PROCEEDINGS
OF THE
CHEMICAL SOCIETY

SEPTEMBER 1958

THE CHEMICAL INDUSTRY IN THE NINETEENTH CENTURY: A SHORT SURVEY OF ITS GROWTH

By L. F. HABER

CHEMISTS have been reluctant to write the history of their industry and academic historians have been unwilling to make anything but passing reference to applied chemistry. As a result, while studies of the cotton and steel industries abound, there have been few dealing with the evolution of the chemical industry. Lately, however, it has become the subject of several monographs and the sudden interest in a hitherto neglected field of economic history is mainly due to the following three factors: the emergence during the inter-war years of huge concerns naturally attracted attention; their prosperity when other branches of the economy languished was sufficiently unusual to arouse admiration or envy; above all, the tangible evidence of the rôle of industrial chemistry in everyday life inevitably raised the question of how it had all come about and why the industry's structure differed so markedly from that of others.

It would be out of place in this brief survey to review the bibliography of the chemical industry. Suffice it to say that Williams Haynes has written the definitive work on that of America which should serve, but so far has not served, as an example to others.[1] A Stalin prize was awarded to Lukianov for his immensely long treatise on the Russian chemical industry to the end of the Nineteenth Century.[2] But developments in other countries have often been described so sketchily that gaps remain in our knowledge of the growth of chemical manufacture in Britain, France, and Germany.[3]

The term chemical industry covers, as a rule, a heterogenous group of manufactures, often only loosely connected with each other, but in the following pages it is interpreted very narrowly to comprise sulphuric acid, alkalis, fertilizers, and dyestuffs. This arbitrary limitation greatly simplifies the task of focusing attention on the main features of the industry's growth. Moreover, industry is here taken to mean the manufacture of products on a sufficiently large scale

---

[1] Haynes, "The American Chemical Industry," 6 vols., van Nostrand, New York, 1945—54.

[2] Lukianov, "Istoria khimicheskikh Promyslov i Khimicheskoi Promyshlennosti Rossii do kontsa 19 Veka"; 4 vols., Akademia Nauk Moscow, 1948—52.

[3] For Britain, Miall, "A History of the British Chemical Industry," Benn, London, 1931, and A. and N. Clow, "The Chemical Revolution," Batchworth Press, London, 1952, are the best sources. Developments in France have been described by Fauque, "L'Évolution de la grande industrie chimique en France," Éditions Universitaires, Strasbourg, 1932, while for Germany a useful introduction is given by Rassow, "Die chemische Industrie," Flamberg, Berlin, 1925.

to be economically significant. The adoption of these definitions enables us to exclude the Eighteenth Century forerunners which, despite their technological interest, are from the economic point of view of little practical significance. The origins of the chemical industry thus go back to the beginning of the Nineteenth Century, and in particular to France during the Napoleonic wars.

That country, then at the height of her power, provided an environment ideally suited to the very rapid development of chemical manufacture. The large requirements for ammunition and indeed all other war stores coincided with acute shortages of essential imports. The most serious were saltpetre from the East, potash from North America and northern Europe, sulphur from Sicily, and vegetable alkali from Spain. Fortunately for France, the skill of her chemists and engineers, many of them students of the École Polytechnique founded during the Revolution, was equal to the occasion. New processes and methods were adopted: the production of saltpetre from indigenous waste matter became highly organised, the deposits of pyrites in the Massif Central were worked, and factories using Leblanc's artificial soda process were established. As a result, within ten to fifteen years a chemical industry had been created. Figures, though never reliable in those days, may illustrate the order of magnitude: a few years after Waterloo, French production of artificial soda amounted to 10,000 to 15,000 tons a year, and that of sulphuric acid to 20,000 tons.[4] But later, output stopped growing at the spectacular war-time rates; the country's industrial and commercial progress was slower than that of Britain and this inevitably affected the expansion of the chemical industry.

The lead-chamber process for making sulphuric acid (invented by John Roebuck in 1746) and various types of chlorine bleaches (the best being Charles Tennant's bleaching powder patented in 1797) were used in Scotland and to a smaller extent in England. They, and minute quantities of artificial soda, represented the extent of British chemical manufacture at the opening of the Nineteenth Century. With the exception of sulphuric acid, the size of the early chemical works was extremely small. Leblanc's process was known, but its adoption was hindered by the salt excise which had been raised to such high levels in 1805 that artificial soda could not be made at prices competitive with those charged for vegetable alkali, which, in any case, possessed all the advantages derived from traditional usage. After considerable lobbying the salt duty was abolished in 1825 and this was followed a few years later by reductions of those on glass and soap and the abolition of import duties.

These fiscal changes were the essential prerequisite for the growth of chemical manufacture and so it is hardly surprising that, from the late 1820's onwards, Leblanc soda works multiplied. Tennant's chemical factory at St. Rollox was easily the largest and the businesses founded by Muspratt, Gamble, and Allhusen (to mention only some of the founders of the alkali industry) soon became substantial enterprises. By the middle of the century, the manufacture of Leblanc soda, invariably associated with the production of sulphuric acid, was established in two main centres—Tyneside and St. Helens, and they accounted for the greater part of the 6,000 workers employed and the 72,000 tons of soda ash produced in 1852.[5]

Britain was then undoubtedly the leading producer of industrial chemicals and many of the important technical improvements were first applied here. Among the more significant were larger decomposing pans, Gossage's tower for hydrochloric acid, and filter tanks for leaching the crude soda by what would now be called a continuous counter-current flow system. Pyrites had largely replaced Sicilian sulphur and in 1853 the first revolving furnace for the preparation of crude soda or "black ash" was built. In general, the Leblanc soda industry was prosperous and progressive. Especially was this the case in Widnes, a hamlet when the first chemical works were established in 1847, but already a bustling, ugly town of 14,000 inhabitants in 1871. Widnes grew quickly owing to its proximity to salt, coal, and limestone and the facilities for transhipping pyrites and exporting alkali. For some years the expansion was almost as rapid in the Newcastle area which specialised in making soda for shipment to London and the Continent. In the 1850's and 1860's exports to northern and western

---

[4] The figures have been derived from Chaptal, "L'Industrie française," Renouard, Paris, 1819, vol. ii, pp. 173, 175.

[5] Muspratt, "Chemistry as applied to and relating to the Arts and Manufactures," McKenzie, Glasgow, 1860; vol. ii, p. 938.

Europe were rising fast and the Cobden treaty (1860), by opening the French market to British alkali, resulted in booming trade. Indeed such were the advantages derived from large-scale production, that British soda could be sold on the Continent at prices generally lower than those quoted by French and German manufacturers. This explains why the production of alkali by Leblanc's process remained small on the Continent. Further inland, where the burden of freight rates was heavy, local manufacturers fared rather better. Thus the Österreichische Verein für Chemische & Metallurgische Production, founded in the Czech town of Aussig in 1856 soon became a profitable enterprise. Across the Atlantic British competition was equally effective, and so the main emphasis of chemical manufacture, then located mainly in and around Philadelphia, was on the production of sulphuric acid. Only one firm, the Pennsylvania Salt Manufacturing Co., established in 1850 and now trading as Pennsalt, made alkali on a significant scale.

Until the middle of the Nineteenth Century the products of the Leblanc process, soda crystals and soda ash, formed the basis of chemical manufacture in Britain and France, then the only countries where the industry had attained considerable size. Substantial quantities of bleaching powder were also produced, but the business in sulphuric acid (except as required for decomposing salt to sodium sulphate) was still fairly small, as was the output of caustic soda and bicarbonate of soda. But important, indeed fundamental, changes caused by the emergence of a new branch of chemistry—organic chemistry—were now to transform the character of the industry. The most important results of these changes in the field of applied chemistry during the second half of the century were the establishment of the fertilizer and dyestuffs industries.

Justus von Liebig (1803—1873), more than any other chemist, gave both their original impetus: directly by his sustained interest in agricultural chemistry and his numerous writings on the subject, indirectly by establishing at Giessen a systematic laboratory course on organic chemistry. The energy and enthusiasm of the professor was imparted to his students, and they, in turn, disseminated the new teaching methods far and wide.

Liebig's work on agricultural chemistry, though incomplete owing to his underestimating the rôle of nitrogen, and controversial since he relied on laboratory demonstrations rather than on extended field tests, was nevertheless epoch-making. In particular he drew attention to the importance of phosphatic fertilizers. Bone meal had been used for many years, but now Liebig and one of his students, J. H. Gilbert, recommended the employment of mineral phosphates. These were rendered soluble by treatment with sulphuric acid, and the first works to prepare superphosphate was started at Deptford in 1843. Eleven years later, there were six fertilizer works in Britain and several on the Continent, the first being opened in Germany in 1850. Later, large deposits of phosphate rock were found in Florida and towards the end of the century those in North Africa began to be mined. In 1900 superphosphate was quantitatively the most important fertilizer, world production being about 4·5 million tons; the principal manufacturing countries were Germany, Britain, France, and the United States.[6]

French agriculturists had drawn attention to the use of farm manure and prepared night soil and Britain began importing guano on a large scale in the 1830's. The consumption of these nitrogenous fertilizers grew rapidly during the next twenty to thirty years and was supplemented after about 1850 by Chilean sodium nitrate. The ammoniacal liquors from gas works were initially considered a waste product, though the Gas Light & Coke Co. was selling sulphate of ammonia as early as 1833. But even as late as 1871 world production of this fertilizer was estimated at only 42,000 tons. Thereafter output grew quickly and by 1900 roughly half a million tons was manufactured, chiefly in Britain and Germany.[6]

The third important fertilizer was potash. Liebig strongly recommended the use of wood ash on light soil, but in later editions of his book on agricultural chemistry this was altered to potash salts. These had been discovered in enormous quantities in the Duchy of Anhalt and were worked commercially from 1861 onwards:

---

[6] Kubierschky, "Die künstlichen Düngemittel und ihre Bedeutung für die Weltwirtschaft," *Z. angew. Chem.*, 1913, **26**, 724, 727.

production increased from 2,200 tons in that year to 288,000 tons in 1870 and rose further to about 3 million tons in 1900.[7] Potash remained a German monopoly throughout the period and the mining and processing works in the Harz district of central Germany employed many thousands of workers.

Amongst Liebig's students several were to become closely connected with the dyestuffs industry. In particular A. W. Hofmann transplanted the Giessen tradition to the College of Chemistry in London, where C. B. Mansfield isolated the principal constituents of coal tar and W. H. Perkin (1838—1907) prepared the first aniline dye, mauvein, in 1856. That same year a French chemist, Natanson, discovered another coal-tar dye, Aniline Red, which was sold from 1859 onwards under the name of "Magenta" or "Fuchsine" by Renard Frères & Franc, of Lyons.

Perkin began manufacturing his dye at Greenford, near London, in 1857, and within a year or two several other works started in Britain and France. They had to contend with great difficulties: the chemistry of dyestuffs was still in its infancy, the purification of raw materials was laborious and expensive, and it was not always possible to prevent the accidental adulteration of a batch of intermediates. The finished aniline dyes, though often exceptionally brilliant, tended to fade and dyers could, at first, only use them on silk.

Yet twenty years later the situation had been transformed; the British and French enterprises had closed or were leading a precarious existence, while in Germany a vigorous dyestuffs industry was yearly growing more powerful. This sudden change of fortune has been ascribed to a variety of causes. In Britain the initial impetus soon spent itself, a contributory factor being, no doubt, the return of many German chemists (among them Hofmann, Caro, and Martius) to the fatherland, while some of their British colleagues (notably Perkin, Nicholson, and Greville Williams) withdrew from the business to devote themselves to private study or other occupations. Moreover, industrial research was neglected and the quality of the young chemists reflected the teaching of chemistry at universities and colleges which left much to be desired. At a later date abuses of the patent law worked to the detriment of British manufacturers. In France, meanwhile, the causes of the decline were clearer and the decline itself more abrupt than in Britain. The original fuchsine patent was challenged, but the courts upheld the claims of Renard Frères, and they and their successors thereby obtained a monopoly position which, in practice, stifled competition and forced other firms to abandon manufacture or move to Switzerland.

No such difficulties appeared on the German side. The chemists and financiers who combined to establish aniline colour works carefully husbanded their resources, did not stint money on research, and certainly took advantage of the absence of a patent law by copying British and French specifications.* The earliest businesses were founded in 1861: one, initially located near Mannheim, was transferred four years later across the Rhine to Ludwigshafen where it has since traded as the Badische Anilin- & Soda-Fabrik; the other was established by F. Bayer at Barmen (Rhineland), but later moved to Elberfeld and then to Leverkusen. The third company to attain great significance was founded in 1865 at Höchst near Frankfurt under the name of Meister Lucius & Brüning, and is now called Farbwerke Hoechst.† The growth of Badische and Hoechst, at first rather slow, gathered momentum when their chemists, working independently of each other, achieved the synthesis of alizarin (1869). The manufacture of this dye, which quickly replaced madder, was extremely profitable and gave the two companies the leading position in the German dyestuffs industry.

The successes of the German firms were matched, albeit on a smaller scale, by their Swiss rivals at Basle, and at the end of the century, having virtually eliminated all but a handful of British and French enterprises, they effectively dominated the dyestuffs industry. It is impossible to detail here the scale of operations; suffice it to

---

[7] Krische, "Das Kali," Part 1, F. Enke, Stuttgart, 1923, p. 134.

* The first patent law for the Reich as a whole was passed in 1877. The patent laws of the individual states seem to have been of little consequence as far as chemicals were concerned.

† There were several other important dyestuffs firms, notably Kalle & Co. founded in 1863, Cassella & Co., which began making aniline colours in 1867, and the Aktiengesellschaft für Anilinfabrikation (commonly called Agfa) established that same year in Berlin.

say that they were large by comparison with other branches of manufacturing industry.* Of greater interest is a review of their chief characteristics—the rôle assigned to research, technical integration, commercial organisation, and labour relations. The combination of these four was then rarely encountered, and their development by an extremely able team of chemists and businessmen working in close harmony, imparted to the dyestuffs companies quite exceptional thrust. It is profitable therefore, even at this distance, to look a little more closely at these characteristic features, for here we may discern the beginning of the chemical concern of the Mid-twentieth Century.

From the outset, the German dyestuffs manufacturers (with the notable exception of Bayer whose business suffered thereby) appreciated the necessity of having properly run research laboratories and as soon as possible these were lavishly equipped and staffed by large numbers of well-paid chemists, aided by assistants and technicians. Good relations were established with the Universities and especially with the Technische Hochschulen. From the 1880's onwards the scale of the research effort increased rapidly, culminating in the lengthy and very costly work on the indigo synthesis. Badische claimed to have spent about £1 million over a period of ten years before achieving a satisfactory process in 1897. Hoechst probably spent equally large sums on their indigo synthesis which was completed in 1904.

On the technical level the companies were equally successful: they did not, it is true, contribute significantly to the progress of electrochemistry, nor were they concerned with the ammonia–soda process, but Badische took the lead in perfecting the contact sulphuric acid process.† Less spectacular, but in the long run perhaps even more significant, was the pursuit of technical integration. The large manufacturers invariably produced dyestuffs intermediates in their own works and, excepting soda ash, manufactured all the process chemicals. As their requirements were large, these installations soon attained considerable dimensions and comprised electrolytic plants for making caustic soda and chlorine, sulphuric acid works (in which the lead-chamber or the contact process was used), as well as power stations, gas works, and refrigerating plants. Extensive engineering workshops and foundries rounded off the picture. The multiplication of these ancillary works soon caused congestion and at a fairly early date the need for an orderly lay-out of buildings and good internal transport was recognised. The most ambitious project of this kind was launched by Bayer and resulted in the construction, between 1895 and 1907, of a huge works at Leverkusen on a site of 760 acres, and its grid-iron lay-out has now become the standard pattern for chemical plants and oil refineries.

The Germans were ingenious and competent salesmen, and foreign manufacturers paid them the compliment of imitating their methods. In particular they replaced the then traditional method of selling through brokers and agents by direct sales to customers. Their salesmen were presently assisted by specially trained techno-commercial staff whose main function was to promote the use of new dyestuffs and dyeing techniques. In this manner a mutually valuable link was established between manufacturer and customer. These commercial practices were reinforced by a number of more or less formal agreements between manufacturers which, though not eliminating all competition, nevertheless facilitated the orderly marketing of products. A general understanding was reached with other chemical businesses whereby the dyestuffs firms undertook not to sell substantial quantities of inorganic chemicals, while the alkali and potash works on their part did not produce coal-tar dyes.

Labour relations were excellent and the paternalistic policy of the employers contributed importantly to the creation of an *esprit de corps* which, in turn, was of great value to the business. The workers in the dyestuffs industry were amongst the best paid in the country; they benefited additionally from subsidised housing and extensive welfare services comprising hospitals, bath-houses, rest homes, and pensions. Much attention was devoted to industrial

---

* For instance employment at Badische rose from 520 in 1870 to 6,700 in 1900, while gross sales increased from £166,000 to about £2 million.

† Peregrine Philips of Bristol is credited with this invention (1831). C. Winkler in Germany and R. Messel in Britain, working independently of each other, rediscovered the method in 1875 and R. Knietsch of Badische adapted it for large-scale production.

hygiene, two instances being the issue of overalls and the provision of canteens. Great care was taken over the recruitment and promotion of foremen and mechanics, and indeed the elaborate arrangements now made for training within industry can be traced back to the last quarter of the Nineteenth Century.

While the German dyestuffs industry was thus progressing, the Leblanc soda trade was facing increasingly difficult conditions. In particular the ammonia–soda process developed by Ernest Solvay (1838—1922) proved to be a formidable rival. Solvay succeeded where others had failed but, though he patented a workable process in 1861, several years elapsed before he began large-scale manufacture at Couillet in Belgium. His method yielded better and cheaper soda ash than Leblanc's, and his subsidiary and associated companies grew at a remarkable pace: in the 1870's factories were established in France and England, during the 1880's others followed in the United States, Germany, Austria, and Russia.

The British Leblanc soda manufacturers had been riding the alkali boom for many years and were, at first, inclined to discount the threat from Solvay. But about 1880 home demand fell off, while many of the valuable overseas markets began to be supplied from local Solvay plants. Attempts were made to shift the emphasis from soda ash (which was progressively becoming less lucrative) to caustic soda and bleaching powder. These were successful for a time and led to a more hopeful outlook. But the recovery was short-lived and the alkali makers thereupon sought to retrieve their fortunes by a merger. In 1890 virtually all combined to establish the United Alkali Co. Ltd., a huge concern with an issued capital of £8·5 million. Unfortunately this giant had feet of clay: competition from the Solvay process could not be met and during the 1890's the new electrolytic alkali plants began to encroach vigorously on the company's territory by producing large quantities of caustic alkalis and chlorine.

In Britain the vicissitudes of the United Alkali Co. reflected the obsolescence of the Leblanc process, aggravated, no doubt, by the increasingly protectionist outlook of the United States, France, Russia, and, to a smaller extent, Germany. All four had hitherto been dependent, often to a large degree, on alkali imported from Britain. Now, protected by high tariffs, they quickly adopted the latest processes and developed a heavy chemical industry of their own. Progress was particularly rapid in the United States where the output of caustic soda rose from 15,000 to 150,000 tons between 1890 and 1900, while the steep decline in imports of British alkali indicated that the country was becoming self-sufficient in soda ash. In France the growth of alkali industry was less spectacular, but the utilisation of the water-power resources led to the formation of many new firms specialising in chlorates and the production of calcium carbide. In Russia, meanwhile, the 1890's witnessed the establishment of chemical manufacture on a substantial scale.

While the overall economic growth of the chemical industry during the Nineteenth Century was remarkable, this brief account has shown that there were significant differences between the countries, differences which became more pronounced as the years passed and finally produced distinct characteristics.

France, once the principal manufacturer of inorganic chemicals, yielded that place to Britain where the production of alkali by the Leblanc process reached its highest development. But in the last quarter of the century technical change rendered that process obsolete. Improvements were costly and eventually the industry which had been based on it became unable to compete with other processes and so decayed.

This showed that size alone was not enough to ensure steady progress, let alone high profits. But, in retrospect, it seems that the lesson was appreciated less in Britain and France than in the United States and Germany. The emergence and growing power of the American and particularly the German chemical industry was no accident. Nor was it deliberately planned. It arose from the awareness that successful chemical manufacture required more than merely increasing the output of a few products by well-tried traditional methods. It required heavy investment in building and equipment, the constant support of research regardless of quick returns, and finally a commercial outlook capable of anticipating demand instead of selling along established lines. The Germans found that the systematic pursuit of these objectives, combined with a cautious financial policy and good labour relations, was essential if progress was to be maintained. By 1900 their chemical industry was technically ahead of all other countries. But chemical manufacturers in France and Britain, though aware of the German threat, were slow to respond to it and so their businesses all too often marked time, until, inopportunely under the stress of war, the necessary changes and improvements were taken in hand.

LIVERSIDGE LECTURE*

Some Isothermal Reactions of Free Radicals Studied by Kinetic Spectroscopy

By R. G. W. NORRISH
(THE UNIVERSITY, CAMBRIDGE)

THE method of flash photolysis can be applied to the study of reactions in two ways which may be described as approximately adiabatic and approximately isothermal. This arises from the fact that when an intense light flash of very short duration, say 100 microseconds, is applied to a suitably absorbing gaseous system such as iodine or nitrogen peroxide the absorbed light energy is very rapidly degraded to heat and instantaneous temperatures of several thousands of degrees are generated. Only if there is a relatively large excess of inert gas present to act as coolant, or if the process is carried out in solution can this temperature rise be kept in check and limited to a few, say ten, degrees. Thus under the adiabatic conditions resulting from lack of temperature control thermal cracking or explosion as well as photolysis may be induced in suitable systems and the method of kinetic spectroscopy provides a most valuable means for the analysis of the rapid elementary reactions of free radicals and atoms occurring in explosive media. It is not my purpose to discuss this aspect of the subject in detail today: recently I had the honour to describe its application to the study of combustion and explosive processes in gases at the meeting of the International Union of Pure and Applied Chemistry held in Paris last July.[1]

No less important than the adiabatic is the isothermal application of flash photolysis which makes possible, first, the identification of free radicals by their band spectra in absorption, secondly, the analysis of the rotational structure of such spectra at low temperatures (*i.e.*, *ca.* 300°K), thirdly, the recognition or confirmation of primary photochemical processes, and, fourthly, the production of free radicals in such concentrations that radical–radical reactions can be studied analytically. I propose today to limit myself to the third category in the consideration of a number of simple photochemical gas reactions and to endeavour to show how the new technique can elucidate their finer mechanisms and indeed expose new principles of chemical reactivity.

The technique of flash photolysis and kinetic spectroscopy has been described[2] so often that it is not intended to do more than describe it in outline on the present occasion. It had its origin in the discovery by Porter and myself[3] that large measures of photochemical dissociation can be induced in suitable gaseous photochemical systems by intense light flashes involving the dissipation of 2000—10,000 joules. It was obvious that high concentrations of free radicals or atoms were momentarily generated; and, by using a second flash, triggered at specific short intervals of time after the first, Porter was able to obtain some of their absorption spectra.[4] A simplified form of the apparatus is shown in Plate 1.† The photolysis lamp consists of a quartz tube 50 or 100 cm. in length and about 1 cm. in diameter, with robust tungsten electrodes sealed in at each end, and filled with an inert gas such as argon to about 10 cm. pressure. By discharging a bank of condensers of capacity 40 μF charged to 10 kv, some 2000 joules of energy are dissipated and a powerful flash of about 120 microseconds results. The reaction vessel is the same length as the lamp and consists of a quartz tube about 2 cm. in diameter with plane end-plates, lying close to and parallel to it. The reaction vessel and the flash tube are surrounded by a metal tube coated on its inner surface with magnesium oxide to give good reflection, and suitably wound externally if desired to act as an electric furnace for work at elevated temperatures. The second lamp is constructed similarly to the first but is so designed as to send a beam along the axis of the reaction vessel on to the spectroscope slit. By discharging say 10 μF at 10 kv a flash of about 20 microseconds duration is obtained with a sufficiently continuous

---

* Delivered before the Chemical Society at King's College, London, W.C.2, on February 27th, 1958.

† See p. 248.

[1] Norrish, Conference plenière au XVIe Congres International de Chimie pure et appliquée, Paris, *Experientia*, 1957, Suppl. VII.

[2] See Norrish and Thrush, *Quart. Rev.*, 1956, **10**, 149.

[3] Norrish and Porter, *Nature*, 1949, **164**, 658.

[4] Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.

background strong enough to photograph the momentary absorption of the contents of the reaction vessel. After the reaction vessel has been filled, the two lamps are charged up, and they retain their charges until the first is discharged by a trigger current passed from a small centrally placed electrode. The second lamp is triggered at intervals ranging from 10^{-5} to 1 second after the first by an electronic timer initiated photoelectrically by the light from the first flash. In this way the initiation and the rapid decay of intermediate species can be observed spectroscopically and measured as a function of time by applying methods of plate photometry to successive photographs taken at increasing intervals.

The reactions which I shall consider are based on hydrogen sulphide, the oxides of sulphur, simple aldehydes, carboxylic acids, and ozone, together with allusions to the photochemistry of oxygen, methane, water, and ammonia. The latter group, which (with the exception of ammonia) at present defy the application of methods of flash photolysis present a challenge to future workers, for their study is excluded by the fact that they only respond photochemically to light of wavelengths below 2000 Å, and no suitable material transparent in this region for the construction of the photolysis lamp and reaction vessel has been discovered. The use of a sapphire photolysis lamp by Ramsay[5] in this connection was a notable effort but this, as he himself showed, gave results which, though of considerable interest, could not be attributed to flash photolysis. It is to be hoped that the future discovery of some transparent polyolefin may make it possible for us to penetrate at least to some extent in the desired direction. At present we are limited to quartz with its "cut-off" at about 2000Å.

Let us look again at the gases about which I propose to speak. Together with carbon monoxide and nitrogen they have played a fundamental part in the geochemical evolution of the earth; they are the gases past and present of the atmosphere, and it is their elementary photochemical reactions that have prepared and sustained the conditions for the development of life as we know it on this planet. Perhaps I may be forgiven if I digress for a few minutes to emphasise this point, for it will serve to show that laboratory discoveries may extend far outside the space and time in which they are made.

Our Earth, with the possible exception of Mars, is unique in having an oxidising atmosphere, rather than a reduced or a completely oxidised atmosphere. If the solar system had a common origin from cosmic gas and cosmic dust containing as it does 93% of hydrogen, how did this come about? The atmospheres of Jupiter and Saturn and the outer more massive planets are composed of reducing or reduced gases—hydrogen, methane, ammonia, water, hydrogen sulphide, etc., and are probably in their original state. The atmosphere of the inner planet Venus appears to be completely oxidised and to consist wholly of carbon dioxide.

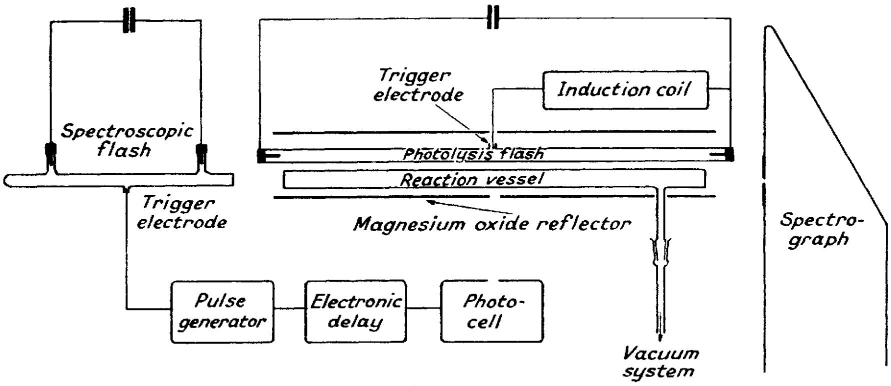


PLATE 1. Typical flash-photolysis apparatus.

Urey[6] and Oparin[7] in their fascinating studies have given us a picture of how this atmospheric evolution from reducing to oxidising conditions took place. Basically it was a consequence of the progressive photolytic action of the sun and the continued loss of the resulting hydrogen gas owing to the relatively weak gravitational fields of the inner planets. Oxides of sulphur, carbon, and phosphorus, etc., were formed later and reacted mainly with the silicates of the lithosphere, while oxygen and nitrogen began to accumulate as the major constituents of the atmosphere. Besides atomic hydrogen, photolysis of the hydrocarbons, ammonia, water, and hydrogen sulphide

[5] Ramsay, *J. Chem. Phys.*, 1956, **25**, 372, 372—373.
[6] Urey, "The Planets," Oxford University Press, 1952.
[7] Oparin, "The Origin of Life on Earth," 3rd edn., Oliver & Boyd, London, 1957.

produced free radicals which either set up polymerisation or reacted together, to form the primordial scum which covered the face of the earth and formed the basis of the organic evolution which prepared the way for the development of life.

Thus the photochemical study of the simple gases which have formed the atmospheres of planets has considerable philosophic interest, beside its intrinsic interest; for a knowledge of the mechanism of their photolyses together with an understanding of the interactions of the radicals and atoms to which they give rise make possible a more and more detailed synthesis of the geochemical and organic evolution of the earth during its four billion years of history.

In Table 1 are shown some of the reactions with which the physical chemist will be concerned in this field of enquiry; we have indeed made but a small beginning, and, for example, can only guess at the primary photolysis products of such simple substances as methane and water. Ramsay,[8] however, has used flash photolysis to establish the primary photolytic reaction of ammonia, and Porter[9] that of hydrogen sulphide. I propose tonight, by taking some of these simple gases as examples, to demonstrate the power of the method of flash photolysis to give new and valuable information about the nature of photochemical processes, and will begin with the oxidation of hydrogen sulphide studied by Dr. Zeelenberg and myself.[10]

In a series of photographs taken at increasing intervals after the photolytic flash (Plate 2*) we see the primary formation of the HS radical coincident with the photoflash, followed by secondary reactions in which the HS radical decays with the formation of S_2 molecules. In view of the quantum yield of unity found by Forbes, Clive and Bradshaw[11] for

TABLE 1. *Photolysis of some constituents of the primitive atmosphere*

Compound	Absorption region	Products	
		Primary	Final
CH_4	1800—1420 (1450—850 faint) Diffuse bands	$CH_3 + H$ (?)	$\left.\begin{matrix} C_2H_6 \\ C_2H_4 \\ C_2H_2 \end{matrix}\right\} + H_2$
C_2H_2	2577—1900 Bands same structure 1520—1020		Polymer (Cuprene ?) Some C_6H_6
H_2O	1785—1550 Continuum	$H + OH$ $(H_2 + O$?)	H_2, O_2 H_2O_2, O_3
	1392—1000 Broad diffuse bands	Excitation of non-bonding electron H_2O^*	
H_2O_2	3100—2700 Continuum	2OH or $H + HO_2$	$H_2O + O_2$
H_2S	2800—1700 Continuum	$H + HS$	$H_2 + S$
H_3N	2430—1515 Diffuse bands	$NH_2 + H$	H_2, N_2 (N_2H_4)
H_3P	2350—2280 Diffuse bands 2250—1850 + Continuum	$PH_2 + H$	H_2, P_2 (red)

* Plates 2—15 for this lecture are collected together and begin facing p. 254.

---

[8] Ramsay, *J. Chem. Phys.*, 1956, **25**, 188.

[9] Porter, *Discuss. Faraday Soc.*, 1950, **9**, 60.

[10] Norrish and Zeelenberg, *Proc. Roy. Soc.*, 1957, *A*, **240**, 293.

[11] Forbes, Clive, and Bradshaw, *J. Amer. Chem. Soc.*, 1938, **60**, 1431.

wavelengths 2080 Å over a wide range of pressure there can be little doubt that the following sequence of reactions is confirmed:

$$\begin{aligned} H_2S + h\nu &= H + HS \\ H + H_2S &= H_2 + HS \\ HS + HS &= H_2S + S \end{aligned}$$

In the presence of oxygen, hydrogen sulphide explodes to form sulphur dioxide, and the sequence of events is shown in Plate 3. The immediate appearance of HS within 30 microseconds is rapidly replaced by that of OH which itself disappears after about one millisecond, and is followed by the delayed appearance of sulphur dioxide which progressively increases in intensity between 2 and 25 milliseconds. If, however, nitrogen is added in excess the system is maintained isothermal, there is no explosion and only limited reaction with the early appearance of the spectrum of S_2O_2 (Plate 4). Under these conditions the initial concentrations of HS radicals produced by the flash is rapidly reduced as the chain reaction develops, but the OH radical never becomes visible—the reaction is rapidly quenched and the OH spectrum appears to be overlaid by strong S_2O_2 bands.

Under isothermal conditions we may conclude that the following reactions take place:

$$\begin{aligned} &H_2S + h\nu = H + HS \\ &H + H_2S = H_2 + HS + 19\ \text{kcal. mole}^{-1} \\ &\left.\begin{aligned} &HS + O_2 = SO + OH + 16\ \text{kcal. mole}^{-1} \\ &OH + H_2S = H_2O + HS + 32{\cdot}7\ \text{kcal. mole}^{-1} \end{aligned}\right\}\text{Propagation} \end{aligned}$$

followed by the process:

$$SO + SO = S_2O_2 + 49{\cdot}5\ \text{kcal. mole}^{-1}$$

Under adiabatic conditions (absence of inert gas) chain-branching reactions develop with rise of temperature, leading to explosion and the formation of sulphur dioxide:

$$\begin{aligned} SO + O_2 &= SO_2 + O + 18\ \text{kcal. mole}^{-1} \\ O + H_2S &= OH + SH + 20\ \text{kcal. mole}^{-1} \end{aligned}$$

In this way S_2O_2 is replaced by SO_2 and the reaction proceeds to completion.

It is not my intention to discuss the explosive reaction of hydrogen sulphide, but one point must be noted and that is the late appearance of the sulphur dioxide spectrum. This delayed appearance is of special interest. It appears to be a temperature effect, for when sulphur dioxide itself is flashed without or with very little inert gas, its spectrum completely disappears for 1—2 milliseconds and is only completely regenerated after some 20 milliseconds (Plate 5). In extending these observations to shorter wavelengths, Mr. Oldershaw[12] has observed a new transient band spectrum to be generated between 2250 and 2400 Å immediately after flashing (Plate 6), together with a strong continuum below 2250 Å. This band spectrum he provisionally assigns to the SO molecule; it agrees approximately with the bands predicted from Martin's[13] results for SO from the known emission bands of longer wavelength. The fading-out of this spectrum is coincident with the reappearance of the SO_2 spectrum, but in the presence of a little added oxygen it fades much more rapidly, as would be expected if the SO radical were removed more rapidly by reaction under these circumstances. The fading of the SO_2 spectrum is to be attributed in the main, however, not to photolysis but to thermal generation of some form of excited SO_2. We have calculated that under the conditions of flashing in the absence of inert gas the temperature may rise instantaneously by about 2500°C. In the presence of a ten-fold excess of nitrogen, when the rise will be only about 250°C, the SO_2 spectrum is only weakened but the process is reversible as shown in Plate 7; and in the presence of a hundred-fold excess of nitrogen the effect is totally suppressed. The continuum which replaces the SO_2 spectrum persists until the original spectrum is regenerated and is independent of added oxygen; it may be attributed to a new species. These results may be correlated with Wieland's observations[14] of a very marked weakening of the SO_2 spectrum on heating in a furnace to 450°C and its restoration on cooling, and we have confirmed this. The effect is greatest when the heating effect is greatest and suppressed when the heating effect is suppressed, and that it cannot be photolytic in character is shown by the fact that there are not enough quanta absorbed completely to affect every SO_2 molecule. It seems possible that some form of triplet state or bond dissociation is generated thermally and reversibly within the SO_2 molecule, which is stabilised by high temperatures:

$$SO_2 \rightleftharpoons SO_2'$$

since SO_2 itself is not affected photochemically by light of wavelength longer than 2200 Å, and since the reactions

$$2SO_2 = SO + SO_3 \quad - 51{\cdot}5\ \text{kcal. mole}^{-1}$$

and

$$2SO_2 = 2SO + O_2 \quad - 150\ \text{kcal. mole}^{-1}$$

are strongly endothermic. The SO spectrum may be generated by photolysis of the metastable SO_2', but the details remain to be established.

On the other hand, Mr. Oldershaw finds that the

---

[12] Norrish and Oldershaw, unpublished work.

[13] Martin, *Phys. Rev.*, 1932, **41**, 167.

[14] Wieland, *Trans. Faraday Soc.*, 1934, **30**, 260.

photolysis of sulphur trioxide follows a more normal pattern. Sulphur trioxide was shown by Kornfeld[15] to be decomposed into sulphur dioxide and oxygen by light of 2750 Å and she concluded the primary reaction to be:

$$SO_3 + h\nu = SO_2 + O$$

Immediately after flashing, however, under isothermal conditions the spectrum we have just attributed to SO appears. This disappears very rapidly and its place is taken by SO_2 bands within about 100 microseconds (Plate 8). If sulphur trioxide is flashed without coolant gas, the same SO spectrum is observed at the shortest delay time but the SO_2 spectrum appears some 5—10 milliseconds late in accord with its high-temperature behaviour outlined above.

These observations lead to the conclusion that the photolysis of sulphur trioxide is described by the following scheme:

$$\begin{aligned} SO_3 + h\nu &= SO + O_2 \\ SO + O_2 &= SO_2 + O + 18{\cdot}8 \text{ kcal. mole}^{-1} \\ O + SO_3 &= SO_2 + O_2 + 34 \text{ kcal. mole}^{-1} \\ SO + SO_3 &= 2SO_2 + 51{\cdot}5 \text{ kcal. mole}^{-1} \end{aligned}$$

rather than that previously postulated.

As the photolytic processes of the atmosphere proceeded with the progressive loss of hydrogen small concentrations of oxygen would begin to accumulate, especially in the upper atmosphere, and the formation of partly oxidised products would become possible. In this way formaldehyde would make its appearance by reactions such as:

$$\begin{aligned} CH_4 + OH &= CH_3 + H_2O \\ CH_3 + O_2 &= [CH_3O_2] = CH_2O + OH \end{aligned}$$

while formaldehyde itself would be subject to further oxidation to formic acid. It thus becomes of interest to study the photolysis of these two compounds, and recently Mr. McKellar[16] has confirmed the appearance of the CHO radical first observed by Ramsay[17] as weak bands at 5624 and 6138 Å in absorption on flashing formaldehyde, and Mr. McKellar has also recorded its formation as a primary product in the flash photolysis of formic acid and acetaldehyde under isothermal conditions. Thus we may conclude that the three following primary reactions occur:

$$\begin{aligned} HCHO + h\nu &= H + HCO \\ HO{\cdot}CHO + h\nu &= OH + CHO \\ CH_3{\cdot}CHO + h\nu &= CH_3 + CHO \end{aligned}$$

The subsequent reactions of the CHO radical will not be discussed at length here; it is short-lived and very probably subject to decomposition:

$$HCO = H + CO \text{ (slightly exothermic)}$$

owing to the tendency of the carbonyl group to reorganise to carbon monoxide. In the presence of oxygen, however, the HCO spectrum is suppressed and there is good reason to believe that the reaction

$$HCO + O_2 = HO_2 + CO + ca.\ 45 \text{ kcal. mole}^{-1}$$

occurs.

The precise process by which higher paraffins, olefins, and acetylene were generated in the primitive atmosphere of the solar system still awaits elucidation. That they originated by the photolysis of methane and the derived free radicals CH_3 and CH_2 seems not to be in doubt, and it is probable that the subsequent photolysis of these hydrocarbon products played a most significant part in providing the first organic compounds on the surface of the earth. Before we can know just how, it is necessary to find some means of studying the photolysis of these hydrocarbons, the reactions of their derived radicals with each other, and with other compounds such as H_2O, NH_3, OH, and NH_2. At present a barrier to this is set by the transparency of quartz, as has already been said.

There is, however, one place in our solar system where these photochemical reactions relevant to our evolution can be observed, namely, in the tails of comets. According to the conclusions of Whipple[18] and Urey[6] the comet head consists of a mass of finely divided cosmic dust, possibly 10—100 km. in diameter, which originated by coagulation in the confines of the solar system in much the same way as planetesimals. Besides matter of low volatility such as silicate and metal phases, these conglomerates—formed as they were at very low temperature—must contain the so-called Whipple ices—solid methane and other hydrocarbons, ammonia, water, etc., condensed from the primitive gases of the solar system. It is believed that comets originating in this way are brought close to the sun by initial captures due mostly to Jupiter and that they continue thereafter to circulate round the sun in elliptic orbits until they disintegrate. At each approach to the sun some of the Whipple ices are evaporated at low pressure and form a tail which spreads out as a fan, always away from the sun owing to the pressure of radiation. In this luminous tail, emission spectra of the following molecules, free radicals, and ions may be observed: CH, CH^+, CH_2, CO, NH, NH_2, OH, OH^+, C_2, C_3, N_2^+, and CN, the products of direct photolysis of, or the reactions of radicals formed photochemically

---

[15] Kornfeld, *ibid.*, 1937, **33**, 614.
[16] McKellar and Norrish, unpublished work.
[17] Ramsay, *J. Chem. Phys.*, 1953, **21**, 960.
[18] Whipple, *Astrophys. J.*, 1950, **111**, 375.

from, methane, ammonia, acetylene, and water.

At the risk of departing from my strictly isothermal theme I am tempted to compare this array with the radicals which are obtained in absorption by the sensitised explosion of acetylene or ethylene mixtures with oxygen in the presence of nitrogen peroxide by flash photolysis,[19] namely, CH, NH, OH, C_2, C_3, CN, and in emission CH, NH, NO, and OH. Such reactions as

$$\mathrm{CH + NO = CN + OH}$$
$$\mathrm{CN + OH = CO + NH}$$

were strongly indicated as taking place, and the conditions may well be compared with those believed to obtain in the comet tail, as the comet approaches the high-temperature regions of the sun.

Now I come to what I would describe as the ozone story, a story of interest not only to the photochemist but also to the student of reactions in the atmosphere. Twenty-eight kilometers above the surface of the earth, the ozone layer is maintained as a photochemical stationary state by the two opposed overall reactions:

$$3\mathrm{O}_2 + h\nu = 2\mathrm{O}_3 \quad (\lambda = 1900\text{—}1200\ \text{Å})$$
$$2\mathrm{O}_3 + h\nu = 3\mathrm{O}_2 \quad (\lambda = 6500\text{—}5500 \text{ and } 3000\text{—}2000\ \text{Å})$$

This layer forms a light-filter, preventing all light below 3000 Å from reaching the surface of the earth. Together with water vapour which absorbs below 2000 Å it protects all forms of organic life from complete destruction by the short-ultraviolet radiation of the sun, for very few of the organic compounds upon which life depends—even the simplest—can survive exposure to such radiation.

Ozone absorbs at both the red end of the visible spectrum, and at the ultraviolet end between 3000 and 2000 Å. In both these regions it is photochemically decomposed by the reactions:

$$\mathrm{O_3} + h\nu = \mathrm{O_2 + O}$$
$$\mathrm{O_3 + O = O_2 + O_2}$$

The quantum yield in the visible part of the spectrum, as shown by Kistiakowski,[20] is approximately 2, and in the ultraviolet can reach as much as 6·7 for dry ozone, as shown by Heidt and Forbes.[21] The existence of a chain reaction necessitated the postulation of the following series of reactions by Schumacher and Beretta,[22] Ritchie,[23] and Heidt:[21]

$$\mathrm{O_3} + h\nu = \mathrm{O_2 + O}$$
$$\mathrm{O + O_2 + M = O_3 + M'}$$
$$\mathrm{O + O_3 = O_2 + O_2^*}$$
$$\mathrm{O} + \text{Surface} = \tfrac{1}{2}\mathrm{O_2}$$
$$\mathrm{O_2^* + O_3 = 2O_2 + O}$$
$$\mathrm{O_2^* + M = O_2 + M'}$$

This mechanism is almost unique among modern mechanisms proposed for chain reactions, involving as it does propagation by an activated molecule of oxygen, though no indication of the nature of this activation was possible. Recent work on the flash photolysis of ozone by Dr. McGrath and me[24] has not only given the answer to this problem but has fully confirmed the correctness of the reaction scheme.

Plate 9 shows the result of flashing pure ozone with increasing quantities of nitrogen as diluent. Above a certain ratio of ozone to diluent the ozone exploded almost instantaneously (within 30 microseconds after the flash) and all that was visible was the absorption spectrum of thermally excited O_2 consisting of the lower levels of the Schumann Runge bands populated to a high rotational temperature. Addition of more inert gas suppresses this by reducing the temperature, and the ozone is then destroyed but slowly. The passing below the explosion limit is also characterised by the appearance of the absorption spectrum of highly vibrationally excited oxygen molecules showing bands ranging from $v'' = 12$ to $v'' = 16$ (more recently $v'' = 17$) in the Schumann–Runge series, which now becomes visible for the first time as high up in the quartz ultraviolet region as 3700 Å (Plate 10). These bands exhibit rotational fine structure characteristic of low temperatures, and we are here producing molecules vibrating with as much as 17 quanta in the ground state, which are cold in all other respects. This excitation corresponds to 66 kcal. mole^{-1}; it represents a large fraction of the exothermic energy of either of the reactions by which it could be produced, *i.e.*:

$$\mathrm{O\,{}^3}P + \mathrm{O_3 = O_2 + O_2} + 93 \text{ kcal. mole}^{-1}$$
$$\mathrm{O\,{}^1}D + \mathrm{O_3 = O_2 + O_2} + 138 \text{ kcal. mole}^{-1}$$

The chain, however, must be propagated by a ^1D oxygen atom, for the following reasons:

(1) No chain is propagated in the photolysis by visible light where only ^3P oxygen can be produced in the primary reaction:

$$\mathrm{O_3} + h\nu \overset{6000\ \text{Å}}{=} \mathrm{O_2 + O\,{}^3}P - 24 \text{ kcal. mole}^{-1}$$

---

[19] Norrish, Porter, and Thrush, *Proc. Roy. Soc.*, 1953, *A*, **216**, 165; 1955, *A*, **227**, 423.

[20] Kistiakowski, *Z. physik. Chem.*, 1925, **117**, 337.

[21] Heidt and Forbes, *J. Amer. Chem. Soc.*, 1934, **56**, 2365; Heidt, *ibid.*, 1935, **57**, 1710.

[22] Schumacher, *ibid.*, 1930, **52**, 2377; *Z. phys. Chem.*, 1932, *B*, **17**, 405; Beretta and Schumacher, *ibid.*, p. 417.

[23] Ritchie, *Proc. Roy. Soc.*, 1934, *A*, **146**, 848.

[24] McGrath and Norrish, *Proc. Roy. Soc.*, 1957, *A*, **242**, 265.

The limiting quantum yield of 2 in this region is a consequence of this.

(2) If ${}^1D$ oxygen atoms are formed in the primary ultraviolet reaction:

$$\mathrm{O_3} + h\nu \overset{2500\,\text{Å}}{=} \mathrm{O_2} + \mathrm{O}\,{}^1D$$

and are necessary for chain propagation, then regeneration in the reaction

$$\mathrm{O_2}^* + \mathrm{O_3} = 2\mathrm{O_2} + \mathrm{O}\,{}^1D - 69\ \text{kcal. mole}^{-1}$$

requires oxygen molecules excited to an energy greater than 69 kcal. mole^{-1}, *i.e.*, 18 quanta or more in the ground state. Thus we may conclude that the oxygen molecules excited to 17 quanta or less, which we observe, are not sufficiently energised to propagate the chain: they decay slowly and do not take part in the reaction. Molecules with more than 17 quanta react rapidly in the chain reaction, their concentration is kept low, and they are not observed in absorption. If they did not react however, we might expect oxygen molecules vibrationally excited up to the limit of dissociation, *i.e.*, 117 kcal. mole^{-1}, for the reaction

$$\mathrm{O}\,{}^1D + \mathrm{O_3} = \mathrm{O_2} + \mathrm{O_2}$$

is 138 kcal. mole^{-1} exothermic.

That the ${}^1D$ oxygen is indeed generated in the ultraviolet dissociation of ozone is strikingly demonstrated by our most recent results.[25] It was shown by Forbes and Heidt[25a] that in the presence of water vapour the quantum yield of ozone in the ultraviolet region can rise as high as 130, compared with 6·7 for dry ozone. On flashing moist ozone in the presence of nitrogen we found the answer. It is seen in Plate 11. In the presence of water vapour the excited-oxygen bands characteristic of dry ozone are suppressed completely and their place is taken by strong OH absorption, seen as the 0,0 band in the photograph.

Thus we conclude that chain-propagation no longer takes place by way of excited oxygen, but rather by hydroxyl. In order that hydroxyl radicals may be generated, the reaction

$$\mathrm{O} + \mathrm{H_2O} = 2\mathrm{OH} - 11\ \text{kcal. mole}^{-1}$$

must occur, and since this is endothermic it can only occur spontaneously if the oxygen atom is excited to the ${}^1D$ state (45 kcal. mole^{-1}).

We thus view the mechanism of ozone photolysis in the presence of water as:

$$\begin{array}{l}
\mathrm{O_3} + h\nu \overset{2500\,\text{Å}}{=} \mathrm{O_2} + \mathrm{O}\,{}^1D \\
\mathrm{O}\,{}^1D + \mathrm{H_2O} = 2\mathrm{OH} + 34\ \text{kcal. mole}^{-1} \\
\left.\begin{array}{l}
\mathrm{OH} + \mathrm{O_3} = \mathrm{HO_2} + \mathrm{O_2} + 42\ \text{kcal. mole}^{-1} \\
\mathrm{HO_2} + \mathrm{O_3} = \mathrm{OH} + 2\mathrm{O_2} + 27\ \text{kcal. mole}^{-1}
\end{array}\right\}\text{Propagation} \\
\left.\begin{array}{l}
2\mathrm{HO_2} = \mathrm{H_2} + 2\mathrm{O_2}\ \text{neutral} \\
2\mathrm{OH} = \mathrm{H_2} + \mathrm{O_2} + 12\ \text{kcal. mole}^{-1} \\
2\mathrm{OH} = \mathrm{H_2O_2} + 46\ \text{kcal. mole}^{-1} \\
2\mathrm{HO_2} = \mathrm{H_2O_2} + \mathrm{O_2} + 31\ \text{kcal. mole}^{-1}
\end{array}\right\}\text{Possible termination reactions}
\end{array}$$

The nature of the oxygen molecule generated in the primary dissociation of ozone is not uniquely defined. Certain low lying electronic states such as ${}^1\Delta_g$ and ${}^1\Sigma_g{}^+$ are not excluded energetically, and for spin conservation the reaction:

$$\mathrm{O_3} = \mathrm{O_2}\,({}^1\Delta_g) + \mathrm{O}\,({}^1D) - 91\ \text{kcal. mole}^{-1}$$

is the most probable, the energy corresponding almost exactly to the long-wavelength limit of the ultraviolet absorption.

Referring again to our scheme of photolysis for dry ozone, we see that the primary act can be reversed by the operation of the reaction:

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} = \mathrm{O_3} + \mathrm{M}'$$

This is indicated by the fact that in the presence of inert gases this reaction strongly influences the rate of photolysis. The more efficient M is, the slower is the ozone decomposition. By kinetic analysis of the slow reaction following the flash, as seen in Plate 12, wide variations were found, as shown in Table 2.

TABLE 2. *Relative efficiencies of molecules M for the three-body recombination,* $\mathrm{O} + \mathrm{O_2} + \mathrm{M} = \mathrm{O_3} + \mathrm{M}'$.

M′	He	A	$\mathrm{SF_6}$	$\mathrm{CO_2}$	$\mathrm{N_2}$	$\mathrm{N_2O}$
	1	1	1·5	14	16	17

These variations are extremely interesting; it appears that those molecules exhibiting spherical symmetry show low efficiency compared with the others, but further work is required before any generalisations can be made.

The reaction of oxygen atoms with ozone to produce highly vibrationally excited oxygen molecules is typical of a series of similar reactions which have recently come to light in our studies of flash photolysis. Lipscomb, Thrush, and I,[26] investigating

---

[25] McGrath and Norrish, *Nature*, 1958, **182**, 275.
[25a] Forbes and Heidt, *J. Amer. Chem. Soc.*, 1934, **56**, 1671.
[26] Lipscomb, Norrish, and Thrush, *Proc. Roy. Soc.*, 1956, *A*, **233**, 455.

the photolysis of nitrogen peroxide and chlorine dioxide by this means, were able to show that the mechanism of decomposition involves the following reactions:

$$\begin{aligned} NO_2 &+ h\nu &&= NO + O \\ O &+ NO_2 &&= NO + O_2^* \\ ClO_2 &+ h\nu &&= ClO + O \\ O &+ ClO_2 &&= ClO + O_2^* \end{aligned}$$

in which the oxygen molecules produced in the secondary reactions are excited to the upper limit of eight quanta of vibration. In each case up to about half the exothermic energy of the reaction appears in this way in the oxygen molecule. These results are illustrated in Plates 13 and 14, which show respectively the photolysis of chlorine dioxide with the production and decay of the ClO radical and excited oxygen, and the decay of the excited oxygen as indicated by the fading of the Schumann–Runge spectrum.

By photometric measurement of the decay of a suitable band (we chose the 0·6 band) in such a series as that shown in Plate 14 it is possible to estimate the efficiency of third bodies in effecting deactivation of the excited oxygen. These are summarised in Table 3, for the deactivation of the vibrationally excited oxygen molecule from the sixth to the fifth vibrational level, as compared with Kneser's results[27] for the deactivation of the first vibrational level of oxygen obtained from ultrasonics. As can be seen there is a general similarity between the two sets of values.

TABLE 3.

Deactivating molecule	No. of collisions for deactivation 6 ⟶ 5	1 ⟶ 0	Nearest vibration frequencies (c.m.$^{-1}$)
He	—	$1·5 \times 10^5$	
A	10^7	—	
N_2	10^7	10^5	2159
O_2	—	5×10^5	
CO_2	7000	25,000	1286, 1388
ClO	2000	—	868
ClO_2	2000	—	945, 1106
NO_2	500	—	1320, 1621
CO	—	8500	
H_2O	—	400	

Oxygen frequency interval 6 ⟶ 5 = 1440 cm.$^{-1}$

From these preliminary results it appears that, for the deactivation of the higher levels, molecules with odd electrons or with vibrational intervals approximating to that of the excited oxygen are the most efficient. Much more work is possible along these lines, and we have here for the first time the possibility of studying the transfer of energy from high vibrational levels at low temperatures.

Besides the reactions which we have already mentioned we have found other striking cases of non-equilibrated energy distribution. These are collected in Table 4, together with the only other known case of an analogous character discovered by McKinley, Garvin, and Boudart[28] who were able to show from infrared analysis that when hydrogen atoms are introduced into ozone a great proportion of the total energy liberated appears as vibrational excitation of the OH radical which results.

When mixtures of chlorine and ozone or bromine and ozone were flashed, with a filter which cuts out light absorbed by the ozone, Dr. McGrath found that strong spectra of the 0,0 progressions of ClO and BrO are produced.[29] In addition, however, bands with $v'' > 0$ are observed corresponding to the Gaydon flame bands, previously observed only in emission. Plate 15 shows a typical spectrum obtained by flashing a Br_2–N_2–O_3 mixture of ratio 1:50:1 in which the BrO progression is strongly visible; the higher v'' bands are not easily seen in the reproduction, though easily seen on the negative.

TABLE 4.

	$-\Delta H$ (kcal. mole^{-1})	v'' (max.)	Max. energy of vibration (kcal. mole^{-1})
$O + O_3 = O_2^* + O_2$	93 (O ^3P), 138 (O ^1D)	16	63
$O + ClO_2 = O_2^* + ClO$	61 (O ^3P)	8	34
$O + NO_2 = O_2^* + NO$	46 (O ^3P)	8	34
$Cl + O_3 = ClO^* + O_2$	40 (Cl ^2P), 42·5 (Cl $^2P_{0·5}$)	5	12
$Br + O_3 = BrO^* + O_2$	19·0 (Br $^2P_{1·5}$), 29·5 (Br $^2P_{0·5}$)	4	8
$H + O_3 = HO^* + O_2$	80	9	75

---

[27] Kneser, *Ann. Physik*, 1935, **21**, 682.

[28] McKinley, Garvin, and Boudart, *J. Chem. Phys.*, 1955, **23**, 784.

[29] McGrath and Norrish, *Z. phys. Chem. (Frankfurt)*, 1958, **15**, 245.

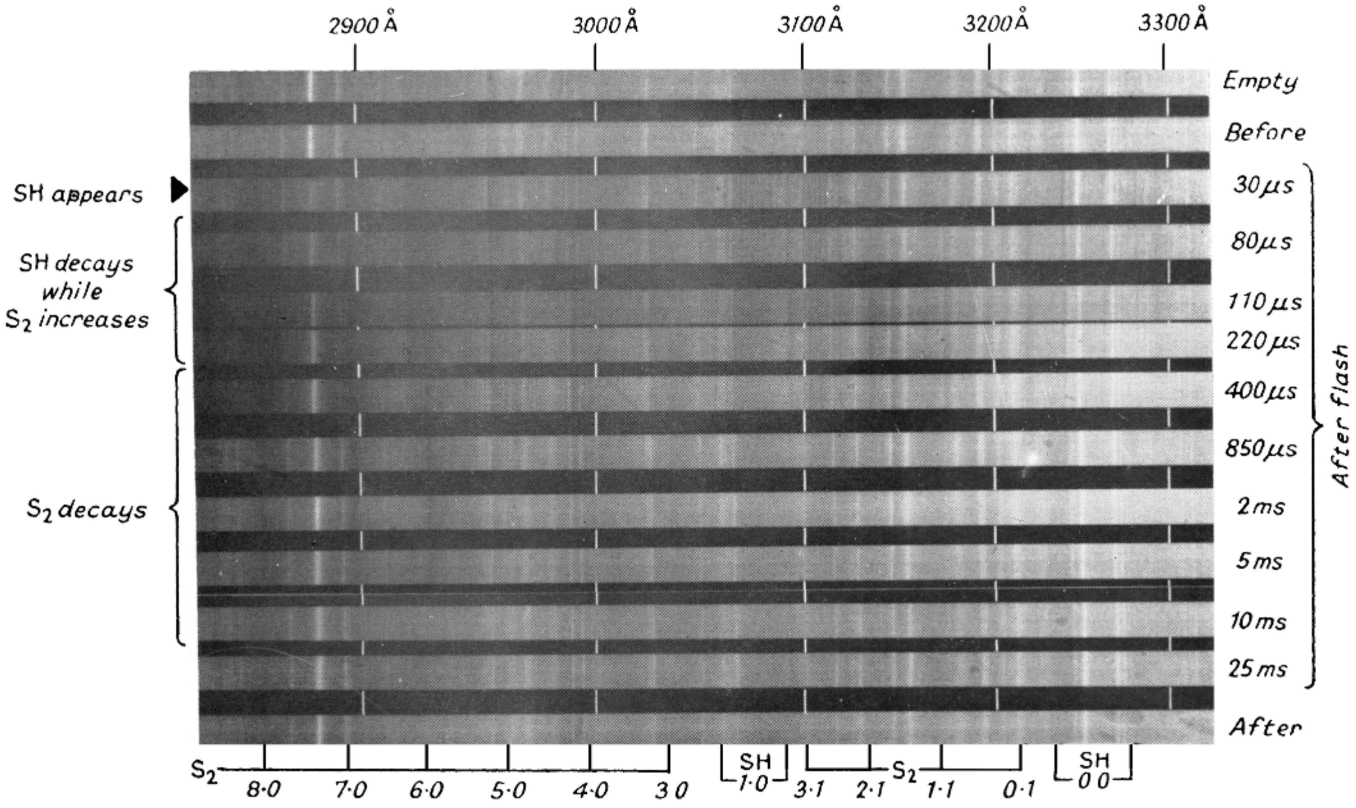


Plate 2. Spectra against time. 1 mm. H_2S. Flash energy = 1500 joules. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1957, *A*, **240**, 293.]

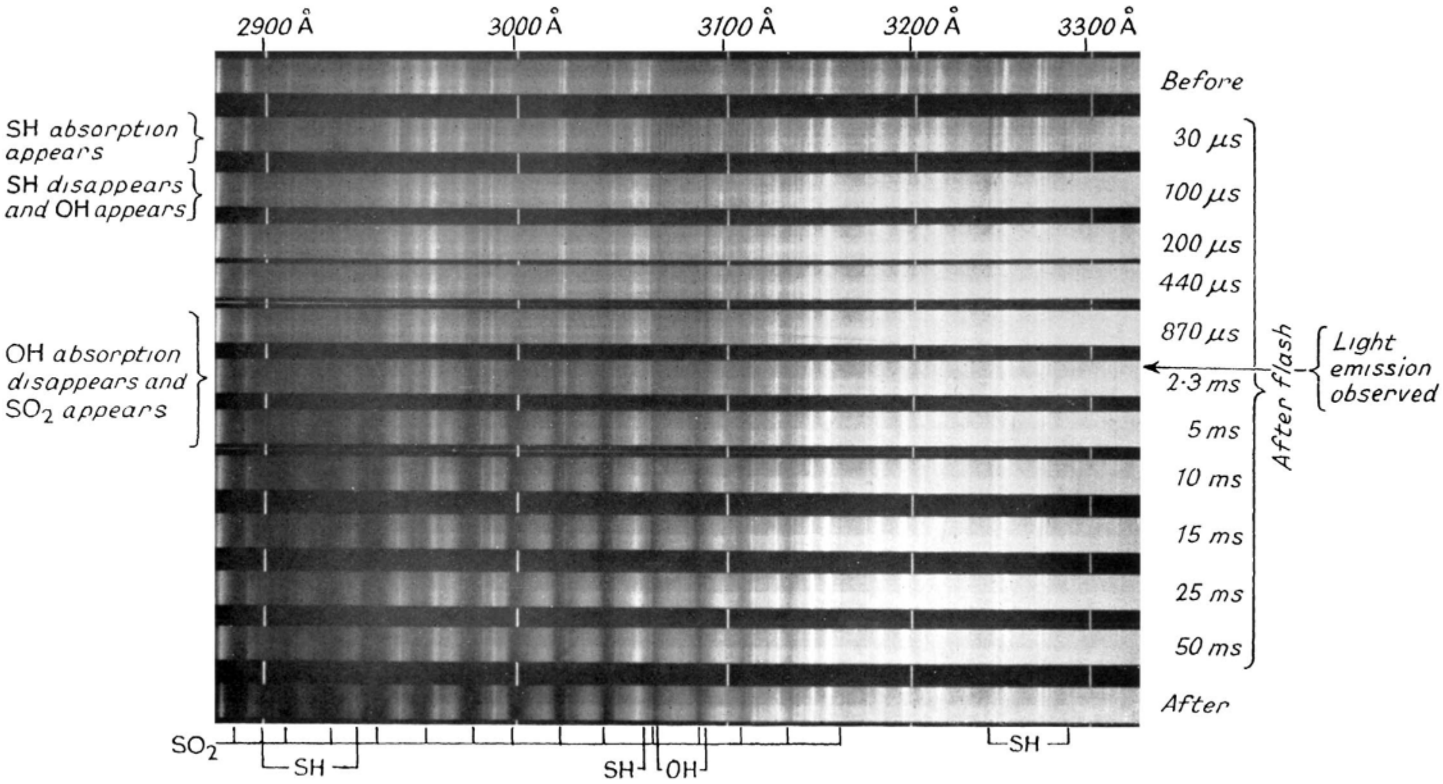


PLATE 3. Spectra against time. 1 mm. H_2S + 3 mm. O_2. Flash energy = 1500 joules. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1957, *A*, **240**, 293.]

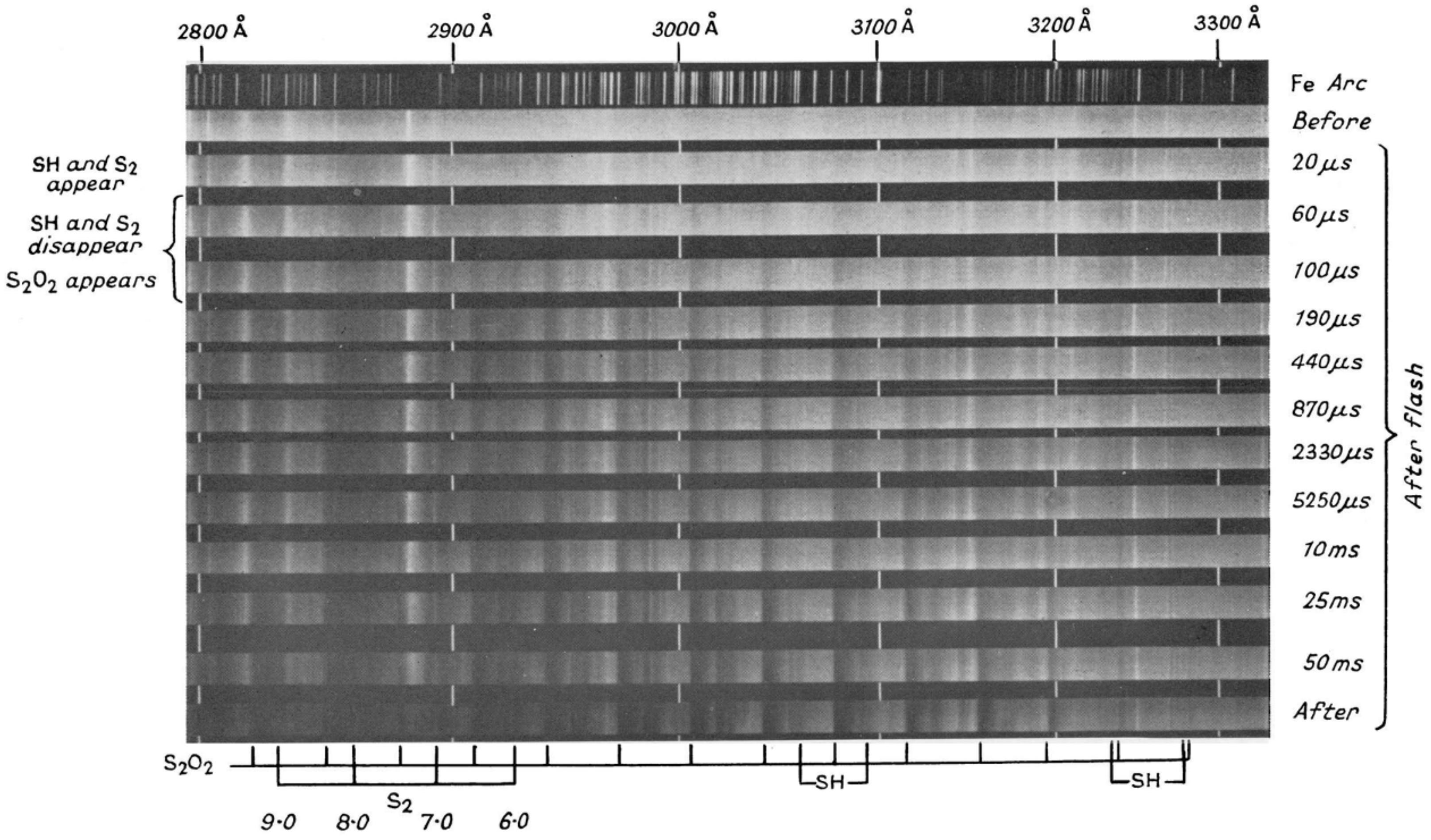


PLATE 4 Spectra against time 1 mm H_2S + 3 mm O_2 + 40 mm N_2 Flash energy = 1500 joules (The S_2 bands unfortunately, do not reproduce clearly) [Reproduced, with permission, from *Proc Roy Soc* , 1957, *A*, **240**, 293]

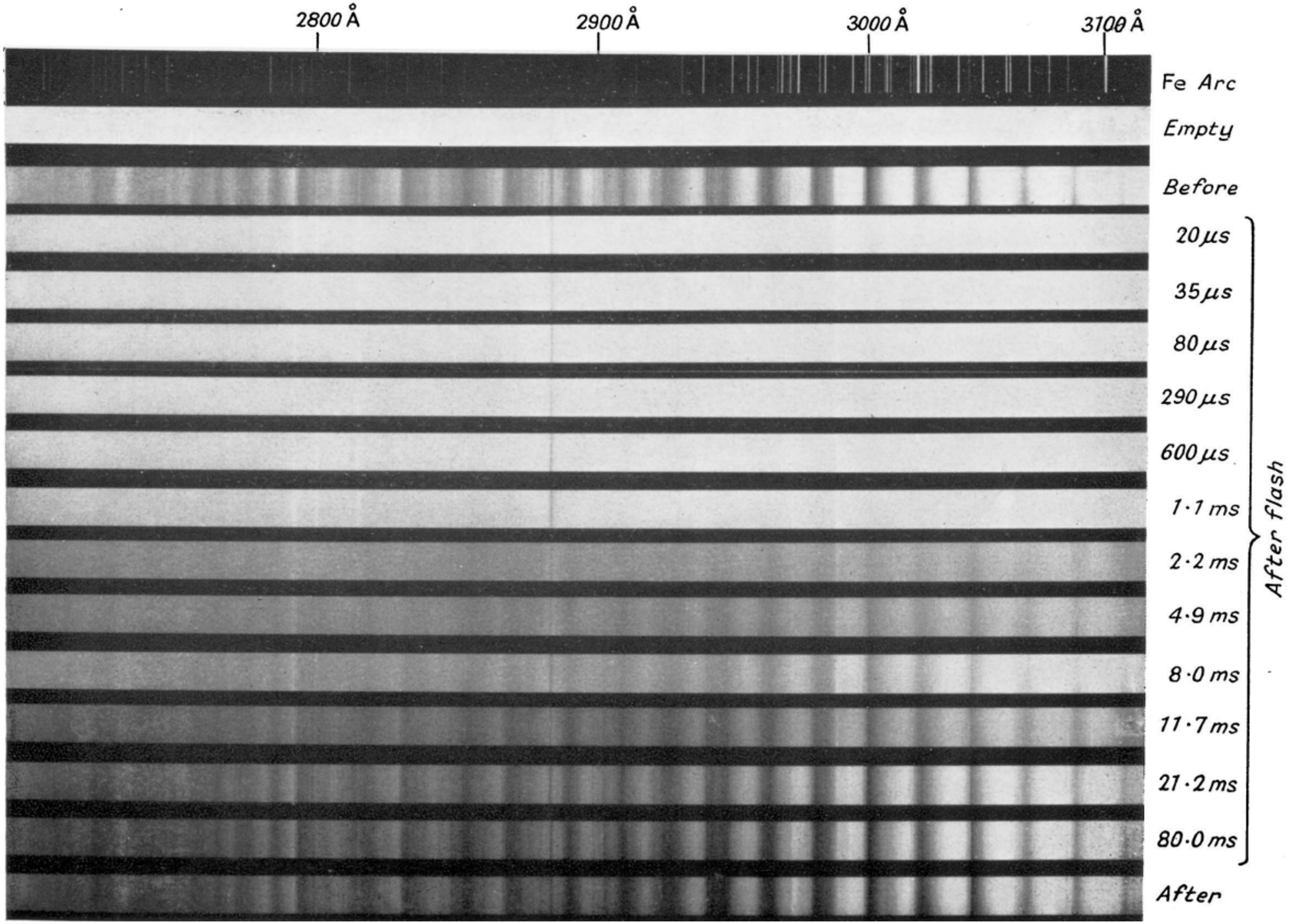


PLATE 5. Flash photolysis of SO_2 1 mm SO_2 Flash energy = 1300 joules

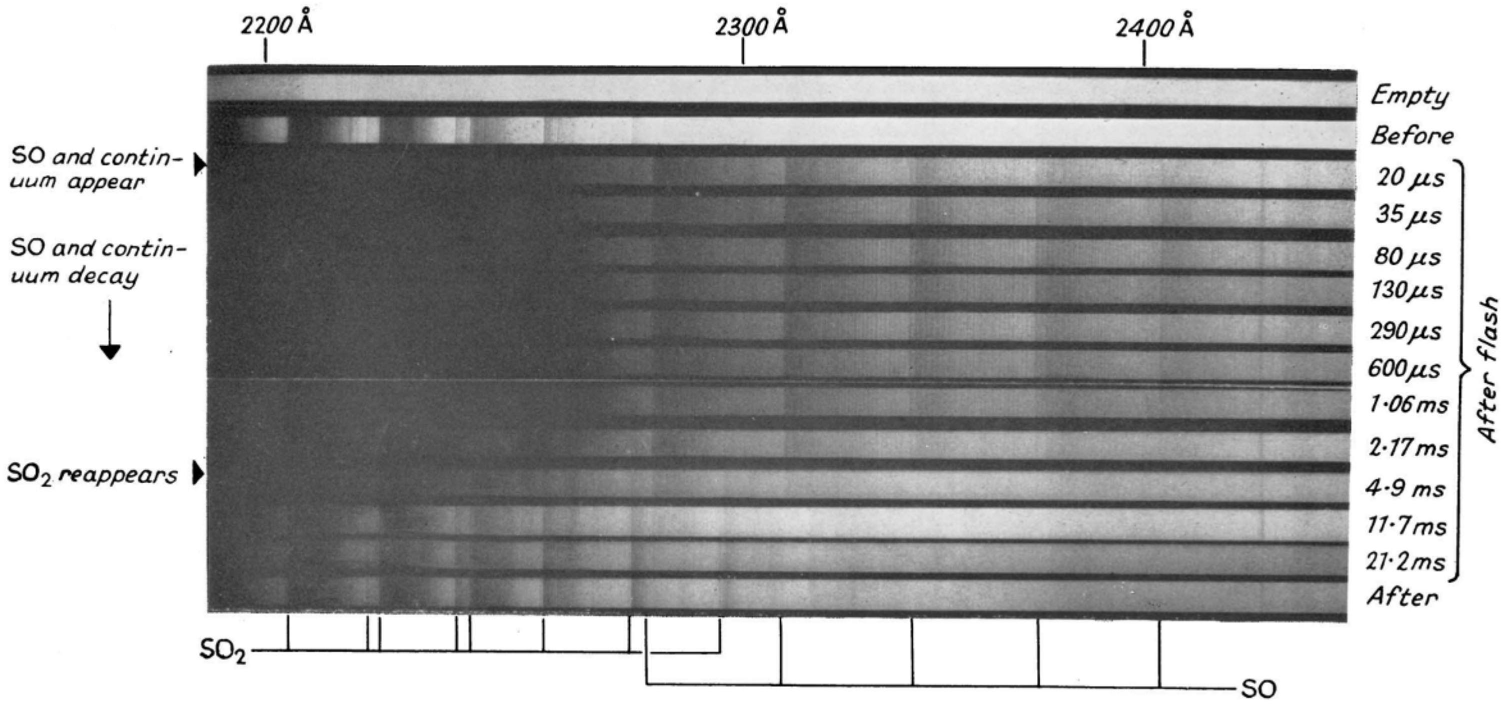


Plate 6. Flash photolysis of SO_2. 1 mm. SO_2 + 3 mm. N_2. Flash energy = 1600 joules.

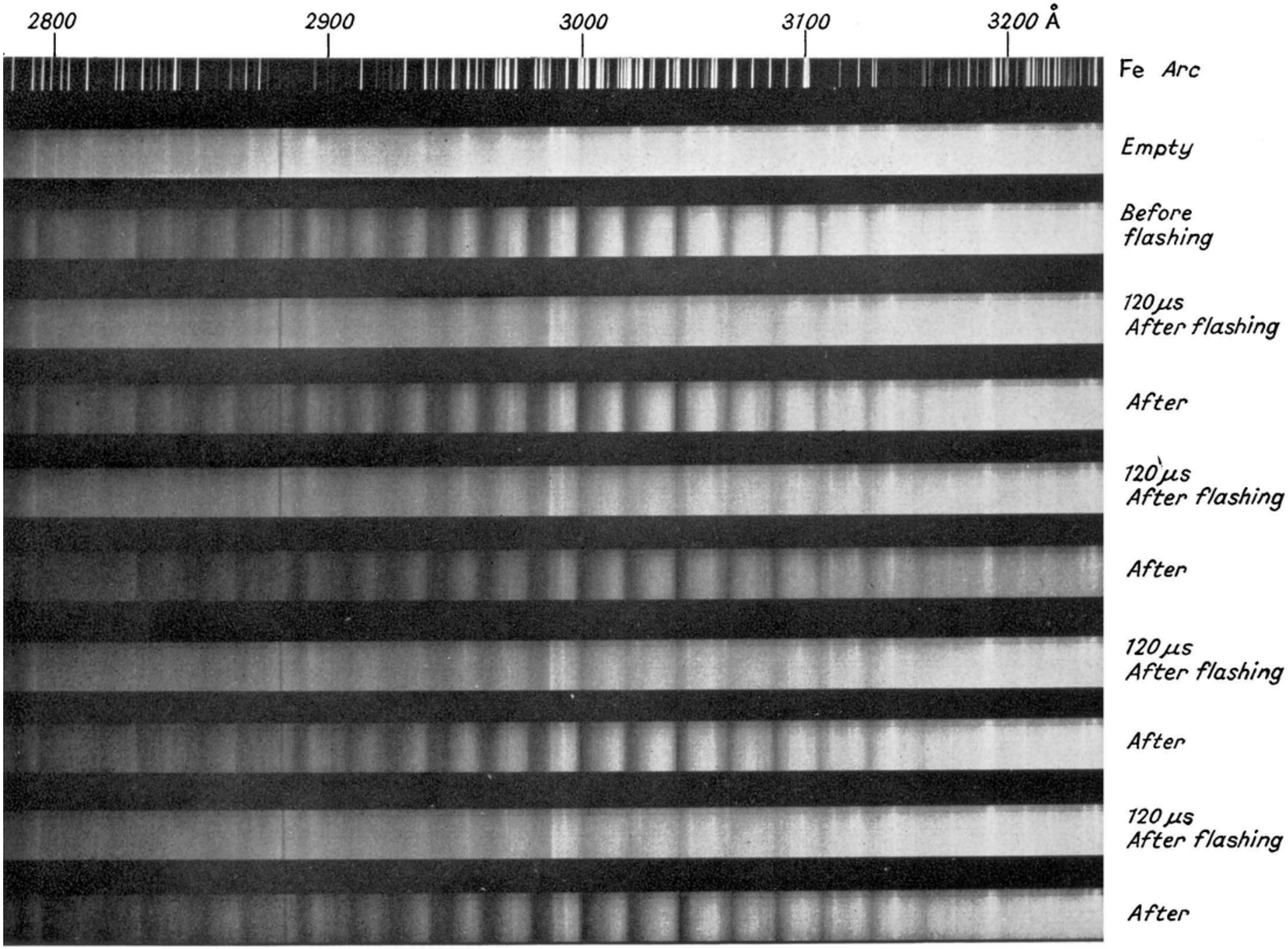


PLATE 7 Flash photolysis of SO_2 Repeated flashing of 1 mm SO_2 + 10 mm N_2 Flash energy = 1500 joules.

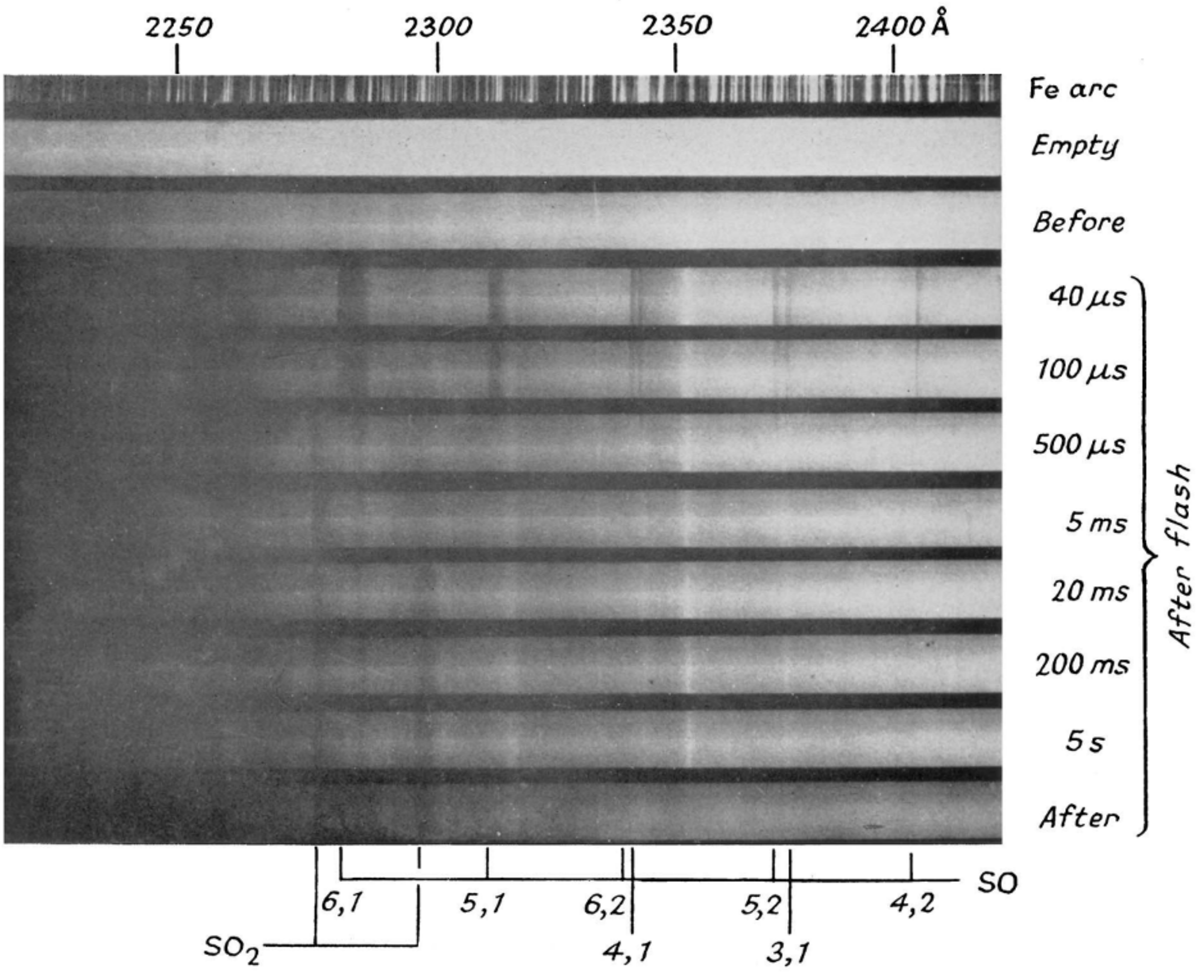


PLATE 8. Flash photolysis of SO_3. 5 mm. SO_3 + 150 mm. N_2. Flash energy = 1500 joules.

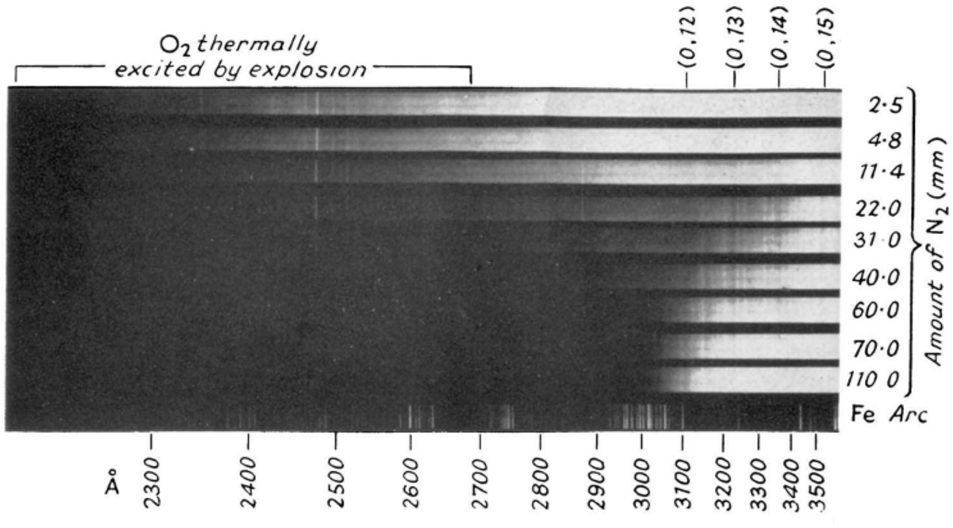


PLATE 9. Effect of nitrogen pressure on the flash photolysis of ozone. Pressure of ozone = 10 mm. Hg. Flash energy = 1280 joules. All spectra taken 30 μs after flash. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1957, *A*, **242**, 265.]

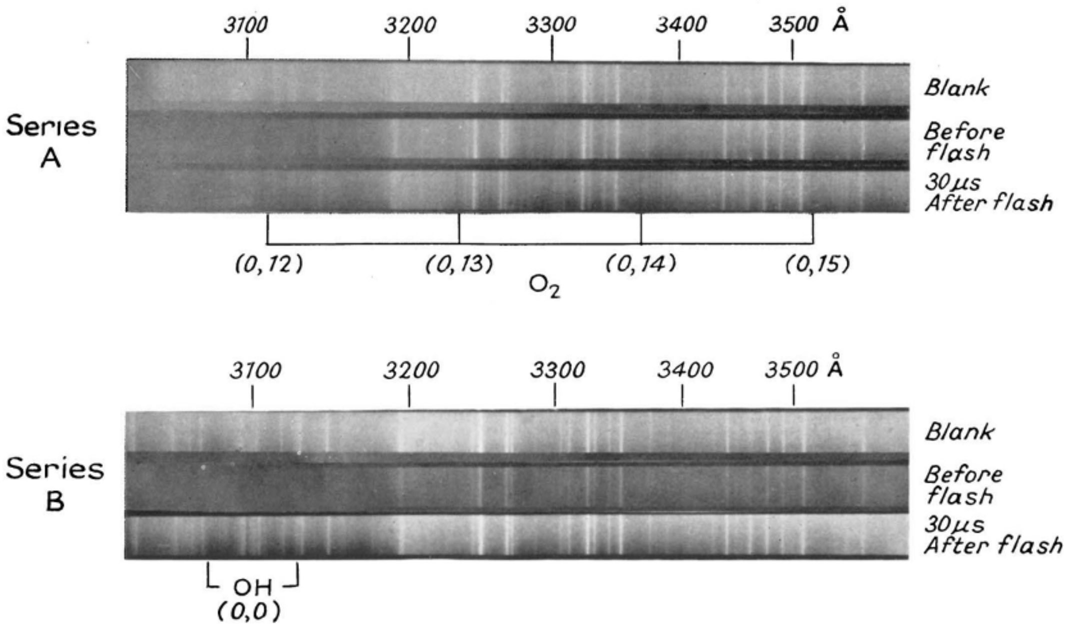


PLATE 11. Flash photolysis of ozone.
Series A. Dry ozone. Mixture ratio O_3–N_2 = 1:100. Ozone pressure = 5 mm. Hg.
Series B. Wet ozone. Mixture ratio O_3–H_2O–N_2 = 1:3:100. Ozone pressure = 5 mm. Hg. Flash energy = 1620 joules.
[Reproduced, with permission, from *Nature*, 1958, **182**, 235.]

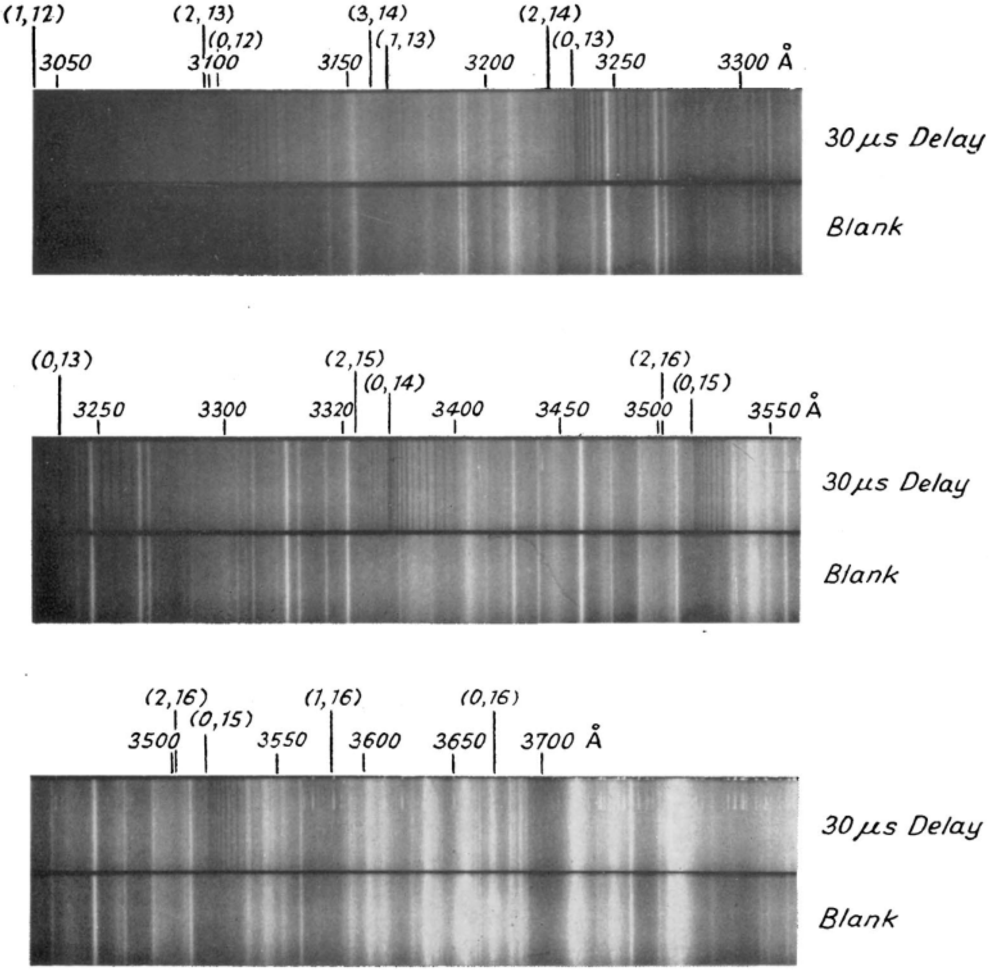


PLATE 10. Schumann–Runge absorption spectrum of vibrationally excited oxygen produced during the flash photolysis of ozone. O_3 pressure = 20 mm. Hg. O_3–N_2 ratio = 1:40. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1957, *A*, **242**, 265.]

PLATE 11. See opposite page.

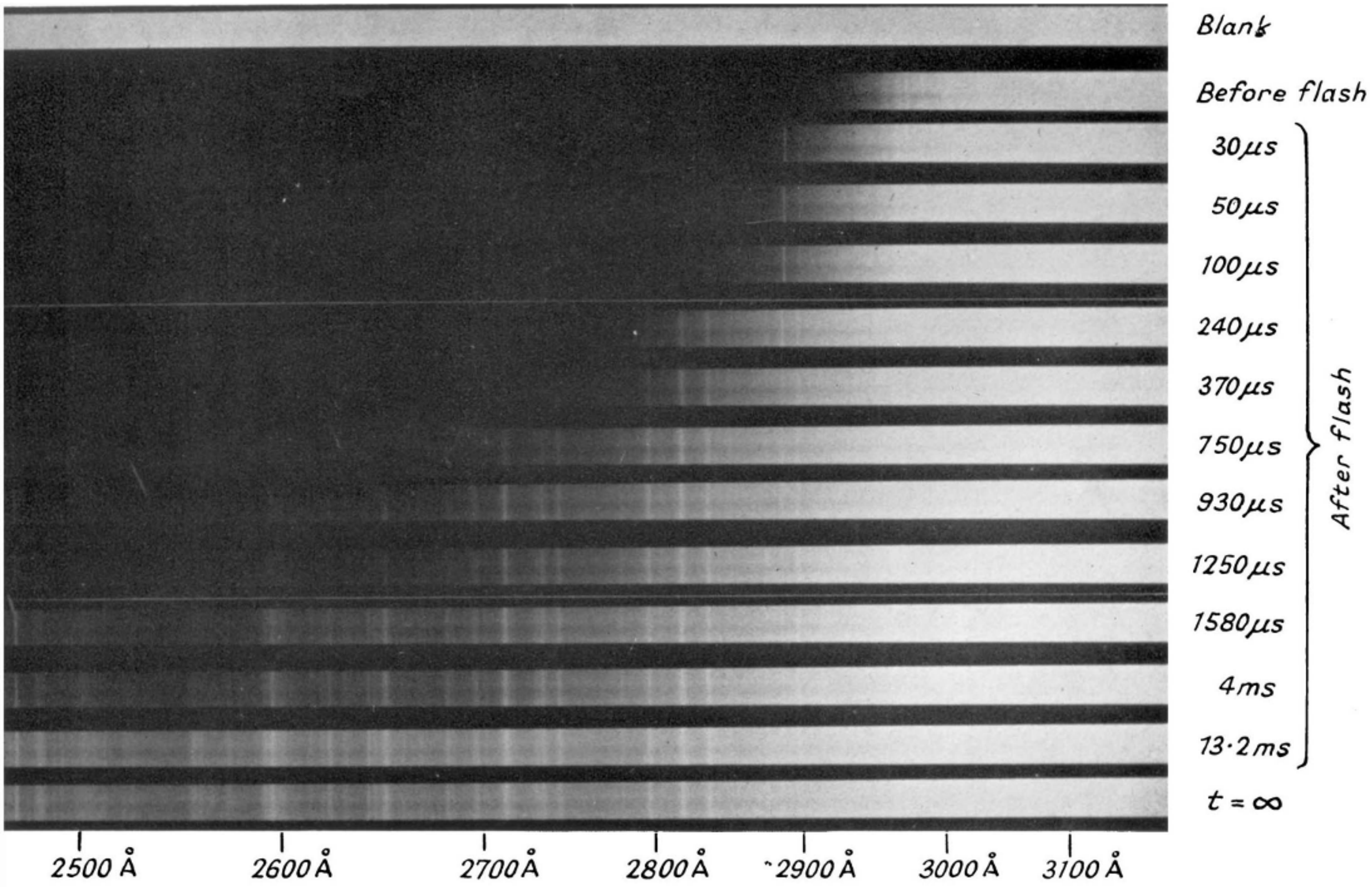


PLATE 12. Disappearance of ozone absorption spectrum with time, after flash. Flash energy = 1180 joules. O_3–N_2 mixture ratio 1:163. 2·9 mm. O_3. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1957, *A*, **242**, 265.]

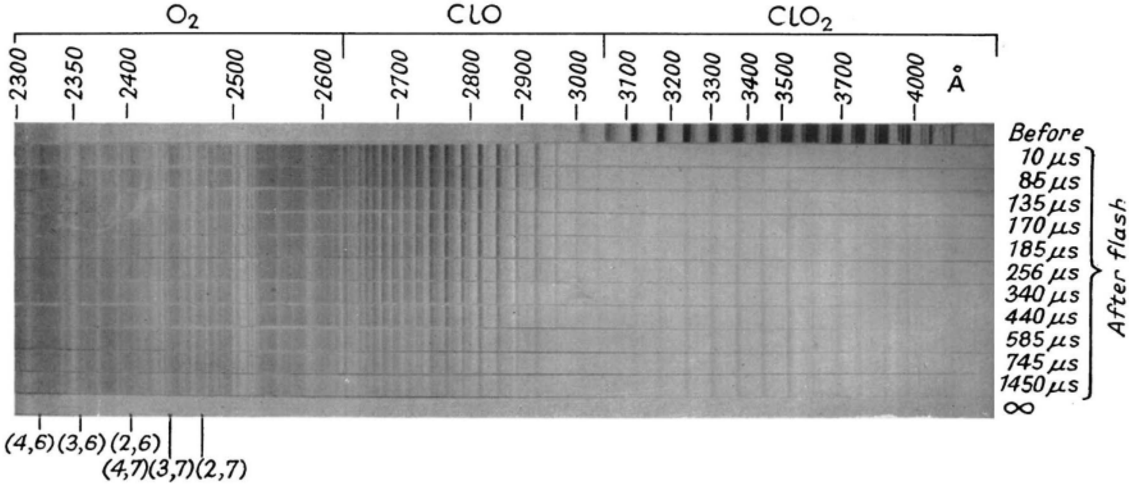


PLATE 13. Spectra of chlorine dioxide and its photolysis products. 1 mm. ClO_2. 200 mm. N_2. [Reproduced, with permission, from *Proc. Roy. Soc.*, 1956, *A*, **233**, 455.]

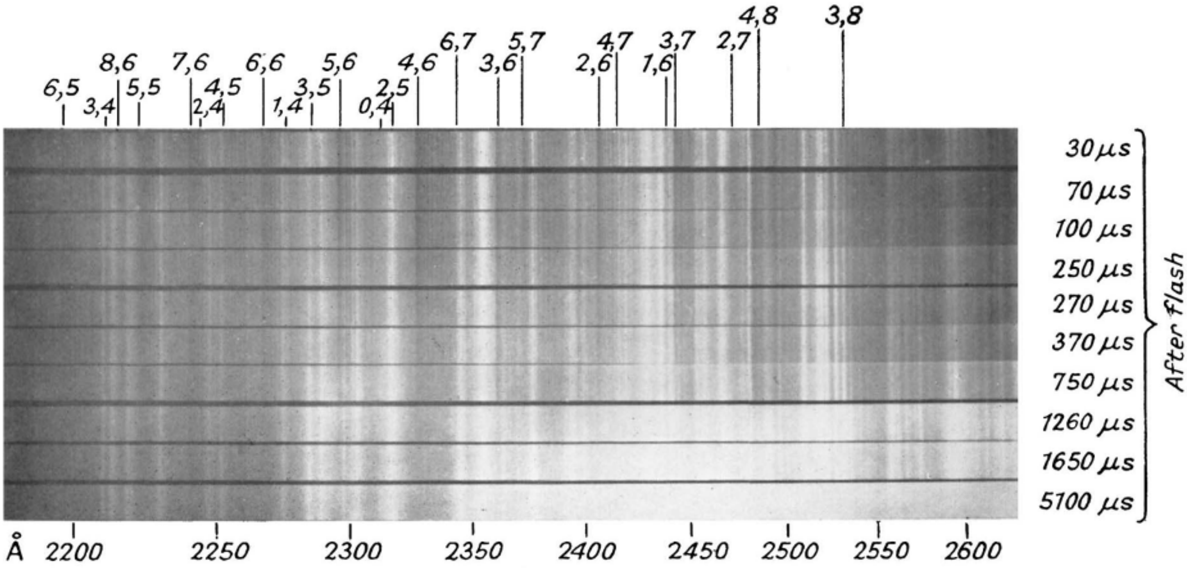


PLATE 14. Decay of vibrationally excited oxygen derived from photolysis of ClO_2. 0.5 mm. ClO_2, 150 mm. N_2.

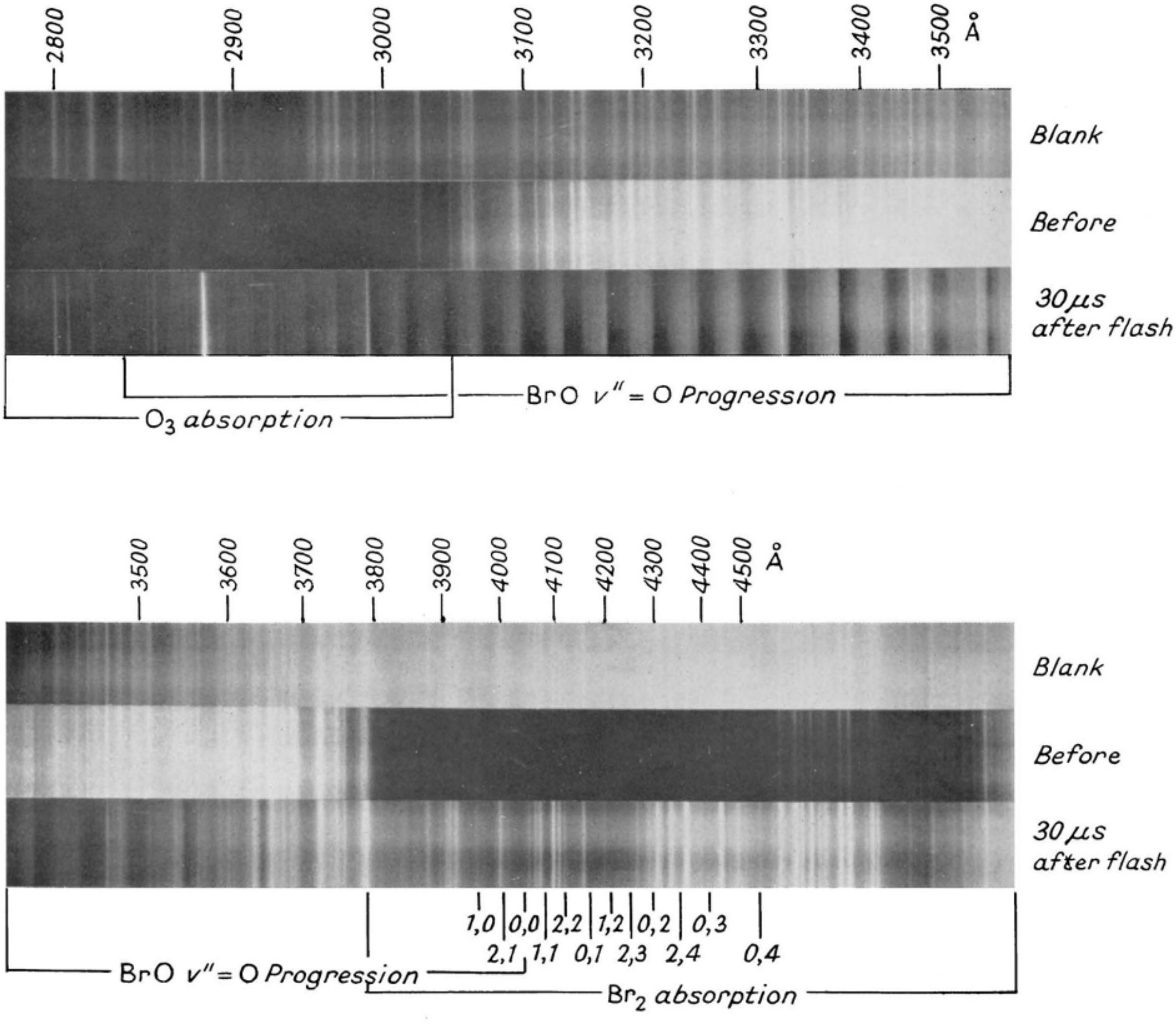


Plate 15. Absorption spectrum of BrO obtained from the flash photolysis of Br_2–O_3–N_2 mixture ratio = 4 : 1 : 40. [Reproduced, with permission, from *Z. phys. Chem* (*Frankfurt*), 1958, **15,** 245.]

It thus seems clear that when an exothermic reaction of the type:

$$A + BCD = AB + CD$$

takes place there is a strong tendency for a major part of the energy of reaction to *remain unequilibrated in the newly formed bond.* Such reactions should form an interesting subject of study for the theoretical chemist: they must have much in common with the stabilisation of a molecule such as HO_2* by a third body, and with reactions such as

$$I + Na_2 = NaI^* + Na$$

studied by Evans and Polanyi[30] in their sodium-flame reactions, where NaI* is vibrationally excited and takes nearly all the energy of the reaction from which it is formed. The study of the highly vibrating molecule produced at low temperatures cannot but be of importance to the better understanding of the propagation of chain reactions, but here for the present we must leave the subject.

When your Council did me the honour of asking me to deliver the Liversidge Lecture I was requested to keep where possible to the tradition of emphasising new lines of thought and new fields for study. The limitations of our methods are at present great and we have made only a small beginning, but it should be obvious that the new technique is able to tell, not only much about the photolysis of simple compounds, but also about the reactions of one radical with another when these are generated in the same tube, and still more when we can extend our observations to the spectral regions of the infrared and far ultraviolet. It is a matter of finding the right conditions for study and of interpreting the spectral record in terms of chemical and physical relations when found. There is plenty of room for many workers in this wide field of investigation and I hope that the very limited part of it to which I have referred tonight will have made this clear.

I make no apology for referring to the planetary atmospheres. So far we have only touched upon the problem of their photolysis and evolution, but when I tell you that the sun supplies enough energy of the right wavelength to have destroyed the whole of the oceans of the earth in about one billion years—that is, about one-quarter of their whole life—the importance of the ozone screen, delicately balanced between two opposed photochemical reactions, is surely manifest; and so too must be the importance of those photochemical reactions which went before in the making of our world.

When you look upon the daffodil and the rose and think on the beauty and melody that is life, think too upon the dance of the oxygen atoms, high in the sunlit empyrean, weaving as they dance that beneficient canopy which makes possible this temple of life and the green pastures of Earth; for indeed, without it, Earth like Venus would be a burnt-out world. So let us take care lest by infantile scheming we stultify the protective function of our atmosphere upon which earthly life with all its endeavour and achievement depends.

---

[30] Evans and Polanyi, *Trans. Faraday Soc.*, 1939, **35**, 178.

COMMUNICATIONS

Alkoxides as Initiators of Anionic Polymerisation of Vinyl Monomers

By ALBERT ZILKHA, BEN-AMI FEIT, and MAX FRANKEL
(THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL)

THERE has been no significant study of alkoxides as initiators for polymerisation of vinyl monomers. Ethyl crotonate[1] and allyl cyanide[2] polymerise under the influence of sodium ethoxide, and the use of sodium methoxide for the polymerisation of acrylonitrile has been reported.[3]

We investigated such aspects of the polymerisation of vinyl monomers by alkoxide catalysts as monomer reactivities, strength of catalysts, effects of surface area of the catalyst, polymerisation medium, temperature, time, and concentration.

Monomers having strong electronegative groups attached to the double bond, such as acraldehyde and acrylonitrile, were polymerised readily.

The order of reactivity of different alkoxides depended on their basic strength, *i.e.* was proportional to the degree of ionisation. Thus acrylonitrile was not polymerised by potassium hydroxide but was polymerised by potassium methoxide (autoprotolysis constant of water 14, of methanol 16·7[4]). Alcohols having a longer side-chain with greater autoprotolysis constants yielded still more active catalysts. Catalytic

---

[1] Pechmann, *Ber.*, 1900, **33**, 3329.

[2] Bruylants, *Bull. Soc. chim. belg.*, 1923, **32**, 317.

[3] Bullet, U.S. 2,608,554—5; cf. *Chem. Abs.*, 1953, **47**, 1430; Schildknecht, "Polymer Processes," Interscience Publ., New York, 1956, p. 225.

[4] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons Ltd., London, 1953, p. 726.

activity was also proportional to the electropositivity of the metal. Thus aluminium *iso*propoxide and *tert.*-butoxide were ineffective, whereas the alkali metal alkoxides strongly polymerised acrylonitrile, with the following order of reactivity, potassium > sodium > lithium; lithium alkoxides, being more covalent, were very weak catalysts. Even alcoholic solutions of sodium or potassium hydroxide, having a small amount of alkoxide ion in equilibrium, polymerised acrylonitrile strongly.

In a typical experiment (under nitrogen), methanolic sodium methoxide (5·3N; 5 ml.) was added to light petroleum (b.p. 40°—60°) (75 ml.) at −15°. This suspension was stirred (5 min.), distilled acrylonitrile (40 ml.) added in one portion, and the mixture stirred for 90 min. at −15°. There was a short induction period. Polymerisation was stopped by addition of cooled hydrochloric acid (1:1). A white polymer (26·5 g., 83%) was obtained.

Under otherwise constant conditions increase in amount of catalyst gave an increase in yield of polymer to a certain limit (see Table in which the period of polymerisation was 120 min. and catalyst was added to the monomer). A threshold concentration of alkoxide was needed to initiate polymerisation, and smaller concentrations of catalyst caused a long induction period.

Catalyst (ml.) ..	1	2	3	5	6	10	15
Polymer (g.) ..	0	7·8	13·3	16·2[a]	21·3	23·2	15·4[b]

[a] 10 ml. of monomer gave only 5.2 g. of polymer (65%) showing a lowering in yield with a relative increase in amount of catalyst; compare *b*.

The surface area of the catalyst was a very important factor. Comparative polymerisations of acrylonitrile by solid sodium methoxide (Matheson, U.S.A.) and by methoxide solution yielded 3 g. and 23·2 g. of polymer respectively. Precipitation of the catalyst from solution by light petroleum gave particles of much greater surface area than that of the solid sodium methoxide. Longer stirring, by increasing the surface area, had a similar effect on yield. Thus, under the conditions of the typical experiment with no stirring and with 5 minutes' stirring gave 16·2 g. and 24·8 g. of polymer, respectively.

Controlled polymerisation occurred only between −40° and 0°. The yield increased strongly with time to about 2 hr. (typical experimental conditions without preliminary stirring of the catalyst; yield 24·8 g.) after which no significant increase was noticed (4·30 hr., yield 25·9 g.).

Such non-polar solvents as light petroleum were the best media for polymerisation. Addition of a polar liquid did not interfere with the polymerisation below a certain limit; thus, with 5 ml. of catalyst (conditions as in the Table), 65 ml. of light petroleum and 10 ml. of methanol, 13 g. of polymer were obtained after 90 min., whilst with 50 ml. of light petroleum and 25 ml. of methanol there was no polymerisation.

Molecular weights of the polymers, as determined from their intrinsic viscosities, were of the order 10^3—10^4.

(*Received*, *August 7th*, 1958.)

The Significance of a Hydrogen-isotope Effect in the Orientation of Electrophilic Substitution in Glyoxaline

By A. GRIMISON and J. H. RIDD

(UNIVERSITY COLLEGE, LONDON, W.C.1)

IN a discussion of the orientation of electrophilic substitution in heterocyclic compounds, the possibility of a kinetic isotope effect in the reaction is usually considered irrelevant. This communication presents evidence to suggest that the detailed mechanism of substitution, as reflected in the presence or absence of a hydrogen-isotope effect, can be the decisive factor in determining the main position of attack.

The kinetic form of the iodination[1] and diazo-coupling[2] of glyoxaline suggests that both reactions require the prior formation of the conjugate base of glyoxaline, and this conclusion is supported by the fact that *N*-methylglyoxaline is unreactive. The kinetic isotope effect in the iodination of glyoxaline and in the coupling of glyoxaline with diazotised sulphanilic acid has been studied by comparing the reaction rates of normal and deuterated glyoxalines. The preparation of 2-deutero-, 4:5-dideutero-, and 2:4:5-trideutero-glyoxaline, and their identification by nuclear magnetic resonance is being described elsewhere.[3] In the iodination of 2:4:5-trideutero-glyoxaline, there is a large kinetic isotope effect (k_H/k_D = 4·4) for both catalysed and uncatalysed

---

[1] Ridd, *J.*, 1955, 1238.

[2] Brown,n, M Duffiaynard, and Ridd, *J.*, 1953, 3937.

[3] Gillespie, Grimison, Ridd, and White, *J.*, 1958, 3228.

reactions. This is similar to the isotope effect in the iodination of the phenoxide ion.[4] In diazo-coupling, the isotope effect is negligible.

The product of the coupling is the 2-azo-compound.[5] The initial product of the iodination has been previously assumed to be the 2-iodo-compound,[6] but direct evidence has been lacking since the main products are the di- and the tri-iodo-compound. However, the studies with the deuteroglyoxalines show that, at least under our conditions, the initial substitution must be mainly at the 4(5)-position: the kinetic isotope effect is present for 4:5-dideuteroglyoxaline, but almost absent for 2-deuteroglyoxaline.

Thus iodination and diazo-coupling lead to different positions of attack, although both apparently occur by substitution in the conjugate base of glyoxaline. This orientational change may occur because the proton loss is partly rate-determining in the iodination. The molecular-orbital calculations offer some justification for this view. The calculations on orientation in the conjugate base of glyoxaline are equivocal: the charge densities suggest that electrophilic substitution should occur at the 2-position, but the localisation energies suggest that such substitution should occur at the 4(5)-position.[7] The charge densities refer to the unperturbed substrate, but the localisation energies refer to a structure further along the reaction co-ordinate, and nearer to the transition state of a reaction in which proton-loss is rate-determining. Hence, of these two reactions, it is the iodination which should certainly not follow the charge densities, and this is the result observed.

These results suggest that for certain substrates it is advisable to consider separately the orientation of those electrophilic substitutions in which proton-loss is partly rate-determining.

(*Received, August* 16*th*, 1958.)

---

[4] Grovenstein and Kilby, *J. Amer. Chem. Soc.*, 1957, **79**, 2972.
[5] Fargher and Pyman, *J.*, 1919, **115**, 217.
[6] Pauly and Arauner, *J. prakt. Chem.*, 1928, **118**, 33.
[7] Bassett and Brown, *J.*, 1954, 2701.

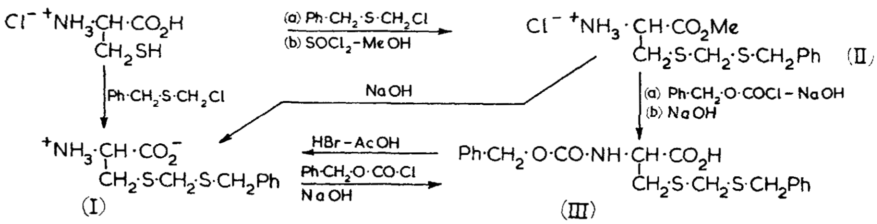
A New Method for the Protection of Thiol Groups

By (Miss) P. J. E. PIMLOTT and G. T. YOUNG
(THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY)

WE report here a new method for the protection of thiol groups, with special application to the synthesis of peptides containing cysteine. By the action of benzylthiomethyl chloride, the thiol is converted into its benzylthiomethyl derivative;[1] such mercaptals are remarkably stable, but are smoothly cleaved by mercuric chloride, giving the mercaptide, from which the thiol may be regenerated in the usual fashion. In the mildness of the conditions required for its removal, the benzylthiomethyl group possesses an important advantage over the classical benzyl group.

L-Cysteine hydrochloride in dried methanol reacted readily with benzylthiomethyl chloride[2] on the boiling-water bath, and after 30 minutes the solution contained a mixture of the hydrochloride of *S*-benzylthiomethyl-L-cysteine (I) and the methyl ester hydrochloride (II). Alkaline hydrolysis of this crude product (A) in aqueous dioxan gave the zwitter-ion (I) as colourless needles, in 70% overall yield, m.p. 193°, $[\alpha]_D^{18\cdot5}$ $-39\cdot8°$ (*c* 0·66 in 2·4N-hydrochloric acid) (Found: C, 51·6; H, 5·8; N, 5·1; S, 25·0. $C_{11}H_{15}O_2NS_2$ requires C, 51·4; H, 5·9; N, 5·5; S, 24·9%). The same compound (I) may also be prepared, advantageously, by reducing L-cystine with sodium in liquid ammonia and adding benzylthiomethyl chloride to the resulting solution.

Treatment of the crude product (A) with thionyl chloride and methanol[3] gave the methyl ester hydrochloride (II) as colourless needles (85% overall yield), m.p. 145—146° (Found: C, 46·7; H, 5·8; N, 4·8. $C_{12}H_{18}O_2NClS_2$ requires C, 46·9; H, 5·9; N, 4·6%).



---

[1] Böhme, Fischer, and Frank, *Annalen*, 1949, **563**, 54.
[2] Wood and du Vigneaud, *J. Biol. Chem.*, 1939, **131**, 267.
[3] Brenner and Huber, *Helv. Chim. Acta*, 1953, **36**, 1109.

The action of benzyl chloroformate and sodium hydroxide on the compound (I) gave *N*-benzyloxycarbonyl-*S*-benzylthiomethyl-L-cysteine (III) as a syrup (95%), from which the crystalline di*cyclo*hexylamine salt was isolated, m.p. 118·5—119°, $[\alpha]_D^{18\cdot5}$ + 6·5° (*c* 1·27 in ethanol) (Found: C, 65·1; H, 7·8; N, 4·7; S, 11·1. $C_{31}H_{44}O_4N_2S_2$ requires C, 65·0; H, 7·7; N, 4·9; S, 11·2%).

To remove the protecting group, *S*-benzylthiomethyl-L-cysteine was dissolved in N-hydrochloric acid by warming, and warm aqueous mercuric chloride was added. The precipitated mercury benzyl sulphide was filtered off, and L-cysteine was regenerated by passing hydrogen sulphide into the filtrate. Oxidation with hydrogen peroxide yielded L-cystine $[\alpha]_D^{16\cdot5}$ −230° (*c* 1·12 in N-hydrochloric acid); extrapolation from Toennies and Lavine's equation[4] gives an identical figure for the specific rotation of pure L-cystine at this temperature. Protection and recovery of the thiol had therefore been effected without loss of optical activity. Further, no racemisation had occurred during the preparation of the other named derivatives, as shown by the following sequence of reactions. The ester hydrochloride (II) was converted into its benzyloxycarbonyl derivative, which was hydrolysed to the acid (III); this, on treatment with hydrogen bromide in acetic acid, gave authentic *S*-benzylthiomethyl-L-cysteine.

The *S*-benzylthiomethyl protecting group appears to be completely stable under the conditions normally used in peptide synthesis. For example, *S*-benzylthiomethyl-L-cysteine was recovered unchanged after treatment with 2N-sodium hydroxide at room temperature for 24 hours, with 2N-hydrogen bromide in acetic acid at room temperature for 15 hours, or with 2N-hydrochloric acid at 60° for 5 hours. In each experiment the nitroprusside test was negative.

Compounds (II) and (III) are clearly key intermediates for the synthesis of peptides containing cysteine, and they should be especially valuable where the use of sodium in liquid ammonia, required for the cleavage of *S*-benzyl groups, is undesirable.

One of us (P. J. E. P.) thanks the Department of Scientific and Industrial Research for a Research Studentship.

(*Received, July 28th*, 1958.)

---

[4] Toennies and Lavine, *J. Biol. Chem.*, 1930, **89**, 153.

The Gas-phase Halogenation of Benzonitrile: A Novel Substitution Pattern

By J. W. ENGELSMA and E. C. KOOYMAN
(KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM.
N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ)

PREVIOUS work[1] has indicated that the halogenation of halogenobenzenes in the gas phase leads to dihalogenobenzenes showing a peculiar isomer distribution characterised by large proportions of *meta*-constituent (60–68%).

We have now studied the gas-phase chlorination and bromination of benzonitrile. This seemed of interest in view of the different substituent effects caused by the cyano-group (−*I*, −*M*) compared with those of the halogen atom (−*I*, +*M*).[2]

Using experimental procedures similar to those described earlier,[1] we carried out chlorinations at 300—400° and brominations at 425—500°. Monohalogenobenzonitriles were isolated in high yields by fractional distillation. Formation of carbon was slight; balances of aromatic compounds were better than 90%, compositions of small intermediate fractions being determined mass-spectrometrically. Isomer ratios were established by infrared analyses based on the pure isomers. In addition, competitive chlorination was carried out with an equimolar mixture of chlorobenzene and benzonitrile.

As in the halogenations of the halogenobenzenes, isomer ratios showed little dependence on temperature. They were markedly different, however, from those observed for other substitution reactions of benzonitrile. Some of our results are given in the Table.

Distribution patterns of isomeric halogenobenzonitriles appear to be similar to those of dihalogenobenzenes obtained by gas-phase halogenation; in the latter case, somewhat higher *meta*:*para*-ratios were observed. Isomer ratios in the bromination of benzonitrile seem to be nearly identical with those in chlorination.

The results of the competitive run indicate that overall chlorination rates of chlorobenzene and benzonitrile are of the same order of magnitude; in this run, isomer ratios were about the same as in the separate halogenations.

---

[1] Engelsma, Kooyman, and van der Bij, *Rec. Trav. chim.*, 1957, **76**, 325; Engelsma and Kooyman, *Proc. k. ned. Akad. Wetenschap.*, 1957, *B* **60**, 321.

[2] Cf., *e.g.*, Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N.Y. 1953, Chapter VI, Section 20.

Gas-phase halogenations and other substitution reactions of benzonitrile.

Reaction	Aromatic compound	Temp.	Isomer distribution (%) in substitution products *ortho*	*meta*	*para*	Remarks
Gas-phase chlorination	PhCN	350°	18	49·5	32·5	(*a*)
Gas-phase chlorination	PhCN } 1:1	350	16	53	31	Conversion 39% (*b*)
	PhCl		8	67·5	24·5	Conversion 37% (*b*)
Gas-phase bromination	PhCN	475	21	50	29	—
Liquid-phase nitration[3]	PhCN	−20	17·3	80·5	2·1	Cationic substn.
		0	12·5	86·5	0·8	
Liquid-phase phenylation[4]	PhCN	70	60	10	30	Homolytic substn.

(*a*) Isomer distributions showed a slight increase in the *ortho*-percentages and a decrease in *meta*-contents with increasing temperatures, 25% *ortho*, 45% *meta* and 30% *para* being found at 450°.
(*b*) % Molar of aromatic compound converted, based on mass-spectrometric analysis of product isolated.

The above facts are difficult to account for in terms of known substitution mechanisms and substituent effects. It is believed that one or more of the reaction steps involved are reversible and that, as suggested earlier, thermodynamic stabilities may also play a part in determining isomer distributions rather than kinetic factors only, thereby leading to a novel substitution pattern.

(*Received, July 2nd*, 1958.)

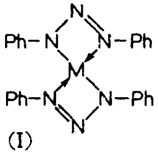
---

[3] Wibaut and van Strik, *Rec. Trav. chim.*, 1958, **77**, 316; cf. Baker, Cooper, and Ingold, *J.*, 1928, 436.
[4] Dannley and Gregg, jun., *J. Amer. Chem. Soc.*, 1954, **76**, 2997.

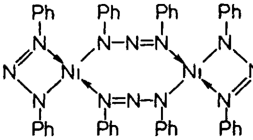
A Diamagnetic Binuclear Compound of Bivalent Copper

By C. M. HARRIS and R. L. MARTIN
(DEPARTMENT OF INORGANIC CHEMISTRY, N.S.W. UNIVERSITY OF TECHNOLOGY)

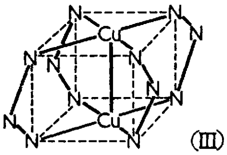
DWYER[1] has shown that diazoaminobenzene, Ph·NH·N:N·Ph, is an effective chelating agent with the metals Ag^{I}, Cu^{I}, Cu^{II}, Ni^{II}, and Pd^{II}, the bivalent metals forming biscomplexes, M^{II} (chelate)$_2$ which were formulated as non-electrolytes. The Pd^{II} and Cu^{II} complexes were considered to possess the uninuclear structure (I) and the diamagnetic and dimeric Ni^{II} compound the binuclear arrangement (II).[2]



(I)



(II)



(III)

Recently we have found the dark green copper(II) derivative is also dimeric (from crysoscopic measurements) and diamagnetic in benzene solution. There is strong evidence that this compound is, in fact, a derivative of cupric copper, for its absorption spectrum is characterised by a broad absorption maximum at 6250 Å which is typical of nitrogen-ligated copper(II) compounds.[3] Bis(diazoaminobenzene)copper(II) is also diamagnetic in the solid state between 80 and 400°K.

We believe that the diamagnetism and the dimeric nature of bis(diazoaminobenzene)copper(II) reveal that this molecule adopts a binuclear configuration, similar to that of copper(II) acetate,[4] in preference to a structure like (II). If this is correct, the diamagnetism arises from direct intramolecular exchange between two copper atoms, supported virtually in contact with one another, by four bridging Ph·N_3·Ph groups as shown in (III) (the eight phenyl groups have been omitted for clarity).

It is interesting to note that the spin paramagnetism, normally associated with the cupric ion, is completely quenched (μ = 0 B.M.) in this compound, in marked contrast to the partial quenching observed[5] in copper(II) alkanoates (μ = 1·38 B.M.), which have a similar structure.

It now seems possible that the diamagnetic nickel(II) compound may also possess a structure analogous to (III).

(*Received, July 8th*, 1958.)

---

[1] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78.
[2] Dwyer and Mellor, *J. Amer. Chem. Soc.*, 1941, **63**, 81.
[3] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.
[4] Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.
[5] Martin and Waterman, *J.*, 1957, 2545.

THE CHEMICAL SOCIETY

PROGRAMME OF MEETINGS*

OCTOBER, 1958 TO JANUARY, 1959

London

Thursday, October 16th, 1958, at 7.30 p.m.
Centenary Lecture, "Spectra of Free Radicals," by Dr. G. Herzberg, F.R.S. To be given in the Large Chemistry Lecture Theatre, Imperial College of Science and Technology, South Kensington, S.W.7.

Thursday, November 6th, at 7.30 p.m.
Irving Langmuir Memorial Lecture. To be given by Sir Eric Rideal, M.B.E., M.A., D.Sc., F.R.S., in the Rooms of the Society, Burlington House, London, W.1.

Thursday, November 13th, at 7.30 p.m.
Centenary Lecture, "Chemical and Technological Aspects of ^{15}N-Chemistry," by Professor Dr. K. Clusius. To be given in the Lecture Theatre, The Royal Institution, Albemarle Street, W.1.

Thursday, December 11th, at 7.30 p.m.
Tilden Lecture, "The Triplet State in Chemistry," by Professor G. Porter, M.A., Ph.D. To be given in the Rooms of the Society, Burlington House, W.1.

Thursday, January 15th, 1959, at 7.30 p.m.
Tilden Lecture, "Nucleotides and Bacterial Cell Wall Components," by Professor J. Baddiley, D.Sc., Ph.D. To be given in the Large Chemistry Lecture Theatre, Imperial College of Science and Technology, South Kensington, S.W.7.

Aberdeen

(Meetings will be held at Marischal College, unless otherwise stated.)

Friday, October 10th, 1958, at 7.30 p.m.
Lecture, "Enzyme Systems in Polysaccharide Degradation," by Professor I. A. Preece. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Friday, October 17th, at 5 p.m.
Lecture, "The Mode of Action of Tetra-ethyl-lead as an Anti-knock," by Professor A. D. Walsh, Ph.D. Joint Meeting with the Royal Institute of Chemistry, to be held at Dounreay Experimental Reactor Establishment.

Wednesday, November 12th, at 7.45 p.m.
Lecture, "Constructional Details of a Petersen Tower Sulphuric Acid Plant," by Mr. J. P. A. McDonald. Joint Meeting of the Royal Institute of Chemistry and the Society of Chemical Industry.

Friday, December 12th, at 7.45 p.m.
Lecture, "Silicones. An Introduction to their Chemistry and Applications," by Dr. G. G. Freeman, F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, January 15th, 1959, at 7.30 p.m.
Lecture, "Some Recent Developments in the Porphyrin Field," by Professor G. W. Kenner, M.Sc., Ph.D. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Birmingham

(Meetings will be held in the Chemistry Department, The University.)

Friday, October 24th, 1958, at 4.30 p.m.
Lecture, "Aspects of Chemotherapy," by Dr. F. L. Rose, O.B.E., F.R.I.C., F.R.S. Joint Meeting with Birmingham University Chemical Society.

Friday, November 14th, at 4.30 p.m.
Lecture, "The Chemistry and Handling of Polonium," by Dr. K. W. Bagnall. Joint Meeting with Birmingham University Chemical Society.

Friday, January 16th, 1959, at 4.30 p.m.
Lecture, "Protein Biosynthesis," by Dr. C. E. Dalgliesh, M.A., A.R.I.C. Joint Meeting with Birmingham University Chemical Society.

Bristol

(Meetings will be held in the Chemistry Department, The University, unless otherwise stated.)

Thursday, October 2nd, 1958, at 6.30 p.m.
Lecture, "Rocket Fuels," by Dr. W. G. Parker. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Friday, October 10th, at 7 for 7.30 p.m.
Dinner and Dance, jointly with the Royal Institute of Chemistry and the Society of Chemical Industry. To be held at The Royal Hotel, Bristol 1.

---

* Reprints may be obtained from the General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

Thursday, October 23rd, at 7.30 p.m.
Lecture, "Plastics in the Shoe Trade," by Mr. J. Bunten. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at the Technical College, Brunswick Road, Gloucester.

Thursday, October 23rd, at 5.15 p.m.
Lecture, "Ruthenium Complexes," by Dr. J. M. Fletcher, M.A. Joint Meeting with the Student Chemical Society.

Thursday, October 30th, at 6.30 p.m.
Lecture, "Transition-metal Complex Hydrides," by Professor G. Wilkinson, Ph.D., A.R.C.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, November 6th, at 5.15 p.m.
Lecture, "Unsolved Problems of the Electrical Double Layer," by Professor D. C. Grahame. Joint Meeting with the Student Chemical Society.

Thursday, November 13th.
Social Evening, jointly with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, November 20th, at 5.15 p.m.
Lecture, "Recent Developments in the Chemistry of *cyclo*Propane and *cyclo*Butane Derivatives," by Professor C. H. Hassall, Ph.D., F.R.I.C. Joint Meeting with the Student Chemical Society.

Thursday, November 20th, at 6.30 p.m.
Lecture, "Plastics in Packaging," by Mr. F. A. Paine. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, November 27th, at 5.15 p.m.
Lecture, "Crystalline High Polymers," by Professor C. E. H. Bawn, C.B.E., Ph.D., F.R.S. Joint Meeting with the Student Chemical Society.

Thursday, December 4th, at 6.30 p.m.
Lecture, "Titanium for Chemical Plant," by Dr. K. W. J. Bowen. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Wednesday, January 7th, 1959.
Christmas Lecture of the Royal Institute of Chemistry entitled, " Chromatography," by Dr. F. H. Pollard. To be given at Royal Fort, Bristol 8.

Thursday, January 22nd, at 6.30 p.m.
Lecture, "Safety in the Use and Disposal of Radioactive Materials," by Dr. B. A. J. Lister, D.I.C., A.R.C.S., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, January 29th, at 6.30 p.m.
Society of Chemical Industry Jubilee Memorial Lecture entitled, "Colonial Research—Products and Pesticides," by Dr. R. A. E. Galley, D.I.C., A.R.C.S., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Cambridge

(Meetings will be held in the University Chemical Laboratory, Lensfield Road.)

Friday, October 24th, 1958, at 8.30 p.m.
Lecture, "Crystal Compounds of Graphite," by Professor A. R. Ubbelohde, D.Sc., F.R.S. Joint Meeting with the University Chemical Society.

Friday, November 7th, at 8.30 p.m.
Lecture, "Some Reactions of Nitrous Acid," by Sir Christopher Ingold, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the University Chemical Society.

Tuesday, November 18th, at 2.30 p.m.
Lecture, "The Physicochemical Investigation of Tautomerism in *N*-Heteroaromatic Systems," by Dr. S. F. Mason, M.A.

Friday, November 28th, at 8.30 p.m.
Lecture, "Natural Polyacetylenes," by Professor E. R. H. Jones, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the University Chemical Society.

Durham

(Meetings will be held in the Science Laboratories, The University.)

Monday, October 13th, 1958, at 5 p.m.
Lecture, "Structural Chemistry and Synthetic Fibres," by Dr. I. Goodman, M.Sc., A.R.T.C. Joint Meeting with the Durham Colleges Chemical Society.

Thursday, October 30th, at 5 p.m.
Lecture, "Homolytic Aromatic Substitution," by Professor D. H. Hey, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the Durham Colleges Chemical Society.

Monday, November 10th, at 5 p.m.
Lecture, "Bond Dissociation Energies in Polyatomic Molecules," by Dr. H. A. Skinner. Joint Meeting with the Durham Colleges Chemical Society.

Monday, November 24th, at 5 p.m.
Lecture, "Some Aspects of the Chemical Structure of Proteins and Nucleic Acids," by Professor H. D. Springall, M.A., D.Phil., A.R.I.C. Joint Meeting with the Durham Colleges Chemical Society.

Monday, January 26th, 1959, at 5 p.m.
Lecture, "Structural Chemistry of Some Complex Halides," by Professor R. S. Nyholm, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the Durham Colleges Chemical Society.

Edinburgh

(Meetings will be held at the North Bristol Hotel, unless otherwise stated.)

Thursday, October 30th, 1958, at 7.30 p.m.
Lecture, "Recent Investigations at the Torry Research Station on the Preservation of Fish for Food," by Dr. A. Banks. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, November 13th, at 7.30 p.m.
Lecture, "Packaging," by Dr. G. L. Riddell, F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, December 4th, at 7.30 p.m.
Lecture, "Recent Studies in Relation to Biosynthesis," by Professor A. J. Birch, D.Phil., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, January 8th, 1959, at 7.30 p.m.
Lecture, "Fluidisation," by Dr. J. F. Richardson. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Tuesday, January 27th, at 7.30 p.m.
Lecture, "The Use of Deuterium in the Study of Catalytic Hydrogenation," by Professor C. Kemball, Ph.D., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, and Edinburgh University Chemical Society, to be held in the Biochemistry Lecture Theatre, Teviot Place.

Exeter

(Meetings will be held in the Washington Singer Laboratories, Prince of Wales Road.)

Friday, October 24th, 1958, at 5 p.m.
Lecture, "Some Recent Advances in the Chemistry of the Vitamins D," by Professor B. Lythgoe, Ph.D., F.R.I.C., F.R.S.

Friday, November 28th, at 5 p.m.
Lecture, "Porous Crystals as Sorbents and Molecular Sieves," by Professor R. M. Barrer, D.Sc., F.R.I.C., F.R.S.

Glasgow

(Meetings will be held in the Chemistry Department, The University.)

Thursday, October 23rd, 1958, at 4 p.m.
Lecture, "Some Problems in the Chemistry and Biochemistry of Plant Gums and Mucilages," by Professor E. L. Hirst, C.B.E., D.Sc., LL.D., F.R.S. Joint Meeting with the Alchemists' Club and the Andersonian Society.

Friday, November 21st, at 7.15 p.m.
Meeting for the Reading of Original Papers.

Thursday, December 4th, at 4 p.m.
Lecture, "Polyhedra in Chemistry," by Dr. A. F. Wells, M.A. Joint Meeting with the Alchemists' Club.

Friday, January 16th, 1959, at 7.15 p.m.
Lecture, "Some Recent Developments in the Porphyrin Field," by Professor G. W. Kenner, M.Sc., Ph.D.

Hull

(Meetings will be held in the Organic Chemistry Lecture Theatre, The University.)

Thursday, October 23rd, 1958, at 6 p.m.
Lecture, "Metal–Ammonia Reductions," by Professor A. J. Birch, D.Phil., F.R.S. Joint Meeting with the University Student Chemical Society.

Tuesday, November 11th, at 5 p.m.
Lecture, "Explosives," by Dr. B. D. Shaw, M.M., T.D. Joint Meeting with the University Student Chemical Society.

Thursday, November 20th, at 7.30 p.m.
Lecture, "Alkyls and Aryls of Transition Metals," by Dr. J. Chatt, M.A., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry.

Irish Republic

Wednesday, December 17th, 1958, at 7.45 p.m.
Lecture, "The Polysaccharides Today," by Professor P. S. O Colla, Ph.D., D.Sc.. F.I.C.I., M.R.I.A. To be given in the Chemistry Department, University College, Dublin.

Liverpool

(Meetings will be held in the Department of Inorganic and Physical Chemistry, The University.)

Tuesday, October 21st, 1958, at 5 p.m.
Centenary Lecture, "Spectra of Free Radicals," by Dr. G. Herzberg, F.R.S.

Thursday, November 27th, at 5 p.m.
Lecture, "Recent Developments in the Chemistry of *cyclo*Propane and *cyclo*Butane Derivatives," by Professor C. H. Hassall, Ph.D., F.R.I.C. Joint Meeting with Liverpool University Chemical Society.

Thursday, January 29th, 1959, at 5 p.m.
Lecture, "Organic Semiconductors," by Professor D. D. Eley, Sc.D., Ph.D. Joint Meeting with Liverpool University Chemical Society.

Manchester

Monday, November 10th, 1958, at 3 p.m.
Centenary Lecture, "Chemical and Technological Aspects of ^{15}N-Chemistry," by Professor Dr. K. Clusius. To be given in the Large Chemistry Lecture Theatre, The University.

Newcastle upon Tyne

(Meetings will be held in the Chemistry Department, King's College.)

Friday, October 31st, 1958, at 5.30 p.m.
Bedson Club Lecture, "The Acetylenic Approach to the Synthesis of Natural Products," by Professor R. A. Raphael, D.Sc., Ph.D., F.R.I.C.

Wednesday, November 12th, at 5.30 p.m.
Centenary Lecture, "Chemical and Technological Aspects of ^{15}N-Chemistry," by Professor Dr. K. Clusius.

Friday, November 21st, at 5.30 p.m.
Bedson Club Lecture, "Recent Developments in Quantum Chemistry," by Professor H. C. Longuet-Higgins, M.A., D.Phil., F.R.S.

Tuesday, January 20th, 1959, at 5.30 p.m.
Tilden Lecture, "The Triplet State in Chemistry," by Professor G. Porter, M.A., Ph.D.

Friday, January 23rd, at 5.30 p.m.
Bedson Club Lecture, "The Molecular and Crystal Structure of Benzene," by Professor E. G. Cox, D.Sc., F.R.I.C., F.R.S.

Northern Ireland

(Meetings will be held at the Queen's University, Belfast.)

Tuesday, October 28th, 1958, at 7.45 p.m.
Lecture, "The Extrusion of Sulphur from Organic Molecules," by Dr. J. D. Loudon, A.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

Thursday, November 27th, at 7.45 p.m.
Lecture, "Analytical Applications of Co-ordination Compounds," by Dr. T. S. West. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry.

North Wales

Thursday, October 30th, 1958, at 5.45 p.m.
Lecture, "The Scientific Examination of Paintings and Antiquities," by Dr. A. E. A. Werner, M.A., A.R.I.C. Joint Meeting with the University College of North Wales Chemical Society, to be held in the Department of Chemistry, University College of North Wales, Bangor.

Thursday, November 27th, at 5.45 p.m.
Lecture, "Reaction Mechanisms," by Professor E. D. Hughes, Ph.D., D.Sc., F.R.I.C., F.R.S. Joint Meeting with the University College of North Wales Chemical Society, to be held in the Department of Chemistry, University College of North Wales, Bangor.

Thursday, November 27th, at 7.30 p.m.
Lecture, "Raman Spectra and Molecular Structure," by Dr. L. A. Woodward, M.A. Joint Meeting with the University College of Wales Chemical Society, to be held in the Edward Davies Chemical Laboratories, Aberystwyth.

Nottingham and Leicester

Tuesday, November 11th, 1958, at 8 p.m.
Lecture, "Water Repellency," by Professor N. K. Adam, Sc.D., F.R.I.C., F.R.S. Joint Meeting with the Society of Chemical Industry, to be held in the Chemistry Department, The University, Nottingham.

Tuesday, November 18th, at 4.30 p.m.
Lecture, "Ionic Polymerisation," by Professor C. E. H. Bawn, C.B.E., Ph.D., F.R.S. Joint Meeting with the University of Leicester Chemical Society, to be held at the University, Leicester.

Monday, December 1st, at 4.30 p.m.
Lecture, "Stereochemistry and the Transition Metals," by Professor R. S. Nyholm, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the University of Leicester Chemical Society, to be held at the University, Leicester.

Tuesday, December 9th, at 5 p.m.
Lecture, "The Chemistry of the Tannins," by Professor R. D. Haworth, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the University of Nottingham Chemical Society, to be held in the Chemistry Department, The University, Nottingham.

Tuesday, January 27th, 1959, at 8 p.m.
Lecture, "The Growth of Fluorocarbon Chemistry," by Professor R. N. Haszeldine, D.Sc., Ph.D., F.R.I.C Joint Meeting with the Royal Institute of Chemistry, to be held in the Chemistry Department, The University, Nottingham.

Oxford

(Joint Meetings with Oxford University Alembic Club to be held in the Inorganic Chemistry Laboratory.)

Monday, October 27th, 1958, at 8.15 p.m.
Lecture, "Fatty Acids," by Dr. J. C. Smith, M.A.

Monday, November 10th, at 8.15 p.m.
Lecture, "Aromaticity," by Professor D. P. Craig, M.Sc.

Monday, November 24th, at 8.15 p.m.
Lecture, "The Stereochemistry of some Ionic Solids," by Dr. L. E. Orgel.

St. Andrews and Dundee

Friday, October 17th, 1958, at 5.15 p.m.
Lecture, "Alchemy, Alchemists, and Music," by Professor J. Read, Ph.D., Sc.D., F.R.S. Joint Meeting with the University Chemical Society, to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Thursday, October 23rd, at 5.5 p.m.
Centenary Lecture, "Spectra of Free Radicals," by Dr. G. Herzberg, F.R.S. To be given in the Chemistry Department, Queen's College, Dundee.

Friday, October 31st, at 5.15 p.m.
Lecture, "The Reactions and Spectra of the Complexes formed between Sodium and Unsaturated Organic Molecules," by Dr. E. Warhurst, M.Sc. Joint Meeting with the University Chemical Society, to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Tuesday, December 9th, at 5.5 p.m.
Lecture, "The Effects of the Size and Shape of Drug Molecules upon Drug Action," by Dr. H. R. Ing, F.R.S. To be given in the Chemistry Department, Queen's College, Dundee.

Friday, January 30th, 1959, at 5.15 p.m.
Lecture, "Some Aspects of the Chemistry of Naturally Occurring Quinones," by Dr. R. H. Thomson, F.R.I.C. Joint Meeting with the University Chemical Society, to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Sheffield

(Meetings will be held in the Chemistry Department, The University, unless otherwise stated.)

Monday, October 20th, 1958, at 4.30 p.m.
Centenary Lecture, "Spectra of Free Radicals," by Dr. G. Herzberg, F.R.S. Joint Meeting with the Royal Institute of Chemistry and Sheffield University Chemical Society.

Tuesday, October 28th, at 7 p.m.
Lecture, "Some Aspects of Corrosion in the Canning Industry," by Dr. H. Liebmann. Joint Meeting with the Royal Institute of Chemistry and Sheffield Metallurgical Club, to be held at the British Iron and Steel Research Association, Hoyle Street, Sheffield.

Thursday, November 6th, at 4.30 p.m.
Lecture, "Some Photochemical Re-arrangements," by Professor D. H. R. Barton, D.Sc., F.R.S. Joint Meeting with the Royal Institute of Chemistry and Sheffield University Chemical Society.

Thursday, November 27th, at 7.30 p.m.
Lecture, "Organic Complexing Agents in Analysis," by Dr. H. M. N. H. Irving, D.Sc., D.Phil., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and Sheffield University Chemical Society.

Wednesday, December 10th, at 7.30 p.m.
Lecture, "Some Aspects of Power Station Chemistry," by Mr. L. A. Huntingdon, A.M.C.T., A.R.I.C. Joint Meeting with the Royal Institute of Chemistry, to be held at the Technical College, Rotherham.

Thursday, January 22nd, 1959, at 4.30 p.m.
Lecture, "The Acetylenic Approach to the Synthesis of Natural Products," by Professor R. A. Raphael, Ph.D., D.Sc., A.R.I.C. Joint Meeting with the Royal Institute of Chemistry and Sheffield University Chemical Society.

Southampton

(Meetings will be held in the Chemistry Department, The University, unless otherwise stated.)

Friday, October 10th, 1958, at 5 p.m.
Lecture, "The Education and Training of Chemists," by Dr. D. W. Kent-Jones, F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and Southampton University Chemical Society.

Friday, October 17th, at 5 p.m.
Centenary Lecture, "Spectra of Free Radicals," by Dr. G. Herzberg, F.R.S. To be given at the Institute of Education, The University.

Friday, November 14th, at 5 p.m.
Lecture, "Aryl Silicon Compounds and Aromatic Reactivity," by Dr. C. Eaborn, A.R.I.C. Joint Meeting with Southampton University Chemical Society.

Friday, November 28th, at 5 p.m.
Lecture, "The Theory of Absorption Spectra of the Transition-metal Compounds," by Dr. J. S. Griffith. Joint Meeting with Southampton University Chemical Society.

Friday, January 30th, 1959, at 5 p.m.
Tilden Lecture, "The Triplet State in Chemistry," by Professor G. Porter, M.A., Ph.D.

South Wales

Monday, October 20th, 1958, at 5.30 p.m.
Lecture, "Recent Advances in Nuclear Resonance," by Dr. R. E. Richards, M.A. To be given in the Chemistry Department, University College, Cardiff.

Monday, October 20th, at 5.30 p.m.
Lecture, "Synthesis of Nucleotide Coenzymes," by Professor G. W. Kenner, M.Sc., Ph.D. Joint Meeting with the University College of Swansea Chemical Society, to be held in the Chemistry Department, University College, Swansea.

Monday, November 10th, at 5.30 p.m.
Lecture, "Natural Tannins," by Professor R. D. Haworth, D.Sc., F.R.I.C., F.R.S. To be given in the Chemistry Department, University College, Cardiff.

Monday, November 17th, at 5.30 p.m.
Lecture, "Applications of Raman Spectra to Chemical Problems," by Dr. L. A. Woodward, M.A. Joint Meeting with the University College of Swansea Chemical Society, to be held in the Chemistry Department, University College, Swansea.

Monday, December 1st, at 3 p.m.
Lecture, "Recent Developments in the Study of Ionic Solutions," by Professor K. W. Sykes, M.A., D.Phil. Joint Meeting with the University College of Swansea Chemical Society, to be held in the Chemistry Department, University College, Swansea.

Monday, January 26th, 1959, at 5.30 p.m.
Lecture, "Crystalline High Polymers," by Professor C. E. H. Bawn, C.B.E., Ph.D., F.R.S. To be given in the Chemistry Department, University College, Cardiff.

NEWS AND ANNOUNCEMENTS

Corday-Morgan Commonwealth Fellowship.—The Fellowship for the year 1958–59 has been awarded to Miss Rama Bhattacharya, who has, since January, 1957, been Junior Research Fellow of the Council of Scientific and Industrial Research, India, at the University College of Science, Calcutta. The Corday-Morgan Fellowship will be tenable in the Department of Chemistry, University College, London, under Professor Sir Christopher Ingold.

The Corday-Morgan Commonwealth Fellowship is not offered for the following academic year, 1959–60.

Local Representatives.—North-Eastern Area. In order to improve the service to Fellows in North-east England the areas of responsibility have now been re-defined as follows:

Durham	*Dr. F. Glockling*
Newcastle	*Dr. F. J. McQuillin*
Tees-side	*Dr. I. J. Faulkner*

It is envisaged that although meetings will be arranged in each of the three parts of the area, a close liaison will be maintained between the Local Representatives, and Fellows living in the area will be fully informed of all activities that may be arranged.

Fellows living near Tees-side are invited to attend a General Meeting which will be held at Constantine Technical College, Middlesbrough, at 7.30 p.m. on Tuesday, September 30th, 1958, when the proposed arrangements will be discussed.

New System for Control of Research Programmes at Two D.S.I.R. Laboratories.—Changes in organisation affecting two D.S.I.R. Laboratories are announced. Small Steering Committees are being set up to bear responsibility for the research programmes at the new Warren Spring Laboratory, at Stevenage, and at the recently re-named National Chemical Laboratory, at Teddington.

Research Boards, which the Steering Committees replace, were hitherto responsible to the Research Council, but there was not necessarily any common membership. Under the new arrangement the Steering Committees are full committees of the Research Council and the Chairman of the Committees are members of the Council.

In addition to the Chairman there will be four members of each Committee: two from industry with experience in research management, as well as the Secretary of D.S.I.R. and the Director of the Laboratory. The Committees are empowered to set up specialist sub-committees as necessary, to advise on the different fields of research covered by the Laboratories.

The Warren Spring Laboratory Steering Committee is as follows: *Chairman*, Sir Harry Jephcott. *Members*, Dr. R. Holroyd, Mr. D. A. Oliver, the Secretary of D.S.I.R., and the Director of the Warren Spring Laboratory.

The National Chemical Laboratory Steering Committee, which will assume responsibility from October 1st, 1958, will be as follows: *Chairman*, Professor C. E. H. Bawn. *Members*, Dr. F. Roffey, Mr. B. Topley, the Secretary of the D.S.I.R., and the Director of the National Chemical Laboratory.

Symposium.—The 4th International Symposium on the Reactivity of Solids will be held in Amsterdam on May 30th to June 4th, 1960, and will be organised by the Netherlands Ceramic Society. Further details may be obtained from the Secretariat, 4th International Symposium on the Reactivity of Solids, Technische Hogeschool Eindhoven, Insulindelaan 2, Eindhoven.

Deaths.—We regret to announce the death of Professor Joliot-Curie, an Honorary Fellow of the Society, on August 14th 1958; also the deaths of the following Fellows: *Mr. Reginald Gordon Doyle* (10.8.58), a Fellow since 1919, and *Dr. Ernest Bowman Ludlam* (13.8.58,) formerly Lecturer at the University of Edinburgh.

Personal.—*Dr. S. Krishna*, Scientific Adviser in London to the High Commission for India and Scientific Liaison Officer for India, will relinquish his post on August 18th. Dr. Krishna's successor has not yet been named. *Mr. B. Sen*, Assistant Educational Adviser, India House, Aldwych, London, will be temporarily in charge of the Department.

The Rt. Hon. the Earl of Halsbury has accepted an invitation to remain in office as President of the Institution of Production Engineers for 1958–59. He will retire as Managing Director of the National Research Development Corporation on March 31st, 1959.

Dr. R. H. Marriott has been elected President of the Society of Cosmetic Chemists of Great Britain.

Mr. E. E. Ayling has been appointed Senior Lecturer in Chemistry at the University College of Swansea.

Dr. A. M. Cook, Senior Lecturer in Pharmaceutics at the School of Pharmacy, London, has been appointed to the University Readership in Pharmaceutics tenable at that School.

Dr. H. J. Dothie has been appointed Head of the Physical Chemistry Section, Tropical Products Institute, with effect from August 1st.

Dr. R. J. Gillespie has relinquished his post at University College, London, on appointment as Associate Professor of Chemistry at McMaster University, Hamilton, Ontario.

Dr. John B. Jepson has been granted leave of absence by the Middlesex Hospital Medical School to be Visiting Scientist for one year from November at the National Heart Institute, Bethesda, Maryland.

Dr. D. D. Perrin has been appointed Senior Research Fellow in the Department of Medical Chemistry, the Australian National University, Canberra.

Dr. D. P. Dodgson has been appointed Chief Chemist to Durham Chemicals Ltd.

Mr. R. Llewellyn Rees has been appointed Director of Research and Development (Operations) to the Central Electricity Generating Board.

OBITUARY NOTICES

JULIAN LEVETT BAKER

(1873—1958)

Julian Levett Baker was born on February 24th, 1873, in London and educated at the City of London School and later at Finsbury Technical College under H. E. Armstrong. Having qualified as an Associate of the Institute of Chemistry in 1894 (Fellow in 1897) he started his professional career with the Beetroot Sugar Association under A. R. Ling, succeeding him as chief chemist in 1898. In 1900 he became Chemist to Combe's Brewery, Long Acre, and in due course chief chemist to Watney, Combe and Reid.

His first appearance as an author of original work was in 1895 (*Trans.*, 1895, **67**, 702) when the first of three papers on "The action of diastase on starch" by A. R. Ling and J. L. Baker appeared, the others following in the *Journal* in 1895 and 1897. Curiously, his last paper (*J. Inst. Brewing*, 1939) was on virtually the same subject, the dextrins and maltodextrins formed by the action of malt diastase on starch. In the first group of papers the existence of Lintner's isomaltose among the fission products was confirmed. But it was shown that mixtures of "maltodextrin β" and maltose from which it had been incompletely freed could simulate isomaltose. This accounted for some of the conflicting claims made by previous workers. The controversy as to the existence or non-existence of isomaltose in starch–amylase fission products was raging afresh in 1927, but it has since been settled in favour of isomaltose, which is taken to be composed of two glucopyranose residues linked by the α-1:6-linkage.

Later communications to the *Journal* were with his colleague H. F. E. Hulton and concerned aspects of the amylase–starch problem (*J.*, 1914, **105**, 1529; 1921, **119**, 805; 1922, **121**, 1929; 1929, 1655). There was also one on a malt enzyme which attacks "furfuroids" (pentosans). But Baker's most important contribution was the paper in 1902 (*Trans.*, 1902, **81**, 1177) on the formation of α-amylodextrin, the limit dextrin remaining after the fission of maltose from starch to completion by β-amylase has been completed. This dextrin has throughout figured prominently in starch–amylase work, even in recent years. It had previously been described as erythrogranulose by Wissmann (1895) but the information had remained confined to a thesis and was unpublished and unknown for over thirty years.

A number of papers appeared also in *J. Inst. Brewing*, perhaps an outstanding one (with H. F. E. Hulton and F. E. Day) in 1912 being the identification of *Bacterium aceti viscosum*, a slime-forming bacterium, pathogenic in beer. Its association with what is now known as *Acetobacter* and its tolerance to hop-antiseptics were quite contrary to general opinion at that time and for long afterwards, but turned out to be correct. Another piece of work concerned the successful use of a mixture of brewers' and bakers' yeast for bread-making: this was during the 1914—1918 war.

One text book, "The Brewing Industry," appeared in 1905.

Baker was very active in the scientific societies: honorary secretary of the Institute of Brewing, 1908—1917, and of the London section of the Society of Chemical Industry, 1903—1909; Editor of the Analyst, 1906—1920, and of the Journal of the Institute of Brewing, 1920—1949; member of the Council of the Institute of Brewing, 1907—1951, and a vice-president. He examined in brewing for the University of Birmingham.

The greatest honour he received was the award of the Horace Brown Medal of the Institute of Brewing (1948), joining the list commenced by his teacher, H. E. Armstrong.

Baker was a man of great charm and a good friend and counsellor, especially to young men. He died in Maidenhead in February, 1958.

In 1901 he married Evelyn Daniels who died in 1945. He leaves two sons and a daughter.

R. H. HOPKINS.

ARTHUR HENRY FORD-MOORE

1896—1958

ARTHUR FORD-MOORE, a Senior Principal Scientific Officer at the Chemical Defence Experimental Establishment, Porton, was born at Ealing, Middlesex on October 11th, 1896, and died suddenly at his home in Salisbury on May 29th, 1958. After service as a Captain with the London Regiment in Palestine between 1915 and 1919 he graduated from Trinity College, Cambridge and joined the Chemical Defence Experimental Station (now C.D.E.E.) direct from the University, in 1921. He was employed there until the time of his death, except for a short break between 1942 and 1944, when he collaborated with H. R. Ing at the Dyson-Perrins Laboratory at Oxford.

Although security considerations restricted publication of his work, Ford-Moore achieved wide recognition and was internationally accepted as an authority on chemical defence problems, and in particular on the chemistry of organic compounds containing phosphorus and sulphur. His work embraced not only these but also a wide variety of other problems in synthetic chemistry. The first published account of his research work appeared in 1934 in a paper on the vanillylamides of fatty acids. Since 1946 he published nine papers in the *Journal* and at the time of his death he was preparing a series of papers describing his more recent results.

In his early researches he gained recognition for his work on the chemistry of mustard gas and related compounds, during which he made himself a master of the chemistry of the organic sulphur compounds. He devoted his later years to the chemistry of organophosphorus compounds and it is in this field, where his brilliant laboratory technique found ample scope, that he will primarily be remembered. He carried through a comprehensive examination of the chemistry of insecticidal and toxic organophosphorus compounds. This included the elucidation of chemical reactions of importance in the preparation of these compounds, the establishment of synthetic routes for producing them in a high state of purity, and the effect of variations in molecular structure on activity.

Ford-Moore also made lesser but valuable contributions to other branches of synthetic chemistry. His publications reveal excursions into chemistry of many other organic compounds with pharmacological activities. Particularly noteworthy is the result of his collaboration with H. R. Ing. The preparation of some forty alkamine esters, mostly of benzilic acids, and the results of their testing as mydriatics was described in a paper in the *Journal* in 1947. An outcome of this work was the manufacture and use of the mydriatic Lachesine.

Arthur Ford-Moore will be remembered by his professional colleagues for his infectious enthusiasm for his work, and his willingness and outstanding ability to explain to others his experiments, their objects, results, and implications. His written reports are a model of lucid reporting, while his vivid use of words brought enlightenment and pleasure to the many audiences he faced during his professional career. He was essentially an experimentalist, whose whole working life was spent either at a laboratory bench or a laboratory table writing up the results of his own work. His output was prodigious and there is no doubt that, were it not for the cloak of secrecy surrounding most of his work, he would have been recognised as one of the leading experimentalists of the day.

His outstanding ability for research was recognised in 1952 by special promotion, a mark of high distinction awarded to scientists in the government service.

He was a man of many interests, playing a very active part in the life of the Chemical Defence Experimental Establishment for many years. His gaiety and enthusiasm are greatly missed by all his colleagues. He is survived by a widow and a daughter, to whom we offer our sincere sympathy.

E. A. PERREN.

APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the publication of this issue of Proceedings. Such objections will be treated as confidential. The forms of application are available in the Rooms of the Society for inspection by Fellows.)

Bigot, Johan Albert, D.Sc. 2A Deltastraat, Amsterdam Z2, Netherlands.
Chuchani, Gabriel, M.S., Ph.D. Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela.
Considine, William James, A.M., Ph.D. 191-16, 35th Avenue, Flushing 58, New York, U.S.A.
Day, Peter, 4 Alma Terrace, High Street, East Malling, Maidstone, Kent.
Evans, Michael Bryan, B.Sc., A.R.I.C. 6 Gorse Close, Hatfield, Herts.
Freiser, Henry, Ph.D. Department of Chemistry, University of Arizona, Tucson 25, Arizona, U.S.A.
Gini, Donald, B.S. 1513, 20th Street, Boulder, Colorado, U.S.A.
Golomb, Dan, Ph.D. Department of Chemistry, Rutgers University, Newark 2, New Jersey, U.S.A.
Greenwood, Harry Hawkshaw, Ph.D. 21 The Crescent, Nunthorpe Station, Middlesbrough.
Grigg, Ronald Ernest. 81 Hammond Road, Southall, Middlesex.
Holm, Richard Hadley, B.S. Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts, U.S.A.
Kubek, Zdenek, Ing.Chem. Spolek pro chemickou a hutni vyrobu, Narodni Podnik, Usti n. Lab., Czechoslovakia.
Lansbury, Peter Thomas, Ph.D. 1802 Inglewood Drive, Fairfax, Wilmington 3, Delaware, U.S.A.
Laurence, Alfred Edward, LL.D. 92 Higher Drive, Purley, Surrey.
Matsuura, Sadao, M.Sc. University House, Canberra, A.C.T., Australia.
Oxtoby, Allan Henry. 28 High Firs Crescent, Harpenden, Herts.
Steele, Derek, B.Sc. 16 Arundel Square, Ashington, Northumberland.
Twigg, Bryan, B.Sc. 13 Granby Road, Mile End, Stockport, Cheshire.
Watson, Alan Alfred, B.Sc. 71 The Commons, Welwyn Garden City, Herts.
Wong, Chi Shing, B.Sc. 95D Robinson Road, Hong Kong.
Wong, Shun Chu, Ph.D. 16 Kennedy Terrace, Hong Kong.

ADDITIONS TO THE LIBRARY

Cinétique chimique appliquée. J. C. Jungers, J. C. Balaceanu, F. Coussemant, F. Eschard, A. Girand, M. Hellin, P. Leprince, and G. E. Limido. (Revue de l'Institut Français du Pétrole, 1952—1956. Selected articles.) Pp. 774. Société des Éditions Technip. Paris. 1958. (Presented by the publisher.)

Les peroxydes organiques. V. Karnojitzki. Pp. 142. Hermann. Paris. 1958. (Presented by the publishers.)

NEW JOURNALS

Acta Biochimica Sinica, from 1958, **1** (in Chinese with English summaries).

Analele Stiintifice ale Universităţii "Al. I. Cuza" din Iaşi. Sectiunea I. Matematica, Fizică, Chimie, from 1955, **1** (in Roumanian).

Biochimica Applicata (Italy), from 1958, **5**.

Dopovidi Akademii Nauk, Ukrains'koi Radians'koi Sotsialistichnoi Resp'liki, from 1957 (with English summaries).

International Abstracts of Biological Sciences (London), from 1958, **9**.

Periodica Polytechnica (Hungary), from 1957, **1** (in English and German).

Práce, Acta Academiae Scientiarum Cechoslovenicae Basis Brunensis, from 1958, **30** (with German summaries).