EMISSION OF ULTRA-VIOLET RAYS BY CHEMICAL REACTIONS.

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In recent years kinetics have been largely applied to the analysis of the various stages of chemical reaction ; unfortunately, the solutions arrived at frequently contain much that is arbitrary : the experimental results can often be interpreted by more than one hypothesis, between which the continually increasing precision of experimental methods allows a choice, the difficulty of which is frequently emphasised by the active discussions aroused by certain problems. It is, therefore, essential to consider these hypotheses from as many different angles as possible : already, for instance, supersonics and, in photo-chemical reactions, the study of spectra, have proved particularly fruitful.

Judging by the early results obtained, the analysis of the ultra-violet radiation emitted by many chemical reactions provides a new means of penetrating the inner mechanism of chemical processes.

The known phenomena of chemi-luminescence are studied by ordinary means: *e.g.*, photographic plates and photo-electric cells, and the determination of the spectral regions of the emission can usually be effected by standard spectrographic methods.

The use of highly sensitive apparatus, such as photo-electric counters, reveals that many reactions, even the simplest, *e.g.*, the neutralisation of a strong base by a strong acid, are accompanied by the emission of ultra-violet light in a region as far as 2000 A, although with an intensity incomparably smaller than that of any known chemi-luminescence; for this reason, the usual means of investigation cannot be used to study these phenomena.

The essential feature of this micro-luminescence is the development of a quantum of high energy. In certain cases it has actually been possible to calculate from a knowledge of the spectral region that the quantum corresponds to 150,000/160,000 calories per gm. mole. Such high values involve considerable difficulties in visualising the chemical mechanism; it is in this respect that the new phenomena are of particular interest.

The photo-electric counter[1] is sensitive to radiation of only a few photons per sec. per cm.^{2}, so that it responds to the transformation of only a few individual molecules.

A brief review will now be given of the principal phenomena so far studied by this method, particular attention being given to those which have been more fully examined.

General.

Ultra-violet emission is obtained not only in strictly chemical reactions, but also during physico-chemical phenomena; many anodic oxidations, the dehydration and hydration of quinine sulphate, and the passage of high tension electric currents through semi-conductors, are accompanied by the emission of ultra-violet rays up to 2000 A.

In certain biological phenomena, also, such as the electrical or mechanical excitation of nerves, these rays are emitted.

After showing with Van Doormal[2] that chemical phenomena emit these photons in quantities too small to be detected by ordinary means (oxidation of bisulphite, of pyrogallol, of alcohols by chromic acid, decomposition of water by K, Na, Am, Mg amalgams; air oxidation of Al, anodic oxidation of Al, Mg, Ta, Si) the writer extended these early results[3] to further chemical reactions, and showed the existence of these radiations in the following cases: neutralisation of strong acids (H_2SO_4, HNO_3) by strong bases (NaOH, KOH), oxidation of potassium oxalate by Br and I, oxidation of glucose by $KMnO_4$, oxidation of sulphites of Na and K by air, thermal decomposition of a great number of substances: KN_3, NaN_3, AgN_3, $Pb(N_3)_2$, $Ca(N_3)_2$, $Ba(N_3)_2$ diphenylnitrosamine, and hexogen.

Many of these emissions are too weak for their spectra to be determined by the method described later for the case of the azides, but it is possible[4] to obtain an idea of the spectral region by the use of counters with variable spectral sensitivity. Table I gives the results of such experiments; differences in the region of emission clearly exist.

By relating the data given in Table I to the corresponding number of molecules reacting in the respective reactions, it is possible to calculate the radio-chemical yield, *i.e.* the ratio of the number of photons emitted

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[1] R. Audubert, *C.R.*, 1933, **196**, 1883; 1935, **200**, 918; *J. Physique*, 1935, **6**, 452.
[2] R. Audubert and Van Doormaal, *C.R.*, 1933, **196**, 1883.
[3] R. Audubert, *J. Chim. Physique*, 1936, **33**, 507.
[4] R. Audubert, *C.R.*, 1936, **202**, 1931.

TABLE I.

Reaction.	CuI Cell.		Al Cell.	
	Energy measured by comparison with resonance lamp. 2,536·52A. erg./sec./cm².	Energy calculated for mean frequency. 2100 A. erg./sec./cm².	Energy measured by comparison with resonance lamp. 2536·52A. erg./sec./cm².	Energy calculated for mean frequency. 2400A. erg./sec./cm².
$NaOH + HNO_3$ . .	$26·6 \times 10^{-8}$	104×10^{-10}	12×10^{-8}	264×10^{-10}
$NaOH + H_2SO_4$ . .	2·7 ,,	108 ,,	14 ,,	308 ,,
Oxidation of Na pyrogallate by O_2 . .	1·3 ,,	51 ,,	17·2 ,,	392 ,,
Oxidation of glucose by permanganate . .	2·0 ,,	80 ,,	Nil	Nil
Oxidation of sodium bisulphite by O_2 . .	1·12 ,,	45 ,,	12×10^{-8}	264×10^{-10}
$K_2SO_3 + O_2$ . .	1·6 ,,	64 ,,	Nil	Nil
$Na_2SO_3 + O_2$ . .	1·7 ,,	70 ,,	,,	,,
Am. amalgam and water	1·4 ,,	56 ,,	15×10^{-8}	330×10^{-10}
Na ,, ,, ,, .	2·3 ,,	90 ,,	14 ,,	300 ,,
Al ,, ,, ,, .	1·12 ,,	45 ,,	10 ,,	320 ,,
Oxidation of C_2H_5OH by chromic acid . .	Nil	Nil	125 ,,	2730 ,,
$C_2O_4K_2 + 2Br$ . .	,,	,,	17 ,,	380 ,,
$C_2O_4Na_2 + 2Br$ . .	,,	,,	10 ,,	220 ,,
$C_2O_4Na_2 + 2I$ . .	,,	,,	7 ,,	150×10^{-8}

to the number of molecules reacted. Table II gives the order of magnitude of the number of photons given out in all directions per second and per unit surface, allowing for the surface of the cathode, and the distance of the latter from the free surface of the reacting body.

TABLE II.—NUMBER OF PHOTONS EMITTED.

	2,000 A.	2,400 A.
$NaOH + HNO_3$	2,000 to 3,000	7,000 to 10,000
$NaOH + H_2SO_4$	2,000 to 3,000	7,000 to 10,000
Oxidation of pyrogallate by O_2 . . .	1,000 to 1,500	10,000 to 15,000
,, glucose by $KMnO_4$ . . .	1,500 to 2,000	
,, sodium bisulphite by O_2 . .	1,000 to 1,500	7,000 to 10,000
$K_2SO_3 + O_2$	1,500 to 2,000	
$Na_2SO_3 + O_2$		
Am. Amalgam + H_2O	1,200 to 2,000	8,000 to 10,000
Oxidation of C_2H_5OH by chromic acid .		70,000 to 100,000
$C_2O_4K_2 + 2Br$		10,000 to 15,000
$C_2O_4K_2 + 2I$		7,000 to 10,000

Among the reactions studied the oxidation of sodium pyrogallate and of sodium bi-sulphite by oxygen are suitable [5] for a simultaneous determination of the energy emitted and of the number of molecules reacting. Table III shows several values of the yield, for various experiments.

When the kinetics of a reaction have been studied, it is also possible, under given conditions, to calculate the value R from the reaction constant and the measured photon emission ; *e.g.* for sodium pyrogallate oxidation, by taking $k = 180 \times 10^{-4}$ for the reaction constant,[6] the value of the

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[5] R. Audubert, *J. Chim. Physique, loc. cit.*[2]

[6] C. G. Max Arthur, *J. physic. Chem.*, 1916, **20**, 546.

TABLE III.—ALUMINIUM CELL.

N (Number of Molecules of O_2 absorbed per second).	*W* (Energy cm./sec. falling on Cathode).	*I* (Number of photons given off by reaction)	*R* (Yield).	Reaction.
173×10^{-17}	$11·6 \times 10^{-9}$	17,000	$1·0 \times 10^{-15}$	Oxidation of pyrogallate.
81 ,,	6·2 ,,	10,000	1·2 ,,	
32 ,,	1·5 ,,	2,000	1·0 ,,	
5 ,,	8 ,,	12,000	$0·5 \times 10^{-14}$	
243×10^{-17}	$14·5 \times 10^{-9}$	22,000	$1·0 \times 10^{-15}$	Oxidation of bisulphite.
153 ,,	7·3 ,,	10,000	0·7 ,,	
54 ,,	5·0 ,,	7,500	1·4 ,,	
20 ,,	5·5 ,,	8,300	4·0 ,,	
15 ,,	1·0 ,,	18,000	$1·2 \times 10^{-14}$	

radio-chemical yield is of the order of 10^{-14} to 10^{-15}. Finally, for the action of Br on K oxalate, taking the values of the reaction constant given by Berthoud and Bellenot,[7] and adopting experimental conditions as nearly identical as possible to theirs, values for the radio-chemical yield are from 10^{-15} to 10^{-16}.

It is of interest that values of the same order are obtained with very different phenomena, such as the hydration of quinine sulphate,[8] the anodic oxidation [9] of Al, and the emission of ultra-violet light by the Reboul effect.[10]

Photogenic reactions accompanying the thermal decomposition of Azides.[11]

Certain known reactions give such an intense ultra-violet luminescence that their spectra can be analysed, and their intensities measured as a function of the experimental conditions ; these data provide new information on the mechanism of these processes. This, clearly the most interesting part of these researches, has only just begun, and it must therefore suffice to quote here only one or two examples where radiochemical analysis has yielded interesting results.

Among the photogenic transformations studied, the thermal decomposition of the azides will first be quoted. The slow thermal dissociation of the azides, NaN_3, KN_3, $Pb(N_3)_2$, AgN_3, $Ca(N_3)_2$, and $Ba(N_3)_2$ gives rise to a radiation which is intense in the case of the first five and much weaker with the two latter.[12] The intensity increases with temperature.[13]

[7] Berthoud and Bellenot, *J. Chim. Physique*, 1924, **21**, 309.

[8] R. Audubert and M. Prost, *C.R.*, 1936, **202**, 1047.

[9] R. Audubert and O. Viktorin, *C.R.*, 1936, **202**, 1504.

[10] O. Viktorin, *C.R.*, 1936, **202**, 941.

[11] It is not possible within the scope of this paper to mention the quantitative results obtained in electrochemical oxidations ; those obtained with Al give reason to suppose the process involves the intervention of the OH radicle.

[12] Incidentally this shows that no relation can exist between the sensitivity to shock and the ultra-violet emission. In support of this conclusion, H. Muraour and the writer observed that detonating explosives, such as basic lead picrate and silver fulminate, give rise on thermal decomposition to no (or, at the most, very feeble) photogenic effects.

[13] R. Audubert, *J. Chim. Physique*, 1937, **34**, 405.

(*a*) Determination of the energy of activation of photogenic reactions.[14]

If we assume the intensity (I) of radiation emitted to be proportional to the velocity constant of the reaction, it is possible to determine the activation energy of the elementary process. This hypothesis, justified, as will be seen below, by the shape of the curves relating the variation of the effect to the temperature, accords with the fact that the curves obtained in air for rise of temperature, are superposed on the curve for falling temperature, provided that certain precautions are taken ; *e.g.* a certain temperature in the neighbourhood of the temperature of deflagration must not be exceeded, for at this temperature the amount decomposed becomes so great that the emitting surface can no longer be regarded as constant.

The curves of log I against $1/T$ (in air) are straight lines (Fig. 1). (ΔN, which represents the increase in the number of discharges, is proportional to I.)

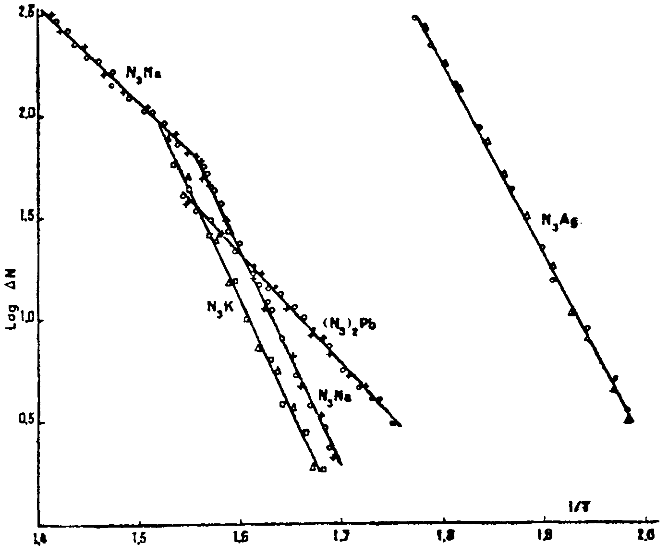

FIG. 1.

The mean slopes correspond to the following activation energies (E) : KN_3 (40/46,000 cal.) ; AgN_3 (40/43,000 cal.) ; $Pb(N_3)_2$ (20/23,000 cal.). With sodium azide there are two linear portions which correspond to two activation energies: 46/50,000 cal. and 20/23,000 cal. F. Mattler has recently determined the activation energies for the slow dissociation of sodium azide in a current of pure nitrogen,[15] and obtained the following figures : 48,000 ± 1500 and 24,500 ± 900, which confirm the results obtained in air. This indicates that the thermal dissociation of sodium

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[14] For the solid state the physical significance of activation energy is by no means clear ; nevertheless, the experimental values obtained constitute important characteristic coefficients.

[15] Experiment has shown that in a closed vessel, whatever be the nature of the gas, the luminous emission from NaN_3 is nil or very feeble, and likewise *in vacuo*. On the other hand, when the gas circulates, an emission is produced. This phenomenon is doubtless due to an inhibition of the sodium nuclei, due to dissociation. Sodium easily loses an electron, and deactivation without emission is thus favoured.. In a current of gas the sodium is carried away owing to its low vapour pressure. In point of fact, this phenomenon is not observed with AgN_3.

azide must take place by one or other of the above photogenic reactions according to the temperature; the velocity of each reaction will obey the Arrhenius law; at temperatures between that at which the emission starts, and the temperature of transition $t_0 = 365°$, the process responsible for the ultra-violet emission has an activation energy of about 46,000 calories, whilst above t_0 this is replaced by a reaction with energy of the order of 20,000 calories.

The fact that for the decomposition of the azides there exist only two types of photogenic reaction (and in particular the behaviour of sodium azide in the decomposition of which both take part) suggests that these processes are independent of the nature of the metal, and depend only on the N_3 group.

(*b*) Radio-chemical Yield.

This has always an extremely small value, which is also roughly constant, lying between $0{\cdot}4 \times 10^{-14}$ and $0{\cdot}7 \times 10^{-15}$ for many very different phenomena, such as anodic polarisation, dehydration of quinine sulphate, and chemical reactions. This fact is interesting, for it seems to be connected with some fundamental property of the mechanism of the transfer of energy. But in view of the usually high absorbing power of liquids and solids for this region of the ultra-violet, it must be admitted that only a surface yield is thus determined; this is probably the case for the above azides.

According to Garner and Marke,[16] the rate of complete decomposition of the azides, in molecules/cm.^{2}/sec., is $5{\cdot}2 \times 10^{15}$ at 270° C. for $Pb(N_3)_2$, $1{\cdot}7 \times 10^{15}$ at 251° C. for KN_3. Using these values and the values for the number of photons emitted under the same conditions, the radio-chemical yield works out at 1000 to 10,000 times as great as those determined above. It seems, therefore, that the decomposition of azides is from this point of view quite different from the other photogenic reactions studied.

(*c*) Emission Spectra.

These have been obtained in the case of NaN_3 at 410° and of AgN_3 at 280°. At these temperatures the energies of activation are different (approx. 45,000 and 25,000).

Ordinary spectrographic methods cannot be employed owing to the very small number of photons emitted. The following arrangement was therefore devised: the azide heated at constant temperature was placed before the slit of a mono-chromator with a quartz prism and Al mirror, in front of the exit slit of which was set up the Cu_2I_2 photo-electric counter, whose spectral sensitivity curve had been previously determined. With this apparatus, a range of wave-length comprised between about 1900 and 2000 A could be explored.

Both in the case of AgN_3 and of NaN_3 the emission consists of three bands whose maxima are situated at:

$$1975 \pm 25, \quad 2150 \pm 25, \quad 2300 \pm 35, \quad 2400 \pm 40.$$

The spectrum is therefore in this region independent of the nature of the cation and of the activation energy.

If the electronic spectrum of molecular nitrogen be examined, states will be found capable of explaining the emission of the observed bands, as shown below:

$A^3\Sigma u \rightarrow X\Sigma g$: 2009 A.
${}^{1\cdot3}\Sigma g \rightarrow {}^{1\cdot3}\Sigma u$: 2113 A.
$C'\Pi u \rightarrow B^3\Pi g$: 2255 A.
$C^3 \rightarrow A^3\Sigma u$: 2549 A.[17]

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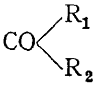
[16] W. E. Garner and D. J. Marke, *J. Chem. Soc.*, 1936, 657.

[17] The bands, discovered by Van der Zeil, *Physica*, 1934, **1**, 513; *Nature*. 1934, **133**, 416, were previously calculated theoretically by A. Recknagel, *Z. Physik*, 1934, **87**, 375.

(*d*) Probable Mechanism of the emission.

These facts allow of an interpretation of the mechanism of emission. It is important, as shown by V. Henri, when seeking an explanation of the primary reactions in photochemical phenomena, to consider the possible electronic activation of radicals.

Henri,[18] on comparing the Raman spectra of such molecules, as for example  $CO\begin{matrix}R_1\\R_2\end{matrix}$ to the fluorescence spectra, has shown that the $=C=O$ group must be in an energy state analogous to the excited $a(^3\pi)$ state of CO, *i.e.*, in an energy level 138,000 cal. above the ground state.

Several radicals ($C=N$, $C=C$, $N=N$ . . .) should show the same property. It may therefore fairly be asked whether the luminous emission may not be due to the deactivation of electronically activated radicals.

The fact that in the case of the dissociation of the azides, the energy levels of electronic activation of the nitrogen molecule can themselves account for the spectral emission bands is a strong presumption in favour of this hypothesis.

It is difficult to arrive at any definite conclusions with regard to the more intimate mechanism of the dissociation reaction. The dissociation might in the case of the azide of sodium be represented :

$$NaN_3 \rightarrow Na - N + (N_2)^*$$
$$N_2^* + NaN_3 \rightarrow Na - N + (N_2)^*$$
$$. \quad . \quad . \quad . \quad . \quad . \quad .$$
$$(N_2)^* \rightarrow (N_2) + h\nu.$$

The existence of two activation energies might be connected with two different modes of rupture, yet to be investigated.

Conclusions.

In this paper, the azides have received particular attention, since they lend themselves to spectral measurements and to quantitative determination of the intensity of the emission. We have been led to attribute the mechanism of emission for these substances to the electronic activation of the radical $N=N$, to which attention was first drawn by Henri, but it must be borne in mind that other processes could account for these large quanta. In the first place, these emissions might be due to those processes in which atoms or radicals take part and which take place with a great variation in internal energy, such as :

$$2O \rightarrow O_2 + 117 \text{ K.cal.}$$
$$2H \rightarrow H_2 + 100 \text{ K.cal.}$$
$$H + O \rightarrow HO + 101 \text{ K.cal.}$$
$$H + OH \rightarrow H_2O + 115 \text{ K.cal.}$$

In certain cases also, these emissions, involving high energies, might be explained by a reaction between two identical molecules having a very high energy content. For example, considering a process such as $A + B \rightarrow C$, a certain number of the C molecules might retain in a metastable condition an energy equal to $E + Q$, where E is the energy

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[18] V. Henri, *C.R.*, 1936, **203**, 67.

of activation and Q the heat of reaction. In this way, the collision of two such superactivated identical molecules might give rise to a single photon :

$$C^{*}_{E+Q} + C^{*}_{E+Q} \rightarrow 2C + h\nu.$$

Although applicable to gaseous or liquid phase reactions, this theory of privileged encounter (collision of the 4th order) does not seem to be applicable to the solid phase : in particular the slow dissociation of the azides (KN_3, NaN_3, $Pb(N_3)_2$,/$Ba(N_3)_2$, $Ca(N_3)_2$), which is accompanied by an emission which is much more intense than that of most of the other reactions studied.

TABLE IV.

Reaction.	E cal./gr.	Q cal./gr.	$E+Q$ cal./gr.	$2E+2Q$ cal./gr.	$h\nu$ emitted.
$K_2SO_3 + \frac{1}{2}O_2 \rightarrow K_2SO_4$.	12,400	61,000	73,500	147,000	145,000 to 150,000
$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$	12,500	69,000	81,500	163,000	145,000 to 155,000
Oxidation Na pyrogallate	16,250	50,000	62,250	132,500	122,000 to 155,000
$C_2O_4K_2+I_2 \rightarrow 2CO_2+2KI$	27,350	36,000	63,350	126,700	122,000 to 145,000
$C_2O_4K_2 + Br_2 \rightarrow 2CO_2 + 2KBr$ . . .	32,250	60,000	93,250	186,500	122,000 to 145,000
Am amalgam + H_2O .	22,400	30,000	52,400	104,800	122,000 to 155,000

For the case of several of the reactions discussed above, under the heading " General," the data of Table IV show that the hypothesis just put forward can account for the magnitude of the emitted photons.[19]

As will be seen, certain intermediate reactions can be shown to exist and can often be identified by radiochemical analysis. Besides the examples already quoted here, the author has shown [20] that the anodic oxidation of Al must take place through an intermediate stage involving OH radicals. Ouellet [21] was able to fix the mechanism of the oxidation of P by means of the photoelectric counter.

In the present state of the method which is often difficult to manipulate, it is not surprising that the number of actual results so far obtained is small, but it is to be hoped that progress in the technique of the use of these instruments will allow of a general application of this method of analysis of the metamorphosis of the molecule itself.

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