THE TRIMETHYLENE BIRADICAL.

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Free radicals may be produced in the homogeneous gaseous reactions of organic halides with atomic sodium in accordance with the general reaction :

$$\mathrm{R\,Hal} + \mathrm{Na} \rightarrow \mathrm{NaHal} + \mathrm{R}.$$

The formation of a number of aliphatic and aromatic radicals in this way from the corresponding halides has been established by their direct interaction with chlorine and iodine,[1] and more recently by their reaction with metallic mirrors.[2]

The experimental method employed in these reactions was that of the diffusion flame method of Hartel and Polanyi,[3] *viz.*, the introduction of sodium vapour at low pressures into a large excess of the organic halide. The probability of the formation of a biradical from a dihalogenated hydrocarbon under these conditions, *viz.*,

$$\mathrm{R\,Hal_2} + 2\,\mathrm{Na} \rightarrow 2\,\mathrm{NaHal} + \mathrm{R} <$$

is very small, since under the usual conditions of the flame the pressure of the halogen compound is many times greater than that of sodium. If the experimental procedure is reversed, however, and the dihalogen compound is introduced into excess of sodium vapour, a biradical may be formed. This method, which was originally used by Bogdandy and Polanyi[4] in their studies of the chemiluminescence of the reactions of halogens and certain inorganic halides with sodium, was employed in the present investigation.

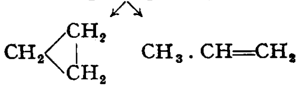
Trimethylene bromide, carried in a stream of nitrogen, was admitted from a small nozzle into a large excess of sodium vapour when the biradical was produced in accordance with the reaction

$$\mathrm{CH_2Br\,.\,CH_2\,.\,CH_2Br} + 2\mathrm{Na} \rightarrow 2\mathrm{NaBr} + \text{—}\mathrm{CH_2\,.\,CH_2\,.\,CH_2}\text{—} \quad \text{(I)}$$

The products of the reaction consisted entirely of *cyclo*propane and propylene, whose formation may be explained (p. 611) on the assumption that the reaction (I) occurs in two steps :

$$\mathrm{CH_2Br\,.\,CH_2\,.\,CH_2Br} + \mathrm{Na} \rightarrow \mathrm{NaBr} + \mathrm{CH_2Br\,.\,CH_2\,.\,CH_2}\text{—} + 29\ \text{Cal. (approx.)} \quad (\mathrm{I}a)$$

$$\mathrm{CH_2Br\,.\,CH_2\,.\,CH_2}\text{—} + \mathrm{Na} \rightarrow \mathrm{NaBr} + \text{—}\mathrm{CH_2\,.\,CH_2\,.\,CH_2}\text{—} + 29\ \text{Cal. (approx.)} \quad (\mathrm{II}a)$$



The interesting isomerisation of the trimethylene biradical to give propylene, involving the migration of hydrogen, has been shown to be mainly a wall reaction. The formation of the intermediate monoradical

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[1] Horn and Polanyi and Style, *Trans. Faraday Soc.*, 1934, **30**, 189 ; Horn and Polanyi, *Z. physik. Chem.*, *B*, 1934, **25**, 151.

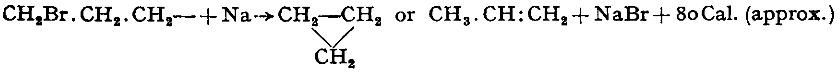
[2] Allen and Bawn, *Trans. Faraday Soc.*, 1938, **34**. 463.

[3] Hartel and Polanyi, *Z. physik. Chem.*, *B*, 1930, **11**, 97.

[4] Bogdandy and Polanyi, *Z. physik. Chem.*, *B*, 1928, **1**, 21.

required by equation (I*a*) has been demonstrated by the production of 1 : 6-dibromo-*n*-hexane. This is formed by the dimerisation of the monoradical under conditions involving a lower concentration of sodium.

The reaction between trimethylene bromide and atomic sodium is accompanied by a marked chemiluminescence, which can be explained if the reaction (II*a*) gives rise either to *cyclo*propane or propylene in a single step, *viz.* :



$$CH_2Br.CH_2.CH_2— + Na \rightarrow \underset{CH_2}{CH_2—CH_2} \text{ or } CH_3.CH{:}CH_2 + NaBr + 80\,\text{Cal. (approx.)} \qquad \text{(III)}$$

Experimental.

The nature of the reaction occurring was ascertained by analysis of the products. In order to reduce the possibility of reaction occurring at the wall of the vessel, the diameter of the reaction zone was maintained small in comparison with that of the reaction vessel. This was accomplished by reducing the distance of penetration of the bromide into sodium by increasing its diffusion resistance by addition of nitrogen. (Normally in the absence of nitrogen, the sodium-trimethylene bromide reaction flame would tend to fill the whole of the reaction tube.) The large pressure of nitrogen also served to increase the diffusion resistance of the radicals to the wall of the vessel, and thereby reduced still further any surface reactions.

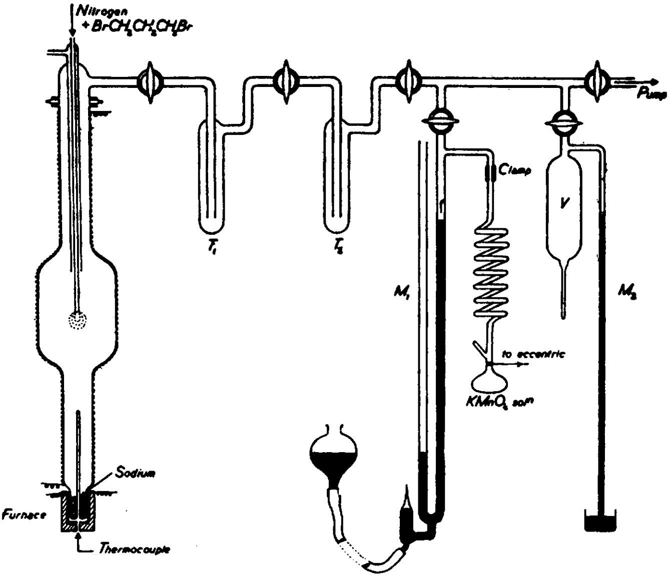


FIG. 1.

The trimethylene bromide was conveyed into the reaction vessel in a stream of nitrogen (Fig. 1), the dimensions of the nozzle and the rate of streaming being such that back diffusion of the sodium into the nozzle was reduced. The chemiluminescence of the reaction enabled the reaction zone to be observed visually, and we have reason to believe that the diameter of the chemiluminescent flame was almost the same as that of the reaction zone. The diameter of the flame was usually about 2-3 cm., the diameter of the reaction vessel being 10 cm. The trimethylene bromide in the saturator was maintained at a temperature of − 40° to − 50°, and the rate of streaming of nitrogen was kept constant throughout any experiment, and was measured by a flowmeter.

The products collected in T_1 and T_2 were transferred to the vessel V (volume 104·2 c.c.) and their volume measured by means of the capillary manometer M_2. They were condensed in the fine capillary attachment of V and the pressure in V determined when the liquid air was replaced by a bath of solid carbon dioxide in acetone. The gaseous products on being pumped off were identified as a mixture of *cyclo*propane and propylene. Under conditions of complete reaction, these were the only products obtained. It should be noted that although both propylene and *cyclo*propane are normally liquids at − 78°, under the conditions of measurement in V at pressures less than 10 cm., both compounds existed as vapours.

If any *cyclo*hexane had been formed in the reaction it would have remained solid at this temperature and would have exerted a negligible vapour pressure. The absence of this compound was repeatedly shown by condensing the products in the capillary attachment of V in liquid air, and warming the capillary to − 78°, when it was found that the gas pressure in V was always the same whether the tip was at − 78° or at laboratory temperature.

By lowering the temperature of the sodium such that the change was incomplete in the reaction vessel, it was possible to attain the condition in which the removal of a single bromine atom from trimethylene bromide was complete, but that a small amount of the monoradical $CH_2Br . CH_2 . CH_2$— so produced escaped further attack by sodium. In this case, a small amount of 1 : 6-dibromo-*n*-hexane was obtained in addition to the gaseous products already referred to. This was a white solid melting at − 2° C. An authentic specimen of this compound had m.p. − 1° C. Further lowering of the sodium pressure resulted in the appearance of unchanged trimethylene bromide in the reaction products.

The analysis of the gaseous products was made by the method of Chambers and Kistiakowsky,[5] who had shown that propylene is readily absorbed by 3 per cent. neutral potassium permanganate solution, while *cyclo*propane is unattacked under these conditions. The residual gas from permanganate absorption on recondensing in V melted at − 124°. This agrees closely with the recorded m.p. of *cyclo*propane of − 126°. A combustion of a sample of this gas over copper oxide gave three times its own volume of carbon dioxide, which conclusively established its identity as *cyclo*propane. A similar combustion of a sample of the original gaseous product also gave three volumes of carbon dioxide for each volume of gas, showing that the fraction absorbed by aqueous potassium permanganate solution consisted of propylene.

Since it is known that *cyclo*propane is converted into propylene by certain catalysts at 300°-400° C., it was necessary to prove that the propylene produced in our experiments was not formed by a reaction of the *cyclo*propane at the wall of the reaction vessel. The gaseous product obtained by passing pure *cyclo*propane through the reaction vessel in a stream of nitrogen under normal experimental conditions, and in the presence of sodium vapour, showed no absorption by potassium permanganate solution. It is therefore clear that there is no interconversion of *cyclo*propane to propylene under the conditions of our experiments. Furthermore, the yield of *cyclo*propane + propylene was quantitative. This was shown by determining the loss of trimethylene bromide from the saturator by weighing before and after a run, and comparing this with the volume of gaseous products formed. The yield of *cyclo*propane +

[5] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.

propylene corresponded to about 95 per cent. of the trimethylene bromide used.

The trimethylene bromide used in these experiments was carefully purified by distillation, the middle fraction B.P. 138°-139° being used. Different preparations of the bromide gave similar results and it is unlikely, therefore, that there were other dibromides in the samples used.

Results and Discussion.

The experimental results are given in the Table.

It is concluded that: (i) the proportion of propylene in the gaseous product is decreased by increasing the pressure of the nitrogen, other conditions being identical. (ii) The proportion of propylene is also dependent on the pressure of the methylene bromide at the nozzle * (determined by the temperature of the bromide saturator). It seems that high nitrogen and small trimethylene bromide pressures lead to low propylene yields. (iii) Reduction of the sodium temperature gives a liquid product in addition to *cyclo*propane and propylene. With a sodium temperature of 345°, this consisted almost entirely of 1 : 6-dibromo-*n*-hexane. This product was first found in experiments in which a slight air leak had developed in the reaction vessel, leading to a reduced concentration of sodium in the reaction zone. On lowering the sodium temperature still further to 335°, some trimethylene bromide passed through the reaction vessel unchanged.

TEMP. OF SODIUM, 362° C. TEMP. OF REACTION VESSEL, 382° C.

Temp. of Saturator.	p_{N_2} (mm.).	Per cent. Propylene.
– 50° C.	1·69	36·5
– 50° C.	1·82	38·2
– 50° C.	2·40	25·0
– 50° C.	2·64	19·5
– 50° C.	2·95	12·8
– 45° C.	1·92	42·8
– 45° C.	2·11	39·5
– 45° C.	2·25	(23·0)
– 45° C.	2·24	30·0
– 45° C.	2·36	28·4
– 45° C.	2·00	24·0
– 40° C.	2·22	32·6

These results can be explained if the sodium atoms react with trimethylene bromide in accordance with the mechanism I*a*-II*a*. The formation of the biradical in II*a* is necessary in order to account for the decrease in proportion of propylene with decrease of trimethylene bromide pressure (decrease of concentration of radicals in reaction zone) and increase of nitrogen pressure (increase in diffusion resistance of the radicals to the walls). These facts are only explicable on the assumption that the propylene is principally formed by the heterogeneous reaction of the biradical at the surface of the reaction vessel. The *cyclo*propane is formed by a direct homogeneous cyclisation of the biradical, but it is not yet certain whether the whole of the propylene is formed heterogeneously, or whether some is produced by homogeneous isomerisation of the biradical—in any case the latter reaction cannot, under suitable conditions, be more than 13 per cent. of the whole.

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* It was difficult to reproduce the experimental conditions exactly on account of two factors: (*a*) over the long period of the experiment (6-8 hours) it was not possible to maintain the bromide cooling bath to better than (± 0·5° C.) and (*b*) the surface part of the reaction varied to some extent with the condition of the surface of the reaction vessel.

The alternative mechanism to I*a* and II*a*, *viz.*, the formation of *cyclo*propane and propylene in a single step, which it is necessary to assume to account for the chemiluminescence cannot explain these facts since no catalytic conversion of *cyclo*propane to propylene occurs.

Chemiluminescence.

The reaction between atomic sodium and trimethylene bromide gives rise to an intense chemiluminescence, which has been identified as that of the D line radiation of sodium. Similar chemiluminescences have previously been observed in reactions involving sodium atoms. The chemiluminescence of the reaction with chlorine, originally observed by Haber and Zisch [6] was made the subject of a detailed study by Beutler and Polanyi,[7] who showed that the mechanism was as follows :

$$\begin{array}{rl} Na + Cl_2 \rightarrow NaCl + Cl & \\ Na_2 + Cl \rightarrow NaCl^* + Na & \quad \text{Type 1A.} \\ NaCl^* + Na \rightarrow NaCl + Na^* & \\ \downarrow \quad & \\ Na + h\nu & \end{array}$$

Similar luminescences were observed in the reactions between atomic sodium and a number of volatile halides, such as mercuric chloride :

$$\begin{array}{rl} Na + HgCl_2 \rightarrow NaCl + HgCl & \\ Na + HgCl \rightarrow NaCl^* + Hg & \quad \text{Type 2A.} \\ NaCl^* + Na \rightarrow NaCl + Na + h\nu & \end{array}$$

These luminescences corresponding to the emission of the D line of sodium which requires an excitation energy of 48·5 K.cal. are all dependent on the fact that the exothermicity of the secondary reaction exceeds this value. An entirely different type of luminescence (Type B) was discovered by Polanyi and Schay [8] in the reaction between atomic sodium and stannic chloride, which consisted of a continuous spectrum whose origin was evidently as follows :

$$\begin{array}{c} Na + SnCl_4 \rightarrow NaCl + SnCl_3 \\ SnCl_3 + SnCl_3 \rightarrow SnCl_4 + SnCl_2 + h\nu. \end{array}$$

A third type of luminescence was observed [9] when cupric chloride vapour was introduced into sodium-mercuric chloride and sodium-chlorine flames, and further examples have been observed when oxygen is admitted to the flames obtained from sodium and carbon disulphides and sodium and the mono- and dichlorides of sulphur.

It is evident that the luminscence observed in our experiments does not belong to either of the last two types, and is therefore probably of the type A. The simplest reaction mechanism, *viz.*, that leading to the liberation of the biradical which we have to assume to account for the products of the reaction, cannot be the cause of the luminescence, since neither of the reactions I*a* nor II*a* are sufficiently exothermic to give the necessary excitation energy. Similarly, no reaction involving sodium molecules, *e.g.*,

$$CH_2Br.CH_2.CH_2— + Na_2 \rightarrow NaBr + —CH_2.CH_2.CH_2— + 11 \text{ K.cal.}$$

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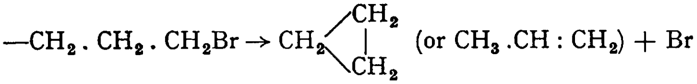
[6] Haber and Zisch, *Z. physik. Chem.*, *B*, 1922, **9**, 302.
[7] Beutler and Polanyi, *ibid.*, 1928, **1**, 3.
[8] Polanyi and Schay, *Z. physik. Chem.*, 1928, **47**, 814.
[9] Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

leads to a liberation of the minimum excitation energy. The only possible reaction seems to be one in which the propylene or *cyclo*propane is formed directly * during the removal of the second bromine atom, according to reaction (III) followed by the subsequent excitation of sodium :

$$\begin{array}{l} NaBr^* + Na \rightarrow NaBr + Na^* \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad Na + h\nu \end{array}$$

The possibility that the monoradical $—CH_2 . CH_2 . CH_2Br$ undergoes a unimolecular dissociation with the liberation of an atom of bromine,



$$—CH_2 . CH_2 . CH_2Br \rightarrow CH_2\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \text{ (or } CH_3 . CH : CH_2) + Br$$

which may then react with sodium atoms or molecules,

$$Na + Br \rightarrow NaBr^*$$
$$Br + Na_2 \rightarrow NaBr^* + Na$$

is also excluded. The former on the grounds that the reaction of the two atoms would take place almost entirely on the wall of the vessel, whereas the luminescence originates from a gas phase reaction, and the latter because visual observations of the light intensity show that this is not reduced by an increase in temperature of the reaction vessel such as would be anticipated for a reaction determined by Na_2 molecules, due to increased dissociation.

It appears highly probable, therefore, that reaction (III) gives rise to the observed luminescence, although it cannot yet be stated whether one or both of the possible reactions is responsible. An estimate of the light yield by comparison with other reactions [4] shows that this corresponds to greater than 1 per cent. but certainly less than 30 per cent. of the reaction occurring in accordance with the mechanism (III).

Summary.

The trimethylene biradical prepared by interaction of trimethylene bromide with atomic sodium gives rise to a mixture of *cyclo*propane and propylene. The latter is formed by a heterogeneous reaction of the biradical.

The mechanism of the chemiluminescence which accompanies the reaction between trimethylene bromide and atomic sodium is discussed.

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* It is highly improbable that the propylene or *cyclo*propane formed directly from the biradical and possessing an excess of energy (50 K.cal.) can excite a sodium atom on collision, since the energy is accommodated among a large number of degrees of freedom of the molecules, and it is unlikely that 49 K.cal. will be given up in a single collision with a sodium atom.