

THE THERMAL DECOMPOSITION OF EXPLOSIVES

PART II. CYCLOTRIMETHYLENETRINITRAMINE AND CYCLOTETRAMETHYLENETETRANITRAMINE

By A. J. B. ROBERTSON

Received 20th May, 1948

The decomposition of both liquid cyclotrimethylenetrinitramine (cyclonite) and cyclotetramethylenetetranitramine follows the unimolecular equation, the Arrhenius frequency factors being very large. The unimolecular uncatalysed decomposition of cyclonite in dilute solution in dicyclohexyl phthalate and trinitrotoluene has a frequency factor approaching the normal value. A more concentrated solution of cyclonite decomposes faster than the dilute solutions; this fact and the anomalous frequency factor for the pure liquid are explained in terms of a chain reaction of short length with a temperature dependent chain length. Analyses of the gaseous products are given, which with the kinetic data show trinitrotoluene to behave effectively as an inert solvent with respect to cyclonite.

In an enquiry into the sensitiveness of explosives to external stimuli it was considered desirable to examine the thermal decomposition of the important explosives cyclotrimethylenetrinitramine (cyclonite or hexogen) and cyclotetramethylenetetranitramine in the liquid phase.

Experimental

The methods used for determining the decomposition rate from the pressure increase due to the gaseous products and for analysis of the gases were those described previously.¹

Decomposition of Cyclotrimethylenetrinitramine.—This was examined above the m.p. (203° C). With quantities of material sufficiently small to avoid explosion, the thermal decomposition of cyclonite followed the unimolecular equation over the whole temperature range 213–299° C, the half-life being 410 sec. at 213° C and 0.25 sec. at 299° C. The reaction rate was the same with the sample in Pyrex glass bulbs or between copper and mica surfaces, and in the presence of air, nitrogen or hydrogen at various pressures up to atmospheric (provided the conditions used did not lead to an explosive decomposition). *In vacuo*, the substance vaporised and distilled from the hot zone before decomposing appreciably. Further recrystallisation of the material from acetone was without effect on the rate. This was also independent of mass at the lower temperatures when quantities from 4–45 mg. were used. At the higher temperatures only a few mg. were used to avoid explosions. From the pressure-time curves unimolecular constants (k) were derived as described before¹ and on plotting $\log_{10} (k \times 10^3)$ against $1/T$ the points shown in Fig. 1 were obtained.

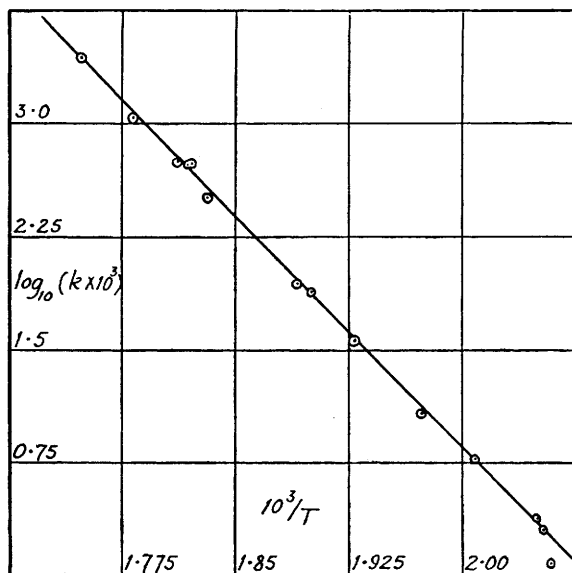


FIG. 1.—Decomposition of cyclonite.

A straight line fitted to the points by the method of least squares gave for the unimolecular constant the expression

$$k \text{ (sec.}^{-1}\text{)} = 10^{18.5} e^{-47.5 \text{ kcal./RT.}}$$

It is necessary to consider whether the high value of the frequency factor could be due to self-heating. The independence of rate and mass at the lower temperatures, with the identity of rate at different inert gas pressures, shows self-heating not to be significant. At the higher temperatures these tests fail as explosion then occurs with larger quantities and at higher gas pressures, but the absence of explosion with a few mg. of material at 10 cm. gas pressure gives

¹ Robertson, *Trans. Faraday Soc.* 1948, **44**, 677.

some indication. It follows from the thermal explosion theories of Semenov² and Frank-Kamenetsky³ that when self-heating becomes of the order RT^2/E , where E is the activation energy of the reaction and T° K the temperature of the vessel, a stable decomposition is no longer possible and explosion ensues. In the glass bulbs the very thin layers of cyclonite could be decomposed at 312°C without explosion, the reaction rate being somewhat too great to determine with accuracy. The degree of self-heating at this temperature should therefore be less than RT^2/E or 14°C . Self-heating should not therefore raise the temperature at 299°C by more than a few degrees. With these considerations the error in E in the above equation was estimated as 2000 cal./mole.

Reaction Products.—Analyses were made of the gases evolved from cyclonite at 225 and 267°C , nitrogen being initially present at 6 cm. pressure to reduce vaporisation. The results expressed as moles of product from one mole of cyclonite are shown in Table I. A considerable solid residue was also obtained. Considerable quantities of formaldehyde and water were also noted. The composition of the products is slightly dependent on temperature. The production of formaldehyde and nitrous oxide suggests the primary step in the decomposition to be the transfer of an oxygen atom from an $-\text{NO}_2$ group to a neighbouring $-\text{CH}_2-$ group, possibly through a transient oxidiazol structure, $\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}\cdot\text{N}\cdot\text{CH}_2\cdot$. The radical remaining after elimination of HCHO could give both nitrous and nitric oxide by direct elimination, or further oxidation of the other neighbouring methylene group to formaldehyde by the $-\text{NNO}$ residue at the end of the chain could lead to the elimination of nitrogen. Further

TABLE I.—DECOMPOSITION PRODUCTS OF CYCLONITE

Temp.	NO	N ₂ O	N ₂	H ₂	CO	CO ₂
225° C	0.54	0.98	1.16	0.09	0.40	0.48
267° C	0.75	0.76	1.03	0.06	0.29	0.44

steps of this kind could occur in the remaining residue accompanied by the formation of complex condensation products.

Decomposition of Cyclotrimethylenetrinitramine in Dicyclohexyl Phthalate Solution.—To investigate further the origin of the very large frequency factor for cyclonite the decomposition in dilute solution was examined. Solutions containing 2 and 5 % of cyclonite in dicyclohexyl phthalate were prepared at 150°C and a 20 % solution at 190°C , the mixtures being subsequently handled as a solid. Visual observation showed the complete solution of the cyclonite. About 1 min. was required for preparing the solutions, the extent of decomposition during this time being negligible. To prevent distillation of the solvent during the decomposition experiments nitrogen was present, usually at 10 cm. pressure.

The pressure-time curves for the 2 and 5 % solutions followed the unimolecular equation closely above 250°C apart from an initial complication due to the 10 sec. or so required for thermal equilibrium to be attained with the large quantity (about 30 mg.) of solvent present, and by a pressure rise due to vaporisation of part of the solvent. In view of these effects any slight autocatalysis at the start of the decomposition would not have been detected in the higher temperature experiments. Below about 250°C some autocatalysis became observable from an initial linear portion of the pressure-time curve, the effect becoming more noticeable at lower temperatures until at 200°C the linear relation persisted while the pressure of products rose to half its final value, the curve then following a first-order equation. In order to justify the derivation of rate constants from the pressure-time curves it was necessary to verify that their shape was not appreciably influenced by supersaturation of gaseous products in the solvent. The pressure-time curves were the same for 2 % and 5 % solutions at gas pressures from 10 to 40 cm. except at the highest temperatures (280 – 290°C) when the unimolecular constant was about 25 % greater at 40 cm. pressure than at 10 cm. pressure. An opposite effect would be expected if much supersaturation occurs; the increased rate was considered to be due to increased

² Semenov, *Chemical Kinetics and Chain Reactions* (Oxford, 1935), chap. 17.

³ Frank-Kamenetsky, *J. Physic. Chem. U.S.S.R.*, 1939, **13**, 738; *Acta Physico-chim.*, 1939, **10**, 365.

self-heating arising from a less vigorous stirring and dispersive action of the bubbles of gaseous decomposition products at the higher inert gas pressures.¹ These observations together with the vigorous bubbling observed and the absence of the deviations in the pressure-time curve to be expected to arise in case of supersaturation according to Pedersen⁴ were taken as indicating this not to be occurring to a significant extent. Unimolecular constants were derived from those pressure-time curves which followed the unimolecular equation throughout with Guggenheim's equation.⁵ Where an initial linear portion of the curve was observed the slope of this with the final pressure rise gave the unimolecular constant for the initial decomposition before the accumulation of autocatalyst.

The temperature variation of the decomposition rate in the ester is shown in Fig. 2. At the highest temperatures the unimolecular constants are rather less than is to be expected from the other results. The reaction may be sufficiently rapid (the half-lives being only a few seconds) to make the rate of disengagement of gas from the solvent an appreciable factor. These high temperature points were therefore disregarded in drawing the straight line shown, which gave for the decomposition rate of cyclonite in 5 % ester solution over the temperature range 201-280° C the expression

$$k \text{ (sec.}^{-1}\text{)} = 10^{15.46} e^{-41 \text{ kcal./RT}}.$$

This expression also represented the decomposition rate in 2 % solution. The decomposition rate in solution is therefore less than that of the pure liquid, the difference increasing with temperature.

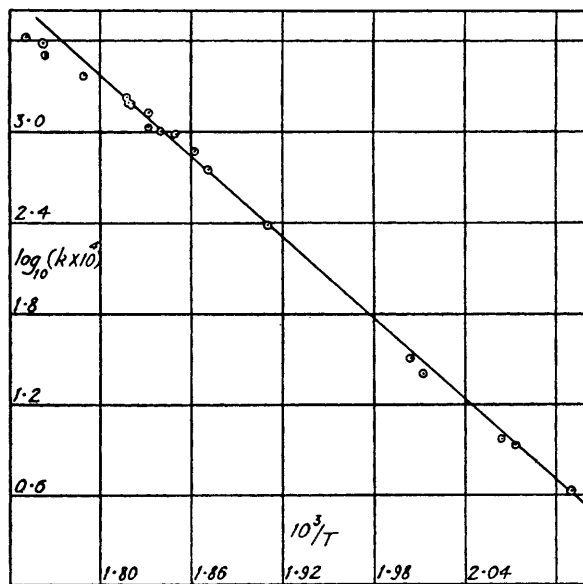


FIG. 2.—Decomposition of cyclonite in dicyclohexyl phthalate.

Decomposition in 20 % Solution.—The diminution of the decomposition rate of cyclonite in dilute solution suggests that a chain reaction of very short length may be involved in the pure liquid-phase reaction, the development of which is impeded by the presence of solvent. In this case more concentrated solutions of the explosive should decompose more rapidly than weaker solutions. The decomposition of a 20 % solution was therefore investigated at 273° C, this temperature being below that at which disengagement of gas may be an interfering factor, but sufficiently high for the difference between the decomposition rate of the pure explosive and the dilute solutions to be readily measur-

⁴ Pedersen, *J. Amer. Chem. Soc.*, 1927, **49**, 2681.

⁵ Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

able (the rates differ by a factor of 3). The decomposition of the 20 % solution followed the unimolecular equation with $k = 0.164 \text{ sec.}^{-1}$, which is some 30 % above the value for 2 and 5 % solutions at this temperature. An increase of this order is in agreement with theoretical expectations as mentioned later.

Autocatalysis.—The formation of a relatively stable catalytic substance by the decomposition of cyclonite in the ester at the lower temperatures was demonstrated by using the liquid remaining from a 5 % solution decomposed at 224°C for 40 min. as the solvent for a new 5 % solution. The new initial rate for the decomposition at 224°C . was then nearly equal to the final catalysed rate for the first experiment, but autocatalysis was less marked in the second experiment. The thermal stability of the catalyst is clearly considerably greater than that of cyclonite. Further recrystallisation of the solvent had no effect on the extent of autocatalysis.

Gaseous Products.—The products from the 5 % solution at 225°C are shown in Table II as moles of product from 1 mole of cyclonite. Nitrogen at 6 cm. pressure was used to prevent distillation of the mixture from the hot bulb. The residual ester was brown and showed a m.p. depression of 4.7°C .

TABLE II.—DECOMPOSITION PRODUCTS OF CYCLONITE IN ESTER SOLUTION

NO	N ₂ O	N ₂	H ₂	CO	CO ₂
0.15	1.13	0.89	0.05	0.16	0.35

The reaction in solution leads to more N₂O and less NO and N₂ as compared with the pure liquid. This is consistent with the intermediate oxdiazol hypothesis already mentioned rather than a scheme involving the breaking of the C—NNO₂ bond as the first step, when the NNO₂ radicals in solution might be expected to rearrange to give two NO molecules.

Decomposition of Cyclotrimethylenetrinitramine in Trinitrotoluene Solution.—1 % and 5 % solutions of cyclonite in T.N.T. were prepared at about 150°C . The T.N.T. was found to behave effectively as an inert

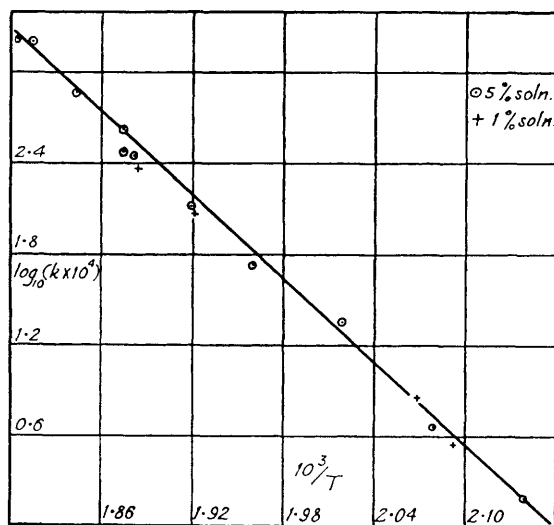


FIG. 3.—Decomposition of cyclonite in T.N.T.

solvent for the cyclonite up to the highest temperatures used (281°C). This observation is in conformity with earlier work of Farmer⁶ and Hinshelwood,⁷ who studied the decomposition of tetryl in T.N.T. as a solvent at much lower

⁶ Farmer, *J. Chem. Soc.*, 1920, **117**, 1603.

⁷ Hinshelwood, *ibid.*, 1921, **119**, 721.

temperatures. The cyclonite decomposition was examined in the presence of nitrogen, usually at 10 cm. pressure up to 250° C, and at 20-40 cm. pressure up to 281° C, to prevent boiling of the T.N.T. (at 10 cm. T.N.T. boils at 267° C).⁸ Similar pressure-time curves were obtained with the 1 % and 5 % solutions and with inert gas pressures from 10 to 40 cm. The shape of the curves closely resembled those obtained in the ester solution; the initial linear portion persisted for about half the decomposition at 200° C, and became less marked with increasing temperature, until above about 250° C no deviation from the unimolecular equation was detectable. After the cyclonite decomposition the pressure continued to increase slowly as the T.N.T. underwent its usual autocatalytic decomposition.⁸ The change in the pressure-time curves from the cyclonite to the T.N.T. decomposition was sufficiently well defined to enable the pressure change due to the cyclonite decomposition to be determined to within 5-10 %. The initial reaction rate constant was determined as before. The temperature variation of k over the range 194.5-281° C is shown in Fig. 3 and is given by the expression

$$k \text{ (sec.}^{-1}\text{)} = 10^{15.65} e^{-41.5 \text{ kcal./RT}}$$

The decomposition rate of cyclonite in T.N.T. solution is again less than that of the pure liquid to an extent dependent on temperature, and in the temperature range examined it is slightly less than that in the ester solution.

Gaseous Products.—Analyses were carried out with 5 % solutions at 220° C with 16 cm. nitrogen initially present and at 264° C with 20 cm. nitrogen. The results are given in Table III as moles of product from 1 mole of cyclonite.

TABLE III.—DECOMPOSITION PRODUCTS OF CYCLONITE IN T.N.T. SOLUTION

Temp.	NO	N ₂ O	N ₂	H ₂	CO	CO ₂
220° C.	0.70	0.63	1.65	0.20	0.57	0.83
264° C.	1.02	0.47	1.33	0.30	0.32	0.85

The variation with temperature of the relative quantities of the various products is very similar to that observed with cyclonite alone (Table I). At both temperatures rather more nitrogen and carbon appears in the gas phase as the products mentioned from the decomposition in T.N.T. There is probably some slight decomposition of the T.N.T. induced by the cyclonite. At 225° C the residual T.N.T. had a light brown colour and its m.p. had been depressed ½-1° C. At 264° C more interaction occurred as the residual T.N.T. had a dark red colour and drops of a red liquid could also be seen.

Decomposition of Cyclotetramethylenetetranitramine.—The decomposition was examined in glass bulbs with 5 cm. air or hydrogen present to prevent vaporisation and distillation of the explosive, and in the copper ovens

apparatus¹ with air present at atmospheric pressure. *In vacuo*, the substance readily vaporised and condensed on the cooler parts of the apparatus without undergoing appreciable decomposition. Above 280° C the explosive melted rapidly, the liquid decomposition following the unimolecular equation. In experiments at 271, 273 and 276° C a time of 20-50 sec. elapsed before complete liquefaction during which an accelerative reaction much slower than the ensuing first-order reaction was observed. It seems possible that some preliminary decom-

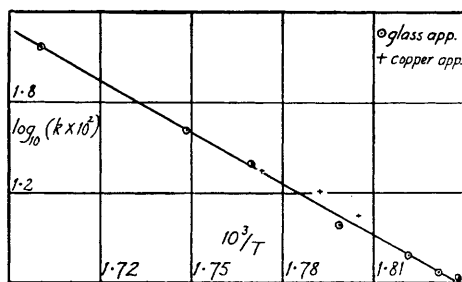


FIG. 4.—Decomposition of cyclotetramethylene-tetranitramine.

position occurs lowering the melting-point. The half-life for the liquid phase decomposition was 16 sec. at 271° C and 0.45 sec. at 314° C. The temperature variation of the unimolecular constant k is shown in Fig. 4 and was represented by the expression

$$k \text{ (sec.}^{-1}\text{)} = 10^{19.7} e^{-52.7 \text{ kcal./RT}}$$

⁸ Robertson, *Trans. Faraday Soc.* (in press).

The frequency factor is even greater than that for cyclonite. No effect of mass was observed on varying the quantity used from 1.7 mg. A non-explosive decomposition was obtained with 2.3 mg. at 337°C, the rate being too rapid to determine accurately. The error in E in the equation above was estimated as 2,000 cal./mole.

Addition of 24 % of cyclotetramethylenetetranitramine to cyclonite made no difference to the decomposition rate of the latter in the temperature range 241–251°C, the mixture decomposing as one substance at the normal rate for cyclonite.

Reaction Products.—From the liquid explosive decomposed at 280°C. for 2 min. the products shown in Table IV were obtained (moles per mole explosive).

TABLE IV.—DECOMPOSITION PRODUCTS OF
CYCLOTETRAMETHYLENETETRANITRAMINE

NO	N ₂ O	N ₂	CO	CO ₂
0.95	1.51	1.16	0.57	0.64

Formaldehyde and water were also formed. The products are similar to those from cyclonite, and a similar decomposition mechanism may be postulated.

Discussion

Both the cyclic nitroamines examined undergo a liquid-phase decomposition which proceeds in accordance with the unimolecular equation, and in the case of cyclonite the independence of decomposition rate with concentration in the 1–5 % range shows the true unimolecular character of the reaction. For both explosives the decomposition rate can be expressed by an Arrhenius equation $Ae^{-E/RT}$ with an extremely large value for the frequency factor. In the case of cyclonite, however, a significant diminution in the frequency factor towards the normal value is observed for the decomposition in dilute solution in two solvents of different chemical type. At the melting point of cyclonite the decomposition rate of the pure liquid is only slightly greater than that of the dilute solutions, but as the temperature is raised the difference between the two becomes steadily greater. At a temperature where the difference is considerable there is also a significantly faster rate of decomposition of cyclonite in 20 % solution in dicyclohexyl phthalate as compared with 5 % solution.

The kinetic expressions for the decomposition of cyclonite in T.N.T. and the ester could be subject to experimental errors arising from autocatalysis and self-heating. Autocatalysis in solution is less marked at the higher temperatures used and is not detectable above 250°C for experimental reasons. Since in deriving the Arrhenius equations initial rates not influenced by autocatalysis were determined at the lower temperatures, and unimolecular constants possibly slightly increased by autocatalysis at the higher temperatures, any errors in the temperature coefficient from this cause would increase both A and E above the true values for the intrinsic decomposition: making the most unfavourable assumptions a possible error from autocatalysis of 2,000 cal./mole in E was estimated, corresponding to a variation in A of about 10 times. Any errors due to self-heating also tend to increase both A and E since the effect is more marked at higher temperatures. It may be noted from theoretical considerations that self-heating is not necessarily diminished by dilution of the explosive with inert material. For infinite slabs, spheres and cylinders of liquid in which an exothermic reaction is taking place with a heat of reaction q per unit volume, the amount by which the

temperature in the centre of the material exceeds that of the boundaries ($T^\circ \text{ K}$) increases with increase of a non-dimensional parameter $d^2(q/K) Ae^{-E/RT} \cdot E/RT^2$ where d measures the size of the material (it is half the thickness of the slab or the radius of the cylinder or sphere) and K is a quantity defined in the same way as thermal conductivity, but which may be numerically increased to allow for forced convection. For a sphere, dilution of the explosive to n times its original volume diminishes q by n times (for the same reaction rate) and increases d^2 by $n^{2/3}$ times, so that if K remains the same self-heating is diminished. For a cylinder, q is diminished n times and d^2 increased n times, so for constant K self-heating is unchanged. For an infinite slab self-heating is increased by dilution. Actually it is probable that K is decreased by dilution on account of the less vigorous stirring by the bubbles of gaseous products, and self-heating of a thin-layer of explosive at the bottom of the bulb may well be increased by dilution. The independence of rate with concentration variations of 1.5 % does not necessarily indicate absence of self-heating, and it is therefore important to make observations at different gas pressures.

Taking these points into consideration it was concluded that the values of E for the reaction in solution were probably not in error by more than 2,000 cal./mole and the most likely errors would increase both A and E . The different kinetic expressions for the decomposition of cyclonite in dilute solution and in the condensed liquid phase were considered to have a sufficiently sound experimental basis to justify theoretical discussion.

The increased decomposition rate of pure liquid cyclonite as compared with the solutions suggests that short chain reactions are involved in the pure liquid. If the probability of one decomposing molecule directly inducing the decomposition of a neighbouring molecule is p , each act of primary activation leads to the decomposition of $(1-p)^{-1}$ molecules. As the explosive molecules are separated by inert solvent the chain development is increasingly inhibited. If the assumption is made that the true decomposition rate of cyclonite uncomplicated by chain reactions is given by the experiments in dilute dicyclohexyl phthalate solution, p can be evaluated. Thus at 205° C , k for pure cyclonite is $0.00076 \text{ sec.}^{-1}$ compared with 0.00058 for the solution, whence $0.00076/0.00058 = (1-p)^{-1}$ and $p = 0.236$. At 273° C the values of k are 0.37 and 0.125 , whence p is 0.662 . Thus in a range of temperature so great that the decomposition rate of cyclonite varies by 640 times, a variation of p by less than 3 times suffices to increase the Arrhenius frequency factor by some 1000 times.

The simplest way of estimating the chain length in solution is to multiply p by the molar fraction M of cyclonite present in solution, each act of activation leading to the decomposition of $(1-Mp)^{-1}$ molecules. For 20 % solutions of cyclonite in the ester at 273° C , $M = 0.27$ and $p = 0.662$, whence the chain length becomes 1.22. The decomposition rate should exceed the limiting rate in very dilute solution by 22 %. By experiment, the rate was 30 % greater. The agreement seems reasonable considering the very simple nature of the calculation. These arguments would also predict the rate in 5 % solution to exceed that in 2 % solution by 3 %. This difference, however, would lie within the experimental error.

It follows from these views that the entropy of activation used in the activated complex theory is not extremely large for the cyclonite decomposition. This is in conformity with the views already expressed concerning the primary decomposition step, which does not involve any great disorganisation of the molecule. The transfer of an oxygen atom from a nitro group to a neighbouring methylene group can occur in six distinct ways, which might suffice to increase the frequency factor to six times the normal value: the experimental value for the dilute solutions can therefore be regarded as showing little anomaly.

The author has much pleasure in thanking Prof. E. K. Rideal for many discussions. This work forms part of a programme carried out at the Department of Colloid Science, Cambridge, jointly with the Department of Chemistry, Bristol, and the author thanks Dr. C. E. H. Bawn, Mr. L. A. Wiseman and Mr. G. K. Adams, for information on their work. This paper is published by permission of the Chief Scientist, Ministry of Supply.

*Davy-Faraday Lab.,
Royal Institution,
Albemarle St., W.1.*