

306. *Thermal Decomposition of Explosives in the Solid Phase. Part I. The Thermal Decomposition in a Vacuum of Certain Mono- and Din nitrobenzenediazo-oxides, with a Note on the Kinetics of Thermal Breakdown of 2-Nitrobenzene-4-diazo-1-oxide.*

By J. VAUGHAN and L. PHILLIPS.

The rates of decomposition, in a vacuum, of certain nitrobenzenediazo-oxides have been studied between 50° and 120°. Under these conditions mononitrobenzene-2-diazo-1-oxides appear to be less stable than the corresponding 4-diazo-1-oxides. A similar conclusion applies to the dinitrobenzenediazo-oxides. This is probably due to restricted resonance in the 2 : 1-diazo-oxides owing to proximity of electrostatic charges. Substitution of nitro-groups in positions *o*- or *p*- to the oxygen atom in 2 : 1-diazo-oxides leads to an increased stability; substitution in the *m*-position appears to be without effect. Similar effects are observed with *o*-substitution on the 4 : 1-diazo-oxides. These effects can be explained on electronic considerations. The kinetics of thermal decomposition of 2-nitrobenzene-4-diazo-1-oxide have been investigated. The results are in agreement with the theory of solid-phase decomposition put forward by Prout and Tompkins (*Trans. Faraday Soc.*, 1944, **40**, 488).

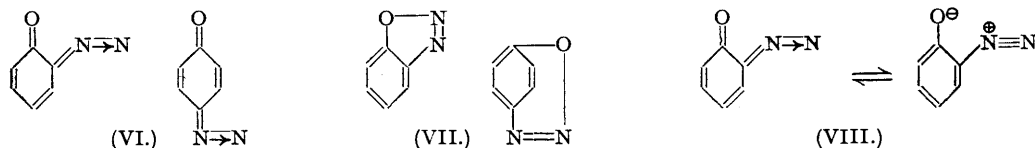
THE following five aromatic diazo-oxides were examined for thermal stability characteristics : 4- (I) and 5-nitrobenzene-2-diazo-1-oxide (II), 2-nitrobenzene-4-diazo-1-oxide (III), 4 : 6-dinitrobenzene-2-diazo-1-oxide (IV), 2 : 6-dinitrobenzene-4-diazo-1-oxide (V).

The method used for following the progress of decomposition was essentially that described by Farmer (*J.*, 1920, **117**, 1432) in which the compound was allowed to decompose in a vacuum and the course of breakdown followed by means of the gas evolution-time curve. The temperature range covered was 50—120°, and the curves obtained in all cases were sigmoid in shape. Addition of the solid end-products did not result in any acceleration of the breakdown, and the gaseous products were also without catalytic effect. The gaseous products of decomposition of these diazo-oxides consist mainly of nitrogen, nitric and nitrous oxides, and carbon dioxide. Since the nitro-groups of mono- and di-nitrobenzene are comparatively stable at temperatures below 120°, the main process in the thermal decomposition of these diazo-oxides would seem to be fission of the diazo-nitrogen, together with some slight secondary reactions depending on the temperature of decomposition. The failure in all cases to obtain 1 mol. of

nitrogen per mol. of diazo-oxide indicated that some coupling may have occurred with the formation of a relatively stable product.

Of the mononitrobenzene diazo-oxides, the 2-diazo-1-oxides (I) and (II) were considerably less stable thermally than (III), a 4-diazo-1-oxide. This characteristic was also demonstrated by the behaviour of the dinitrobenzene compounds, (V) being more stable than (IV). Results also pointed to the following facts: (a) when a nuclear nitro-group is in an *o*- or *p*-position to the oxygen of the diazo-oxide grouping, a stabilising effect is exerted on the molecule; (b) a nitro-group in the *m*-position appears to be without effect on the stability; (c) the presence of two nitro-groups situated as in (a) leads to a stabilising effect greater than that exerted by only one such group.

For many years there was considerable doubt as to whether these internal diazo-oxides had a quinonoid structure (VI) or contained an oxide ring (VII). It is, however, now evident that neither of these structures is correct and that the properties of such compounds are best explained on the basis of resonance hybrids, as in (VIII). This argument is reviewed by Hodgson and

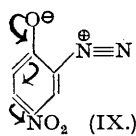


Marsden (*J. Soc. Dyers Col.*, 1943, 59, 271), who point out that such a resonating system explains the superior stability of the diazo-oxides over the diazonium compounds. Thus the diazo-oxides are stabilised by their resonance energy, whilst the diazonium salts, not being resonating systems in this sense, are not stabilised in this manner.

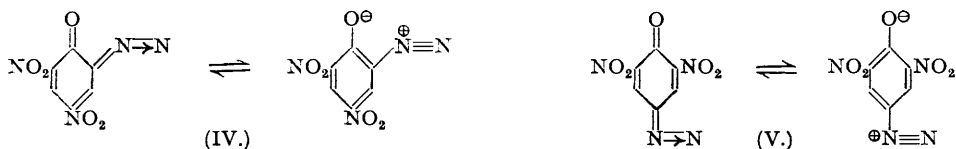
Compounds (I), (II), and (III) can therefore be represented structurally by the general formulæ shown in (VIII). The resonating energy of such systems is, by definition, greatest (*i.e.*, the greatest degree of stability is obtained) when both hybrids contribute equally to the equilibrium state of the molecule. Now in the "ionised" form of the 2 : 1-diazo-oxides, the negatively charged oxygen and the positively charged nitrogen are sufficiently close to set up an appreciable electrostatic attraction, so much so that resonance is probably to some extent inhibited. Consequently, the "ionised" form will preponderate, with the result that the resonance energy assumes a comparatively small value.

On the other hand, resonance in the 4 : 1-diazo-oxides should not be restricted to such an extent because of the greater separation of the electrostatic charges in the ionised form. Consequently, the resonance energy and therefore the stability of the 4 : 1-diazo-oxides should be greater than that of the corresponding 2 : 1-diazo-oxides, as has been found to be the case with (I), (II), and (III). Further support for this theory is afforded by the fact that (II) is less stable than (I). Both compounds are 2 : 1-diazo-oxides, the only difference being that the nitro-group is respectively in the *m*- and the *p*-position. Now, according to the electronic theory of organic reactions, developed by Ingold *et al.*, the nitro-group is an electron-attracting group which exerts mesomeric effects in aromatic compounds. This effect would be expected to operate to reduce the fractional negative charge on the oxygen atom of the ionised form of (I), as in (IX), thereby decreasing the electrostatic attraction between the ionised groups. The contribution to the equilibrium state made by the non-ionised form therefore increases with consequent increase of resonance energy and therefore stability. Since this mesomeric effect cannot operate from a group in the *m*-position, (II) should be less stable than (I). This relative instability in (II) is enhanced by the fact that the nitro-group in (II) is in the *p*-position to the diazo-group. The electron-attracting nature of the nitro-group will tend therefore to increase the positive nature of the diazo nitrogen and will thus inhibit resonance by favouring the "ionic" structure of the molecule.

Introduction of a second nitro-group into the position ortho to the oxygen (where the mesomeric effect can again operate) should tend further to reduce the fractional charge on the oxygen atom. If the major contribution made to the stable structure before introduction of this second nitro-group still comes from the "ionised" form, this second nitro-group should tend to increase stability by bringing the stable structure nearer to the optimum condition, *i.e.* reducing the "amount" of ionised form. Conversely, it follows that if the introduction of a second nitro-group ortho to the oxygen atom in a mononitrobenzenediazo-oxide results in an increased stability, the "ionised" form must preponderate in the latter structure. Thus the fact that (IV) is more stable than (I) confirms that the "ionised" form of the latter preponderates



in the stable structure. Similarly, the fact that (V) is more stable than (III) indicates that, although (III) is more stable than (I), the ionised form still makes the greater contribution to the



relatively stable (III) structure. The destabilising effect of the adjacent charges in the 2 : 1-diazo-oxides is again illustrated by the fact that (IV) is less stable than the corresponding 4 : 1-diazo-oxide (V).

Kinetics and Mechanism of the Thermal Decomposition.—Investigation of the kinetics and mechanism of the thermal decomposition of nitrobenzenediazo-oxide was not the main object of this work. Attempts at kinetic interpretation have only been made, therefore, where data of sufficient accuracy are available. Furthermore, secondary processes other than elimination of diazo-nitrogen played a large part in the decomposition of dinitrobenzenediazo-oxide, so the kinetics were very complex. Satisfactory data were, however, available for compound (III).

The decomposition of all compounds studied in the present investigation is characterised by sigmoid volume-time curves, and microscopic examination of decomposition products indicates that decomposition probably occurs in the solid phase without the incidence of partial melting which can result in autocatalytic reactions. Considerable work has been carried out by Garner and other investigators during the last 15 years on the kinetics and mechanism of thermal decomposition in the solid phase. The position has been reviewed by Garner (*Trans. Faraday Soc.*, 1938, "Symposium on Solid Phase Reactions"; *Science Progress*, 1938—39, **33**, 209), and more recently by Prout and Tompkins (*loc. cit.*), whose treatment of the problem appears to be most complete. Agreement is general that decomposition in the solid phase is initiated at nuclei which are situated mainly at the crystal surface, at lattice imperfections, *i.e.*, where a strain exists, these nuclei being regarded in the widest sense as molecules whose decomposition is highly favoured, *i.e.*, of lower activation energy. The mechanism postulated by Prout and Tompkins (*loc. cit.*), which differs somewhat from that of Garner, is briefly as follows: The surface array of product molecules, which in general have a different unit cell from that of the original substance, sets up strains in the crystal surface which are relieved by formation of cracks (not Smekal cracks, which are produced to relieve strain in the *original* crystals, *i.e.*, they are a property of the crystal itself). At the mouths of these cracks, decomposition will be favoured because of lattice imperfections; reaction therefore spreads down these crevices into the crystal. Covering of the surfaces of these cracks now produces lateral strains which ultimately lead to further cracking from the inner surface. Thus a series of "branchings" will occur and planes of strain will be formed, and along these planes the deformation effect of the product on the electronic structure of an adjacent molecule of unreacted substance will be a maximum and decomposition will be favoured. A chain-like reaction develops, which, however, becomes subject to interference since, when a plane of product molecules is encountered, the chain is broken. By a mathematical consideration of their proposed mechanism Prout and Tompkins derived the relationship

$$\log_{10} p / (p_f - p) = k_1 t + c_1$$

where p is the pressure at a time t , p_f the final pressure, and k_1 and c_1 are constants. This equation should hold from the start of appreciable interference with the branching process (*i.e.*, from the early stages of the reaction) to near the inflexion point of the p - t curve, after which the equation

$$\log_{10} p / (p_f - p) = k_2 t + c_2$$

should hold until the end of the reaction is approached. The graph of $\log p / (p_f - p)$ against t should therefore be two straight lines inclined at an angle to each other. The application of these equations to compound (III) is illustrated in Fig. 3, where $\log v / (v_\infty - v)$ has been plotted against t . The values obtained for k_1 and k_2 at various temperatures are given below:

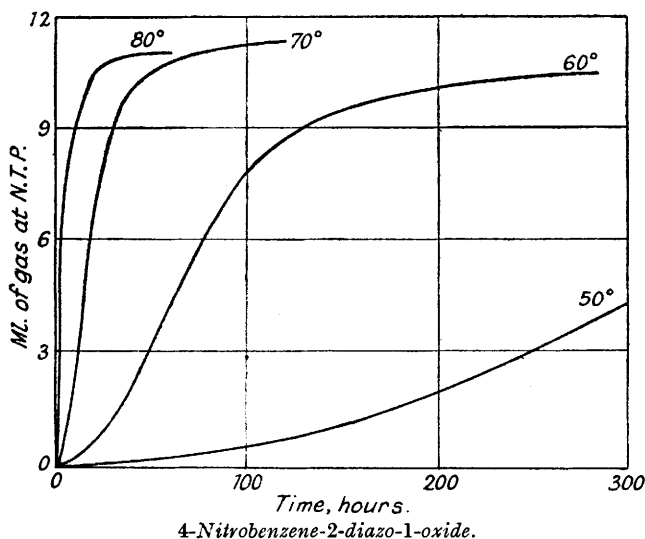
Temp. °	$10^6 k_1$ (sec. ⁻¹), and mean.	$10^6 k_2$ (sec. ⁻¹), and mean.	Temp. °	$10^6 k_1$ (sec. ⁻¹), and mean.	$10^6 k_2$ (sec. ⁻¹), and mean.
90.9°	6.78 } 6.72 6.66 }	8.00 } 8.81 9.62 }	104.4°	38.6 } 39.0 39.4 }	50.1 } 47.7 45.3 }
95.2	11.0 } 11.3 11.6 }	12.4 } 12.0 11.6 }	110.0	74.5 } 72.6 70.6 }	95.1 } 93.6 92.1 }
99.1	20.2 } 19.7 19.1 }	22.4 } 21.4 20.3 }			

The duplication of values of k_1 is good, but that with k_2 is sometimes not very good, owing probably to the relative inaccuracy of pressure recordings during the final period of reaction. Fig. 4 shows the plot of $\log k_1$ and $\log k_2$ against $1/T$ (where T is the absolute temperature). The slopes of the two lines are almost identical, each giving an activation energy of 35.5 k.-cals. per mol. This indicates that the reactions in both stages are identical, thus supplying further evidence in favour of the theory advanced by Prout and Tompkins. The equations derived by these authors have been used in the interpretation of the volume-time curves obtained from the thermal breakdown of other explosives, and it is hoped to communicate the result of some of this work in the near future.

EXPERIMENTAL.

The method and apparatus used for following the progress of decomposition were essentially those of Farmer (*loc. cit.*). Gas analyses were carried out by a method developed at Bristol University, for details of which we are indebted to Dr. C. E. H. Bawn. This comprises separation of the gases by fractional condensation, followed by analysis of the individual fractions. Fractionation and subsequent analyses were carried out in the absence of air, the gases being pumped off by means of a Toepler pump and measured dry. The main fractions obtained were as follows: Fraction I, gases volatile (in a vacuum) at -186° , comprised O_2 , NO , H_2 , CO , and CH_4 ; Fraction II, gases volatile at -120° , comprised CO_2 and N_2O ; the residue consisted of organic vapours, NO_2 , etc. The individual fractions were analysed by

FIG. 1.



accepted chemical methods. The pure samples of diazo-oxides were prepared and supplied by Dr. T. M. Walters of this Department. They were dried in a vacuum over potassium hydroxide and phosphoric oxide before use. Compounds (I) and (II) were photosensitive and had, therefore, to be dried in the dark. Detailed results obtained were as follows.

(a) *4-Nitrobenzene-2-diazo-1-oxide* (I).—Thermal decompositions were carried out at 50° , 60° , 70° , and 80° . The gas evolution-time curves were sigmoid in shape (Fig. 1) and decomposition had practically ceased when *ca.* 0.8 mol. of gas per mol. of (I) had been given off. The gases evolved on complete decomposition at 80° corresponded to 0.84 mol. per mol. of (I) and comprised N_2 , 89.9; NO , 0.7; CO_2 , 8.9; N_2O , 0.5%. It is assumed that the nitrogen is mainly derived from the diazo-group because it is well known that simple aromatic mononitro-compounds are quite stable below *ca.* 120° . The main reaction involves fission of the diazo-nitrogen, together with a small amount of breakdown of the benzene nucleus. Analysis of the gas at about half-decomposition indicated that the reactions involved are probably the same throughout the decomposition. Decomposition of (I) to which had been added 10% by weight of the reddish-black decomposition residue showed that the end-product is not a catalyst for the reaction and, as would be expected, the volatile products of decomposition were found to be without effect on the characteristics of the breakdown. For decomposition of 0.1 g. at 60° , 70° , and 80° , the times required for evolution of half the final gas volume were approx. 71, 17, and $4\frac{1}{2}$ hrs., respectively. It appears, therefore, that the temperature coefficient of the reaction over this temperature range is 3.5–4 per 10° . Thermal decomposition does not involve complete elimination of diazo-nitrogen; *e.g.*, at 80° only 0.76 mol. (or 1.52 atoms of N) are obtained. The blackish-red colour of the residue and the very intense red colour produced in acetone solution suggest that some coupling had occurred to form a comparatively stable product.

(b) *5-Nitrobenzene-2-diazo-1-oxide* (II).—Typical volume-time curves for thermal breakdown at 60° and 70° are shown in Fig. 2. The rate of thermal decomposition was appreciably greater than that of (I) as is shown by the fact that at 70° the times for evolution of $\frac{1}{2}$ mol. of gas per mol. of (I) or (II) were 20.2 and 6.5 hrs., respectively (0.1 g. tested in each case). The volume-time curve at 60° is sigmoid,

although not as markedly so as with (I), probably owing to the slow decomposition of the latter at this temperature. Complete decomposition at 70° gave 0.77 mol. of gas/mol. of (II), and the composition of

FIG. 2.

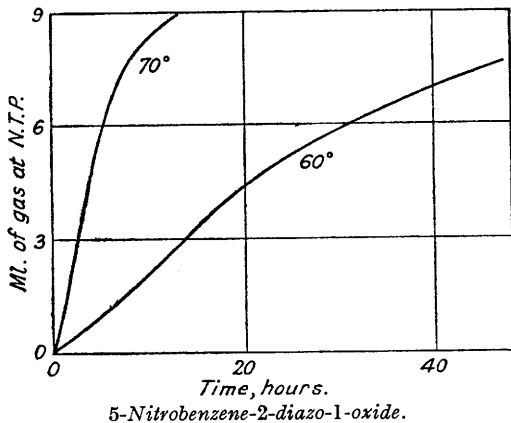
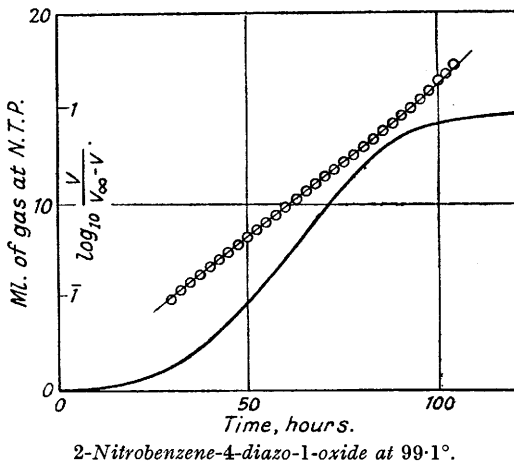
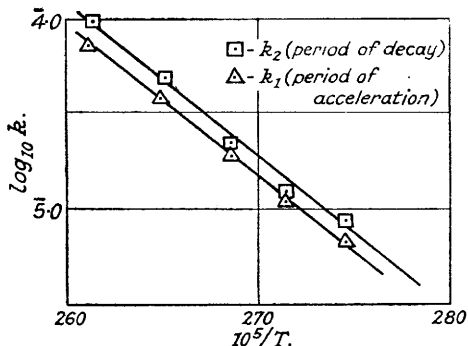


FIG. 3.



this gas was : N₂, 92.0; CO₂, 7.1; N₂O, 0.3; NO, 0.6%. After partial decomposition, the composition of the gases evolved was practically the same, indicating that the same main reaction is occurring throughout the decomposition. Of the original diazo-nitrogen only 0.71 mol. (1.42 atoms of N) is eliminated. As with (I), it is probable that some coupling takes place with the formation of a comparatively stable product containing the residual diazo-nitrogen.

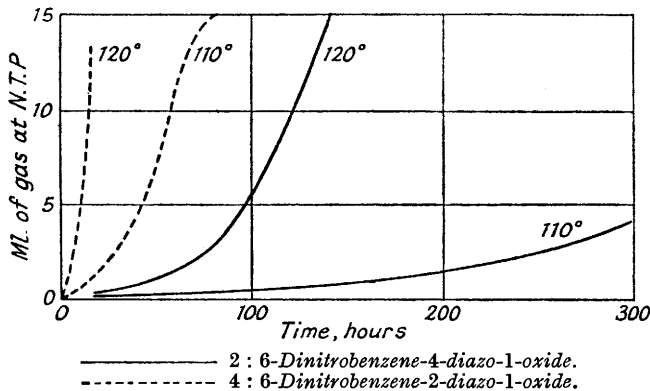
FIG. 4.



(c) 2-Nitrobenzene-4-diazo-1-oxide (III).—Thermal decompositions were conveniently carried out in the range 90–120° and sigmoid volume-time curves were obtained (Fig. 3). On "complete" decomposition at 120°, 1.09 mols. of gas per mol. of (III) were eliminated; the composition of these gases was : N₂, 90.0; N₂O, 1.0; CO₂, 7.6; CO, 1.4%, indicating that approximately 0.99 mol. of diazo-nitrogen is eliminated per mol. of (III). From comparison of the time taken to evolve $\frac{1}{2}$ mol. of gas per mol. of (III), a temperature coefficient of 3.5–4 per 10°, for the range 90–110°, was obtained.

(d) 4 : 6-Dinitrobenzene-2-diazo-1-oxide (IV).—Thermal decompositions were studied in the range 110–120°; typical sigmoid volume-time curves are shown in Fig. 5. The amount of gas evolved on "complete" decomposition is about 1½ mol. per mol. of (IV), *i.e.*, far greater than can be accounted for by elimination of the diazo-nitrogen. The composition of the gases was : N₂, 61.5; NO, 3.0; N₂O, 4.0;

FIG. 5.



CO, 2.5; CO₂, 28.0%, together with a trace of organic vapours; these results indicate that some breakdown and rearrangement of the benzene nucleus occurs, in addition to loss of diazo-nitrogen.

(e) 2 : 6-Dinitrobenzene-4-diazo-1-oxide (V).—The characteristics of thermal decomposition are similar to those of (IV) and the sigmoid volume-time curves obtained are illustrated in Fig. 5. Compound (V) is, however, considerably more stable than (IV); *e.g.*, 1 mol. of gas is evolved per mol. of (V) in *ca.* 121 hrs. at 120°, whilst under the same conditions (IV) evolves this amount of gas in 18 hrs. More gas is evolved on "complete" decomposition than can be accounted for by elimination of diazo-nitrogen, and, as with (IV), analysis of this gas indicates that partial breakdown of the benzene nucleus occurs.

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