620. *Inflammation of Methyl and Ethyl Nitrate Vapours: Characteristics of the Explosion Process and Intermediate Reactions involving Nitrogen Dioxide.*

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The pressure limit of spontaneous ignition (explosion limit) of methyl nitrate vapour in a given vessel is found to depend on the nature of the vessel surface and to be lowered to different extents by different inert gases; explosion is aided more by argon than by carbon dioxide. It is suggested that the explosion of the alkyl nitrates is a chain-thermal process.

The alkyl nitrate vapours can show three modes of decomposition—explosive ignition, faint luminescence (glow) and decomposition unaccompanied by light. These decompositions involve as intermediate processes the oxidation of aldehydes and alcohols by nitrogen dioxide, and the inflammations of such mixtures have been examined separately. Mixtures with nitrogen dioxide of methyl or ethyl alcohol show the same three modes of reaction as methyl nitrate; formaldehyde and acetaldehyde appear to have only two modes of reaction—slow reaction and explosion.

WHEN methyl nitrate vapour is admitted to a hot vessel, decomposition occurs and the nature of the decomposition depends on the pressure of the vapour and the temperature of the vessel. At low temperatures reaction is slow; at higher temperatures (above 250°) above a critical pressure limit, the decomposition is accompanied by a faint, blue glow, and above a second pressure limit spontaneous ignition occurs explosively. If these limits of glow and explosion are plotted as functions of temperature, the regions on the diagram correspond to the three modes of decomposition.

Mixtures of methyl nitrate vapour with argon and nitrogen explode more readily than does the pure vapour itself; this behaviour shows that self-heating is of secondary importance among the factors influencing explosion. As this effect is observed at pressures where there is no tendency for the decomposition reaction to lose its first-order kinetics [the value of k is maintained down to pressures of the order of 2 mm. (Appin, Chariton, and Todes, *Acta Physicochim. U.R.S.S.*, 1936, **5**, 655], the explosion must be explained in terms of autocatalysis involving branched radical-chains. The inert gases aid explosion by impeding the rate at which radicals diffuse to the walls. Such explosions are often sensitive to the influence both of added intermediate products and of small amounts of foreign substances (sensitizers and inhibitors) and to the nature as well as the extent of the vessel surface. The explosion limit of methyl nitrate has been measured in vessels the surfaces of which were coated with different substances, and in the presence both of initially added decomposition products and of some common sensitizers and inhibitors. The influence of some of these factors on the inflammation of ethyl nitrate has also been examined.

Although not of primary importance, self-heating may play some part; to assess its contribution the effects on explosion of diluents with different diffusion constants and specific heats have been measured.

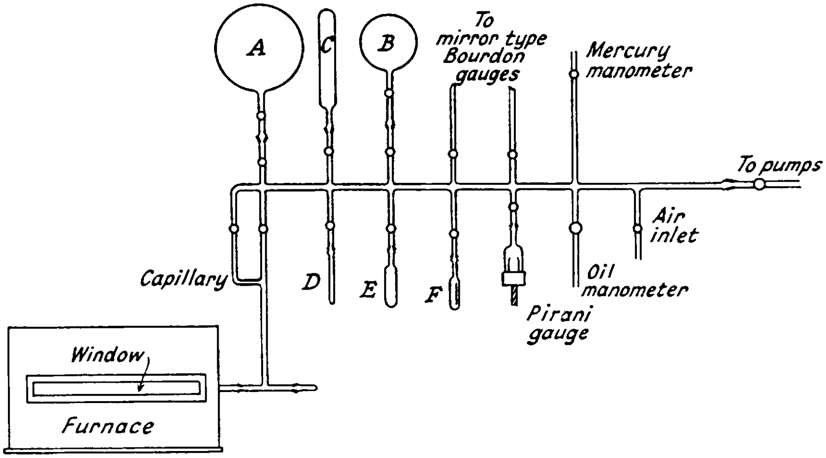
The decomposition of the alkyl nitrates is a complex process, and both glow and explosion processes appear to be due to reactions occurring among the intermediate products formed, *e.g.*, the reactions of aldehydes and alcohols with nitrogen dioxide. The salient features of some of these reactions have been investigated so as to identify glow and explosion processes more nearly; and mixtures with nitrogen dioxide of the simple aldehydes and alcohols show modes of inflammation very similar to those of the pure nitrate esters.

EXPERIMENTAL.

Materials.—Methyl and ethyl nitrates were supplied by the Explosives Research and Development Establishment, Waltham Abbey. They were distilled under reduced pressure, and only the middle fractions were used. Argon and carbon dioxide were taken from cylinders. Nitrogen dioxide was prepared by heating dry " AnalaR " lead nitrate and pumping off the oxygen from the frozen dinitrogen tetroxide. A sample of 98% pure tetraethyl-lead was supplied by the Shell Research Laboratories, Thornton.

FIG. 1.

Apparatus for determining limits of inflammability of vapours.



Formaldehyde monomer was prepared from paraformaldehyde by the method described by Spence and Wild (*J.*, 1935, 338). Acetaldehyde was distilled from a sample of " absolute " acetaldehyde after drying over calcium chloride; samples of " pure " methyl and ethyl alcohols were used direct.

Procedure.—The pressure limits of spontaneous ignition (explosion limit) are measured by determining the partial pressure of explosive vapour necessary for ignition on admission to a hot vessel (method of Mallard and Le Chatelier, *Compt. rend.*, 1880, **91**, 825). The apparatus used is shown in Fig. 1. Mixtures of known composition of the vapours from reactant liquids stored in the small vessels E and F

with the gases stored in the bulbs *B* and *C* can be prepared in the bulb *A* by means of sensitive glass Bourdon gauges. The whole line can be heated electrically to prevent polymerization during experiments with monomeric formaldehyde. All the taps are lubricated with silicone greases to minimise absorption of organic vapours. The reaction vessel is kept at a steady, uniform temperature in the furnace; it can be seen through a window in the side. The furnace is built around an electrically heated, clear quartz tube. To achieve temperature uniformity, power is supplied to different sections independently, and a metal sheath surrounds the reaction vessel. The temperature, which is kept at a steady value by a Sunvic RTI thermostat, is measured with an accurate platinum-resistance thermometer.

Inflammation of Methyl Nitrate Vapour.—The pressure limit of spontaneous ignition in a Pyrex vessel over a temperature range 310—380° was determined. Above about 400° in this apparatus it became difficult to distinguish this explosion from the glow. No induction periods were observed. The explosion limit in vessels of different diameters and with different surface coatings was measured (see Table I). Explosion is more difficult in smaller vessels, as observed by Appin *et al.* (*loc. cit.*); this fact may be explained in terms either of self-heating or of radical chains. Explosion and glow limits were higher in vessels coated with potassium iodide than in one with a potassium chloride surface, and such a result, together with the difference in numerical values for explosion limits obtained by different workers and the phenomenon of "conditioning" the reaction vessel (the irreproducibility of the first few explosion limits in a new vessel or one exhaustively evacuated), provide support for a radical mechanism.

TABLE I.

The effect of the nature and extent of vessel surface on explosion and glow limits of methyl nitrate.

Temperature 350°.

	Pressure limit (mm. Hg).			
	5-Cm. Pyrex vessel: Surface/volume = 0·9 cm.$^{-1}$.	3-Cm. Pyrex vessel: Surface/volume = 0·5 cm.$^{-1}$.		
Process.	Clean.	Clean.	KCl-coated.	KI-coated.
Glow	0·11	—	0·2	0·38
Explosion	1·15	2·0	2·1	2·3

In the vessel coated with potassium iodide the difference between glow and explosion was less clear, and instead of the sharp distinction between a bright yellow flash and a feeble blue glow, as in the quartz vessel (Gray and Yoffe, *Nature*, 1949, **164**, 830; *Proc. Roy. Soc.*, 1949, **200**, *A*, 114) the colour of the explosion itself became blue near the limit.

The effect on the explosion limit of adding intermediate products of decomposition was examined, and mixtures of methyl nitrate with nitrogen dioxide (cf. Appin *et al.*, *loc. cit.*), formaldehyde, and methyl alcohol were examined. Only the methyl alcohol showed any effect, lowering the explosion limit in a 3-cm. Pyrex vessel coated with potassium iodide from 2·3 mm. to 2·1 mm. Mixtures with tetraethyl-lead were also examined, and this compound was found to have no effect.

According to the radical-chain theory of explosions, added inert gases, by impeding the diffusion to the walls of the active radicals, aid explosion, whereas according to the thermal theory, dilution makes explosion more difficult by increasing the thermal conductivity and thermal capacity of the mixture, both effects reducing the intensity and rate of self-heating. Thus the influence on the explosion limit of inert diluents of differing physical properties can give information about the importance of self-heating. Table II lists values in terms of those relative to helium of diffusion constants, *D*, thermal conductivities, *k*, and molecular specific heats, *C*, of three gases, and it may be seen that, although specific heats and diffusion constants do not vary similarly, thermal conductivities and diffusion constants do, being related according to the simple kinetic theory by the relation $k \propto DC$.

TABLE II.

Comparison of specific heats at constant volume, C, *thermal conductivities,* k, *and diffusion constants,* D.

Temperature 375°.

(All magnitudes in terms of helium.)

Gas.	C/C_{He}.	k/k_{He}.	D/D_{He}.
Argon	1	0·13	0·13
Nitrogen	1·7	0·18	0·13
Carbon dioxide	3·2	0·16	0·08

It is for this reason that comparison of behaviour as diluents of the series of gases He, Ne, A, Kr, Xe of identical specific heat does not provide a means of distinguishing between the two mechanisms, since any difference in the effect on explosion limit can be ascribed either to differences in thermal conductivity or to the identical differences in the diffusion constants. In the pair of gases argon and carbon dioxide, however, the distinctions are clear. The specific heat of carbon dioxide is greater than that of argon. If explosion is due entirely to self-heating, carbon dioxide should quench it more easily. However, if the explosion is due entirely to radicals, because carbon dioxide impedes diffusion more than does argon it should aid explosion more. Table III contains the values of the explosion limits of pure methyl nitrate vapour and of mixtures diluted with argon and carbon dioxide.

TABLE III.

Effect of diluents on spontaneous ignition limit of methyl nitrate.

Composition of vapour.	Partial pressure (mm. Hg) of methyl nitrate for explosion.	
	318°.	360°.
Pure $MeO{\cdot}NO_2$	4·2	1·8
0·5 Mole argon	3·5	1·3
0·5 Mole CO_2	3·5	1·6
0·67 Mole argon	3·1	1·2
0·67 Mole CO_2	3·4	—

Both gases lower the explosion limit at all the dilutions examined, and the greater the dilution the lower the explosion limit. As the dilution increases, distinctions between glow and explosion diminish, and in mixtures of 4 : 1 and 9 : 1 carbon dioxide : methyl nitrate ratios it is very difficult to distinguish between the two processes. These observations re-emphasize the primary importance of radical diffusion.

Argon reduces the explosion limit more than carbon dioxide does, and the higher the temperature the greater the difference between them. Since carbon dioxide has a greater specific heat than argon, this may be explained in terms of the difference in the degree of self-heating occurring, which will be less with carbon dioxide than with argon, especially at the higher temperatures where the difference in specific heats is greater.

Inflammation of Ethyl Nitrate Vapour.—It was not possible to observe distinct glow and explosion processes when pure ethyl nitrate vapour was admitted to a Pyrex vessel of 3 cm. diameter at 350°, but only a blue inflammation of continuously varying intensity and duration. This observation is in agreement with the analyses by Bawn and Adams (*Trans. Faraday Soc.*, 1949, **45**, 494), who found the products of inflammation to alter in proportion at different temperatures but to contain very little nitrogen, suggesting that this flame corresponds to a reaction less complete than the explosion of methyl nitrate.

Pollard, Wyatt, and Marshall (*Nature*, 1950, **165**, 564) found that added nitrogen dioxide in widely differing proportions made possible the propagation through the cold vapour of ethyl nitrate of a flame initiated by a spark, and the effect of the oxide on its spontaneous ignition limit was accordingly examined at 350°. A mixture of equal amounts of ethyl nitrate and nitrogen dioxide appeared to behave like pure ethyl nitrate; one with about two-thirds of the proportion of nitrogen dioxide showed clearly the distinct modes of explosion and glow, the bright flame being carried back through the cold mixture in the line. This behaviour is paralleled by that of oxygen mixtures, which also show both the glow and explosive combustion.

Intermediate Reactions occurring in the Inflammation of the Alkyl Nitrates.—The initial step in the thermal decomposition of the alkyl nitrates appears to be the breaking of the O–N bond : $RO{\cdot}NO_2 \longrightarrow RO{-} + NO_2$ (Appin, Chariton, and Todes, *loc. cit.*; Bawn and Adams, *loc. cit.*; Phillips, *Nature*, 1947, **160**, 753; 1950, **165**, 564). Nitrogen dioxide is found as a product of the slow decomposition and may also be isolated (by freezing) after the glow process has occurred. Subsequent reactions of the appropriate alkoxy-radical lead to the formation of formaldehyde polymer from methyl nitrate decomposition and of some ethyl alcohol from ethyl nitrate decomposition, and the further reactions occurring during explosion involve both the reduction of the nitrogen dioxide to nitric oxide and nitrogen and its dissociation into nitric oxide and oxygen. Accordingly, the inflammations of mixtures with nitrogen dioxide of the simplest aldehydes and alcohols have been examined in outline.

Inflammation of Methyl Alcohol–Nitrogen Dioxide Mixtures.—When methyl alcohol vapour is mixed with nitrogen dioxide and the mixture admitted to the hot vessel, modes of reaction are observed which are identical with the modes of decomposition of methyl nitrate, *viz.*, slow reaction, reaction accompanied by a faint blue glow, and explosion. Mixing of the alcohol and nitrogen dioxide, however, is always accompanied by a fall in pressure and reaction occurs. Methyl nitrite has been identified spectroscopically among the products, and the mixed acid anhydride nitrogen dioxide is presumably reacting to give both nitrate and nitrite esters. This is in accord with the results of Harris and Siegel (*J. Amer. Chem. Soc.*, 1941, **63**, 2520), who detected no reduction of the dioxide to monoxide on mixing with methyl alcohol. The minimum pressures required for glow and explosion at 350°, 0·2 mm. and 5 mm., respectively, are comparable with those of methyl nitrate itself, 0·2 mm. and 2 mm.

Fig. 2 shows the explosion and glow limits at 350° of mixtures containing different amounts of nitrogen dioxide. In calculating the mole-fractions in terms of nitrogen dioxide allowance has been made for the association reaction $2NO_2 \rightleftharpoons N_2O_4$, though in this case the interaction of the two components makes the calculated mole-fractions only approximate indications of composition.

Dilution of methyl alcohol nitrogen dioxide mixtures with argon makes both explosion and glow easier, total pressures for these processes in dilute mixtures at 350° being :

Mixture 1, 200 vols. A + 1 vol. $CH_3{\cdot}OH$ + 1 vol. " NO_2," glow limit 5 mm.

Mixture 2, 2 vols. A + 1 vol. $CH_3{\cdot}OH$ + 1 vol. " NO_2," explosion limit 7·4 mm.

Inflammation of Ethyl Alcohol–Nitrogen Dioxide Mixtures.—Mixtures of ethyl alcohol and nitrogen dioxide also show glow and explosion regions, though the explosions are given only by dioxide-rich mixtures which can react to give either a blue glow or a yellow flame; *e.g.*, a mixture of 1 vol. of EtOH + 2 vols. of " NO_2 " (1EtOH : 3·7NO_2), admitted to a hot vessel at 350°, glows at 3 mm. and explodes at 10 mm. Mixtures weaker in nitrogen dioxide show only a blue inflammation which cannot be assigned definitely to glow or explosion process. Reaction also occurs in these cold mixtures, however, and ethyl nitrate may be present.

Inflammation of Formaldehyde–Nitrogen Dioxide Mixtures.—The apparatus was heated to 60° to prevent polymerization of the formaldehyde, and mixtures of the monomer with nitrogen dioxide were made. Very little reaction occurred during the period of mixing in the warm line. Only two modes of reaction were apparent when the mixtures were admitted to the hot vessel—one unaccompanied by any light, and the other accompanied by a bright flame and violent explosion. No induction periods were observed with these mixtures, which exploded more readily the higher the temperature, as found by Pollard and Woodward (*Trans. Faraday Soc.*, 1949, **45**, 767). At 350°, pressures of the order of 20 mm. were required for explosion in the 3-cm. diameter vessel, and rather less in the 5-cm. vessel. No process corresponding to the blue luminescence of decomposing methyl nitrate was observed either at 350° or at 400°.

FIG. 2.

Inflammation of methyl alcohol–nitrogen dioxide mixtures.

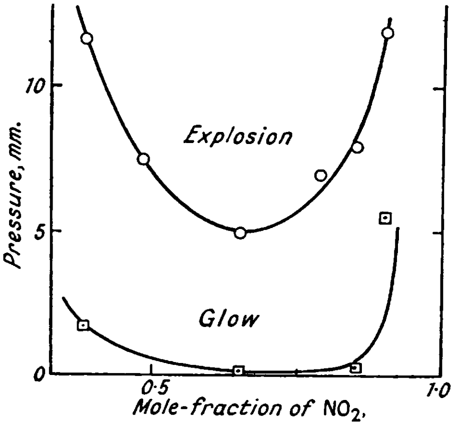
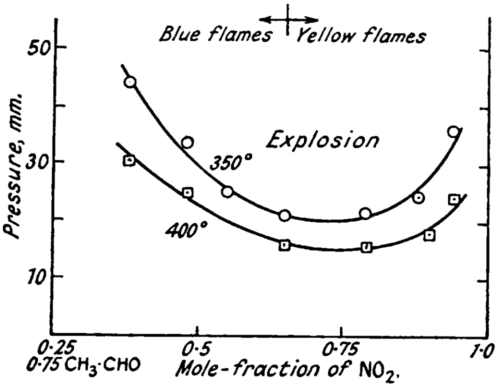


FIG. 3.

Inflammation of acetaldehyde-nitrogen dioxide mixtures.



Inflammation of Acetaldehyde–Nitrogen Dioxide Mixtures.—Mixtures of acetaldehyde and nitrogen dioxide were also examined, and again only two modes of reaction—slow, dark reaction and immediate, explosive ignition—were found at the temperatures (350° and 400°) studied. No difficulties from polymerization were encountered. The variation with mixture composition of the spontaneous ignition limit was measured at these temperatures, and it was found that mixtures with about 0·8 mole of the dioxide (stoicheiometric 0·79) were the most easily ignited (Fig. 3). This is also the mixture found by Hale (Pollard, private communication) to react most readily. The colour of the flames obtained altered from blue to yellow as the composition altered from aldehyde-rich to nitrogen dioxide-rich mixtures.

DISCUSSION.

The different modes of decomposition of methyl and ethyl nitrates correspond to different stages in reactions among the immediate products of decomposition of the original molecule. The reaction producing the glow does not appear to be sharply different in character from the slow decomposition, since nitrogen dioxide remains after the glow (which occurs at pressures and temperatures too low for any oxidation by nitric oxide to be responsible). Furthermore, since aldehyde–nitrogen dioxide mixtures do not show the glow reaction, it is clear that in this process the light-emitting species must itself be produced from either ROH molecules or RO radicals, and it is not unlikely that, as in the case of cool flames in hydrocarbons, the emission of light is incidental to the main decomposition reactions.

The explosion of methyl nitrate is a much more nearly complete decomposition and is normally sharply different from the glow; during it, nitric oxide is reduced to nitrogen, and aldehydes and alcohols are oxidized. As the removal of nitric oxide is made more difficult by extensive dilution of the methyl nitrate, so that its partial pressure is lower and the temperature does not rise so much, the explosion loses its bright yellow flame for a blue one. In decomposition of ethyl nitrate the unfavourable oxygen balance makes the attainment of sufficiently high temperatures for the complete removal of nitric oxide impossible, and bright yellow flames and violent explosion can be obtained only with added oxygen or nitrogen dioxide; similarly, at these pressures, only those mixtures of acetaldehyde or ethyl alcohol with a large proportion of nitrogen dioxide will explode vigorously.

The effect on the explosion of methyl nitrate of the different diluents examined shows clearly that self-heating cannot be neglected in a complete account of its decomposition, though it is of secondary importance; the explosion may be assigned to the class of ignitions called " chain-thermal."

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