

Thermal Decomposition of Organic Nitrates

In an earlier note¹, the basic mechanism proposed for the thermal decomposition of the organic nitrates was :

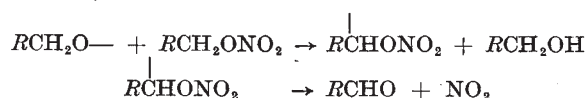


followed by oxidation-reduction reactions between nitrogen dioxide and aldehydes.

It has recently become evident² that the initial step is followed by the recombination reaction :



since nitrogen dioxide, initially added, retards the reaction, the retardation being roughly proportional to the amount added. Furthermore, the disproportionation of the alkoxy radical shown above is improbable since it involves collision between identical radicals, the reactions

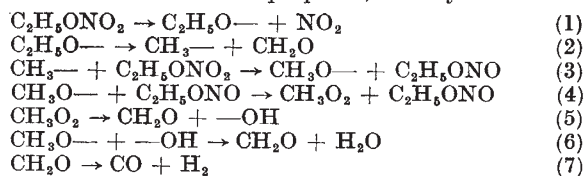


being more probable³.

On the above basis, kinetic equations can be formulated which will account for the retardation of the reactions by nitrogen dioxide, and for the peculiar initial linearity and subsequent first-order behaviour often observed in the p/t curves obtained in overall decomposition studies².

With mono-nitrates of C₃ and above, it appears that the alkoxy radical may also undergo C—C bond fission to form an alkyl radical and formaldehyde, as suggested by Hinshelwood⁴; thus formaldehyde is a decomposition product of *n*-propyl nitrate.

It is noted that Theile⁵ has recently proposed two different mechanisms for the decomposition of ethyl nitrate, of which that for 600° C./1 atm. agrees with the above, except that no recombination is postulated. At 250° C. and 16 mm. pressure, however, a different mechanism is proposed, namely :



The products identified differ from those found by me and by Bawn and Adams⁶, in that they contain ethyl nitrite and no acetaldehyde.

While it is agreed that C—C bond fission may occur in the ethoxy radical at the low pressures used by Theile (vide Rice and Rodowskas⁷), detailed criticism of Theile's work is difficult because of the lack of detail; but the above mechanism is open to doubt on several counts. Thus it is difficult to see why the methoxy radical abstracts oxygen from an ethyl nitrate radical at 250° C. if the ethoxy radical reacts in the normal way, that is, it abstracts hydrogen, at 600° C.

Furthermore, Rice and Teller⁸, in their considerations of probable reactions between free radicals and organic molecules on the basis of the principle of least motion, point out that reactions between radicals and negative groups are less probable than those with positive groups or atoms, a rule which in general is supported by a weight of experimental evidence. On this basis, therefore, it would appear

that reactions (3) and (4) above are improbable, a view which is supported by the fact that methyl radicals readily methylate trinitrotoluene⁹ (cf. reaction (3) above).

Further details of this work will shortly be published elsewhere.

This communication is published with the approval of the Chief Scientist, Ministry of Supply.

L. PHILLIPS

Explosives Research and
Development Establishment,
Ministry of Supply.
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¹ Phillips, *Nature*, **160**, 753 (1947).

² Phillips, Ministry of Supply (unpublished work, 1948).

³ Phillips, Ministry of Supply (unpublished work, 1948).

⁴ Hinshelwood, "The Labile Molecule", Faraday Society Discussions, No. 2, 112 (1947).

⁵ Theile, *Angew. Chem.*, **A**, 65 (March 1948).

⁶ Bawn and Adams, *Trans. Farad Soc.* (May 1949).

⁷ Rice and Rodowskas, *J. Amer. Chem. Soc.*, **57**, 350 (1935).

⁸ Rice and Teller, *J. Chem. Phys.*, **6**, 493 (1938).

⁹ Fieser *et al.*, *J. Amer. Chem. Soc.*, **64**, 2052 (1942).

Retarding (Inhibiting) and Sensitizing Effects of Nitrogen Dioxide in Alkyl Nitrate Decompositions

THE primary step in the decomposition of alkyl nitrates is considered to be the breaking of the O—N bond^{1,2,3}. Phillips⁴ has shown that such decompositions are retarded by initially added nitrogen dioxide, and he has suggested that this primary step is an equilibrium reaction



We have shown that this is so in the case of ethyl nitrate by determining the initial rates of decomposition when increasing amounts of nitrogen dioxide are added to a fixed partial pressure of the nitrate. The expected relationship holds up to a certain concentration for the added nitrogen dioxide, when the rate begins to increase again. Since the final products, due to oxidation of acetaldehyde and ethanol by nitrogen dioxide, are not affected by the initial addition of nitrogen dioxide, this increase in rate points to a catalytic process, similar to the effect of nitric oxide on the decomposition of acetaldehyde⁵.

Phillips⁴ also showed that nitric oxide did not affect the rates of decomposition, and we have confirmed this for ethyl nitrate. It appears that the recombination process $RCH_2O\cdot + NO \rightarrow RCH_2ONO$ occurs at a much slower rate. Steacie⁶ did not report any experiments of adding nitric oxide to decomposing alkyl nitrites, but no effect is to be expected; and the crucial experiment to substantiate the similarity in the two groups of decompositions will be to test the supposition that nitrogen dioxide will retard the decomposition of alkyl nitrites.

Though a flame can be initiated on sparking methyl nitrate vapour in the closed system⁷, no flame can be induced in ethyl nitrate vapour, at least, not up to 7.5 cm. mercury initial pressure. But if 2–3 per cent of nitrogen dioxide is added to the nitrate vapour, a flame will be propagated, and if the percentage of nitrogen dioxide is increased, the flame goes faster. Norrish and Foord⁸ showed that methane increased the induction period for the nitrogen dioxide sensitized hydrogen-oxygen reaction, and if methane is added to a mixture of nitrogen dioxide and ethyl nitrate so that the composition of the mixture is 6 per cent methane, 6 per cent nitrogen dioxide and