325. *Esterification by Dinitrogen Tetroxide.*

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The reaction at room temperatures between dinitrogen tetroxide and ethyl and methyl alcohol in the liquid and the vapour phase has been examined in outline. Reaction is rapid, and it has been found that very little alkyl nitrate is produced, the products being nitric acid and the alkyl nitrite : $R \cdot OH + N_2O_4 \longrightarrow R \cdot O \cdot NO + HO \cdot NO_2$. Oxidation is slight. The importance of this to studies of inflammation of alcohol–nitrogen dioxide mixtures is discussed.

STUDIES of the thermal decomposition in the vapour phase of methyl nitrate (Gray and Yoffe, *Nature*, 1949, **164**, 830; *Proc. Roy. Soc.*, 1949, *A*, **200**, 114) revealed the existence of three distinct modes of reaction, *viz.*, explosive ignition, faintly luminous decomposition, and slow decomposition unaccompanied by light. To obtain information about the behaviour of the nitrates, an investigation was made of the inflammation of gaseous mixtures with dinitrogen tetroxide of the vapours of simple alcohols and aldehydes (*idem, J.*, 1950, 3180). It was found that, although mixtures made by adding an excess of dinitrogen tetroxide to alcohol vapour showed the same three modes of reaction as the alkyl nitrate itself, yet mixtures of dinitrogen tetroxide with aldehydes did not exhibit the chemiluminescent reaction. At these temperatures (350°) the oxide is probably reacting as NO_2.

However, it was noticed that when equivalent amounts of methyl alcohol and dinitrogen tetroxide vapours, separately at pressures of about 2 cm., were mixed, decolorization was complete in a few minutes, showing that a rapid reaction was occurring in the cold. The products were all easily condensable and nitric oxide was not found among them by Harris and Siegel (*J. Amer. Chem. Soc.*, 1941, **63**, 2520).

At room temperature nitrogen dioxide and dinitrogen tetroxide exist together in equilibrium and it was thought that the chemical change occurring was not oxidation by

nitrogen dioxide, as at higher temperatures, but esterification by the mixed acid anhydride dinitrogen tetroxide to give both nitrate and nitrite :

$$2R \cdot OH + N_2O_4 \longrightarrow R \cdot O \cdot NO_2 + R \cdot O \cdot NO + H_2O \quad . \quad . \quad . \quad . \quad . \quad (1)$$
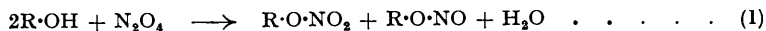
The reaction was therefore carried out both in the gas and in the liquid phase, and the products examined for nitrites and nitrates.

EXPERIMENTAL.

Gas-phase Reaction.—A slight excess of alcohol vapour was mixed in a 4-l. bulb with a few cm. pressure of dinitrogen tetroxide, and reaction allowed to proceed until no brown colour remained. Under these conditions there was a fall of pressure, and at higher concentrations, a mist formed and condensed on the wall.

The mixture was pumped out, condensed in a trap at $-170°$, and then allowed to warm. It was an acidic liquid and was neutralized with calcium carbonate. During these operations volatile methyl nitrite (b. p. $-17°$) bubbled off. The residue was examined for methyl nitrate. None was found, and combined nitrogen was not detected by analysis in the fraction distilling below $70°$. Nor was ethyl nitrate found among the products of reaction of dinitrogen tetroxide and ethyl alcohol.

Absorption spectra of reaction products (dissolved in ethyl alcohol) compared with absorption spectra of gaseous methyl and ethyl nitrites.
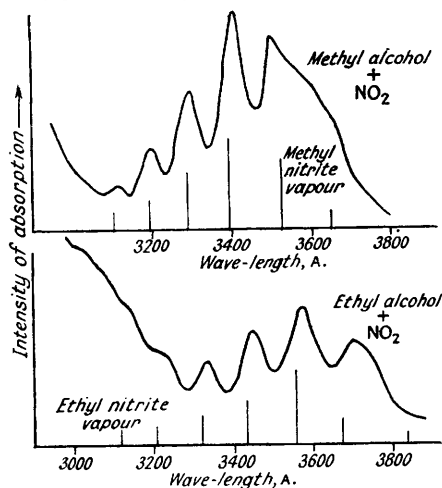
However, both methyl and ethyl nitrites were formed in good yield and were identified spectroscopically by measurements * of light absorption in the wave-length range 2500—4000 A., where the nitrites possess a very characteristic set of maxima in their absorption spectrum (Thompson and Purkis, *Trans. Faraday Soc.*, 1936, **32**, 674; Style, private communication). In the figure the absorption spectra of the reaction products dissolved in ethyl alcohol are compared with the spectra of the gaseous nitrites.

The equation representing the changes occurring is therefore of the form

$$MeOH + N_2O_4 \longrightarrow Me \cdot O \cdot NO + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (2a)$$
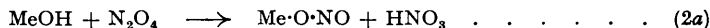
Liquid-phase Reaction.—The reaction between ethyl alcohol and dinitrogen tetroxide was also examined in the liquid phase. About 5 ml. of pure liquid dinitrogen tetroxide were distilled into a slight excess of pure ethyl alcohol in a glass tube cooled to $-170°$. The tube was sealed off and after being allowed to warm gradually to $20°$ was left for some days. Two layers formed and a pressure above atmospheric was released when the tube was opened. The two layers were separated by cooling and pouring off the upper liquid from the frozen crystals below. On melting, the crystals formed a non-inflammable liquid containing nitric acid.† The upper layer was a pale yellow, odorous, inflammable liquid of low freezing point; it could be distilled below $25°$, leaving only a few drops of liquid to distil at $76°$ with slight charring. It was composed almost entirely of ethyl nitrite (b. p. $+17°$) though a faint smell of acetaldehyde suggested that very slight oxidation had occurred.

From these experiments it may be inferred that the principal reaction occurring here is
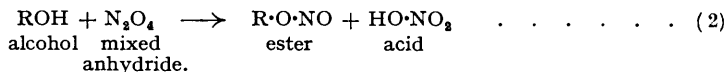
$$EtOH + N_2O_4 \longrightarrow Et \cdot O \cdot NO + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

* We are grateful to Dr. R. N. Haszeldine for these measurements.
† Whitehurst (private communication) also found nitric acid among the products of this reaction.

<div align="center">DISCUSSION.</div>

The products of the reaction occurring between these simple alcohols and dinitrogen tetroxide in both the gas and the liquid phase are nitric acid and the nitrite ester. The reaction may best be represented by equation (2) and not by (1), since although some aldehyde and nitrate

$$ROH + N_2O_4 \longrightarrow R\cdot O\cdot NO + HO\cdot NO_2 \quad \ldots \ldots \quad (2)$$

$$\text{alcohol} \quad \text{mixed} \qquad\qquad \text{ester} \qquad \text{acid}$$
$$\text{anhydride.}$$

may be formed they are present only in small amounts. [Dinitrogen tetroxide is referred to as a mixed anhydride (nitrous + nitric) although its structural formula is $O_2N\cdot NO_2$ and not $ON\cdot O\cdot NO_2$.] Formally, equations (1) and (2) differ only in the extent to which the reaction $ROH + HO\cdot NO_2 \longrightarrow R\cdot O\cdot NO_2 + H_2O$ has proceeded, and since the equilibrium for this change lies well on the right-hand side, the difference in yields of nitrite and nitrate esters may not be ascribed primarily to the differences in their free energies of formation by these reactions but rather to differences in the activation energies of reactions (1) and (2).

These observations are important to the study of the inflammation of the alkyl nitrates. The initial step in the thermal decomposition of methyl nitrate has been assumed (Appin, Chariton, and Todes, *Acta Physicochim. U.R.S.S.*, 1936, **5**, 655) to be $CH_3\cdot O\cdot NO_2 \longrightarrow CH_3\cdot O- + NO_2$ (cf. $CH_3\cdot O\cdot NO \longrightarrow CH_3\cdot O- + NO$ in the decomposition of the nitrite; see, *e.g.*, Steacie, " Atomic and Free Radical Reactions," Reinhold, 1946, p. 141). The $CH_3\cdot O$ radical itself gives rise to alcohol and aldehyde molecules; this fission and subsequent reactions of oxidation by the nitrogen dioxide are responsible for the complex behaviour of the nitrates. The glow process is associated with the formation and removal of the $CH_3\cdot O$ radicals, and the explosive ignition with the reduction of the nitrogen dioxide to nitric oxide and nitrogen.

Differences between the inflammations of mixtures of nitrogen dioxide with aldehydes on the one hand (2-stage processes) and with alcohols on the other (3-stage processes) are due to the ease with which the latter yield the RO radical, whether directly or through the nitrite ester. In the high-temperature reaction with aldehydes the reactive species is probably NO_2 and its prime reactions the abstraction of a hydrogen atom from the aldehyde giving $R\cdot CO$ radicals (McDowell and Thomas, *J.*, 1950, 1462) which yield $R\cdot$ but not the $RO\cdot$ apparently necessary for luminescence. The nitrite ester itself when mixed with oxygen or with dinitrogen tetroxide shows the same three modes of decomposition as methyl nitrate itself. The table sets out the limits of inflammation of such mixtures.

Spontaneous ignition limit of methyl nitrite–nitrogen dioxide mixtures and related systems.

	Partial pressure (mm. Hg) required for inflammation in hot Pyrex vessel (surface/volume = 0·9 cm.$^{-1}$).		
Temp. 350° c.		Mixture.	
Process.	MeO·NO + NO$_2$.	MeO·NO$_2$ + NO.	Pure MeO·NO$_2$.
Glow	1·4	1·3	0·07
Explosion	2·5	2·2	1·3

The two equimolecular mixtures (MeO·NO$_2$ + NO) and (MeO·NO + NO$_2$) which yield identical initial products of decomposition (*viz.*, $CH_3O- + NO + NO_2$ in each case) are seen to behave very similarly.

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