Mechanism of the Reaction of Nitrogen Dioxide with 2-Methyl-2-nitrosopropane

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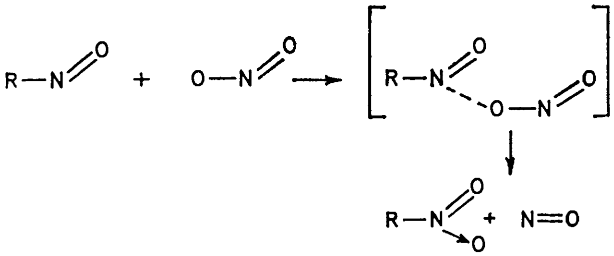
By means of a mass-spectrometric and isotopic labelling technique it is shown that the reaction $Bu^tNO + NO_2 \longrightarrow Bu^tNO_2 + NO$ occurs *via* an oxygen-atom transfer, and not by a displacement mechanism.

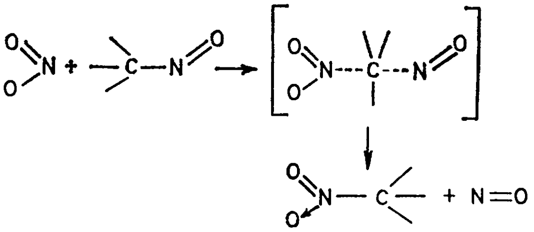
IT has been reported[1] that reaction (1) is rapid in the gas phase where R = Me, but the mechanism of the reaction is unknown.

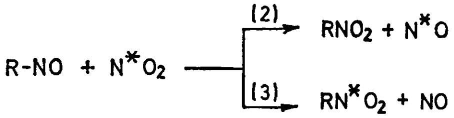
$$RNO + NO_2 \longrightarrow RNO_2 + NO \qquad (1)$$

There are two possible mechanisms, namely an oxygen-atom transfer (2) and a displacement mechanism (*i.e.*, S_H2 at the C atom).


(2)

In principle it should be possible to study such a system using isotopically labelled nitrogen dioxide.


(3)



In practice a refinement of the normal mass-spectrometric analytical method is required because the nitro- and nitroso-compounds and nitrogen dioxide all fragment at 50 eV or greater to give large mass-spectral peaks corresponding to NO^+, and the parent ion is absent for RNO and RNO_2. Analysis of the products therefore requires

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[1] L. Phillips and R. Shaw, Tenth Symposium (International) on Combustion, 1965, 453.

mass spectroscopy at low electron voltages where the contribution from these compounds to the NO^+ peak is negligible.

EXPERIMENTAL

trans-Dimeric 2-methyl-2-nitrosopropane was prepared by the method of Gowenlock and Trotman,[2] purified by recrystallization, and subjected to a number of distillations *in vacuo*. The *trans*-dimer was converted into the monomer before use and stored at 77 K in a blackened bulb.

[^{15}N]Nitrogen dioxide was prepared by the action of copper turnings on [^{15}N]nitric acid (99% isotopic purity). The gases evolved (a mixture of nitrogen dioxide and nitric oxide) were passed over phosphoric oxide and stored in a blackened bulb. The nitric oxide was converted into nitrogen dioxide by the repeated addition of aliquot portions of oxygen, until the solid at 77 K was colourless, and no nitric oxide could be detected mass spectrometrically. The $^{15}NO_2$ was distilled *in vacuo* before each experiment.

A conventional greaseless high-vacuum system was used. The reaction was carried out at room temperature in a 250 ml glass bulb. 2-Methyl-2-nitrosopropane was admitted to the reaction bulb at pressures of 1—10 Torr, and a nearly equal pressure of $^{15}NO_2$ added. The reaction system was connected through a Metrosil sinter and a needle valve to the direct inlet port of an AEI MS10 mass spectrometer, so that samples of the reactant mixture could be admitted directly for analysis. Most analyses were carried out at 10 eV, measured by a Hewlett–Packard 3439A digital voltmeter. At this low electron accelerating voltage, no peak due to NO_2^+ or NO^+ could be detected when pure nitrogen dioxide was admitted to the mass spectrometer. Pure samples of 2-methyl-2-nitrosopropane and 2-methyl-2-nitropropane were also analysed mass spectrometrically at 10 eV. The results are in Table 1.

TABLE 1

m/e	30	56	57	58
Bu^{t}NO	1·3	33	100	8
Bu^{t}NO$_2$	4	100	17	7

The values obtained for the *m/e* 30 peak for these two compounds are almost identical to the residual background before the admission of the compound.

Thus the use of an electron accelerating voltage of 10 eV enables nitric oxide (appearance potential = 9·25 eV) to be detected in the presence of the nitroso- and nitro-compounds and nitrogen dioxide. Comparison of the peaks at *m/e* 56 and 57 enables the nitroso- and nitro-compounds to be distinguished.

RESULTS AND CONCLUSIONS

Upon mixing the 2-methyl-2-nitrosopropane with [^{15}N]nitrogen dioxide, a steady reaction occurred at room temperature. During *ca.* 10 min the initial dark brown colour due to the nitrogen dioxide diminished in intensity until, if an excess of nitroso-compound was used, the reaction flask appeared colourless. A mass spectrum at 10 eV of the contents of the reaction bulb after reaction showed a base peak at *m/e* 56, characteristic of the nitro-compound, and a peak at *m/e* 31 due to $^{15}NO^+$. Condensation of the products of the reaction at 77 K showed the absence of the blue colour characteristic of the nitroso-compound. Typical mass spectral analyses of the reaction mixture are in Table 2. The reaction mixture was usually analysed twice, the first sample being withdrawn after *ca.* 5 min, the second after 20—30 min.

The large *m/e* 56 value shows that during the reaction between [^{15}N]nitrogen dioxide and 2-methyl-2-nitrosopropane, the nitroso-compound is converted into the nitro-compound. The appearance of a mass spectral peak at *m/e* 31, rather than at *m/e* 30, indicates the production of [^{15}N]nitric oxide. Intercomparison of *m/e* 31 and *m/e* 56 from Table 2 with the cracking patterns shown in Table 1 indicates that fragmentation of [^{15}N]2-methyl-2-nitropropane could not be responsible

TABLE 2

m/e	30	31	56	57	58
Run 2B	4	46	100	45	4
Run 3B	3	45	100	78	7
Run 5A	4	18	100	38	3
Run 7B	3	29	100	47	4

$$\mathrm{Bu^tNO} + {}^{15}\mathrm{NO_2} \longrightarrow \mathrm{Bu^tNO_2} + {}^{15}\mathrm{NO} \qquad (2)$$

for the formation of this ion. Thus the experimental evidence shows unambiguously that the reaction occurs by the oxygen-atom transfer mechanism (2; R = Bu^t). It is of interest to consider also the theoretical calculations[3] for the reaction (4), which permit no discrimination between the O-atom transfer and

$$\mathrm{NO} + \mathrm{NO_2Cl} \longrightarrow \mathrm{NOCl} + \mathrm{NO_2} \qquad (4)$$

the Cl-atom transfer. Reaction (1) will be exothermic for nitrosoalkanes[4] by *ca.* 80 kJ mol^{-1}. It seems likely to us that the O-atom transfer reaction (2) is more favourable than (3) on steric requirements for R = Bu^t. It does not necessarily follow that all nitrogen dioxide oxidations of *C*-nitroso-compounds will follow this route. It is possible that small alkyl groups such as methyl could offer less interference to the entering group.

We thank the S.R.C. for a maintenance grant (to P. J. C.).

[2/329 *Received, 14th February, 1972*]

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[2] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1956, 1670.

[3] D. R. Herschbach, H. S. Johnston, K. S. Pitzer, and R. E. Powell, *J. Chem. Phys.*, 1956, **25**, 736.

[4] P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *Internat. J. Chem. Kinetics*, 1972, in the press.