The Structure of Dinitrogen Trioxide

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A direct demonstration has been obtained, through ^{14}N n.m.r., of the nitroso–nitro structure $ON–NO_2$ for dinitrogen trioxide.

Liquid N_2O_3, although well known from its deep blue colour,[1] is a pure compound only near its f.p., $-100·7°$.[2] At higher temperatures both the equilibria

$$N_2O_3 \rightleftharpoons NO + NO_2$$

$$\text{and} \quad 2NO_2 \rightleftharpoons N_2O_4$$

become important, the second being favoured inasmuch as the N–N bond dissociation energy is higher for N_2O_4, 13·7 kcal./mole,[3] than for N_2O_3, 9·5 kcal./mole.[4] N_2O_4 is undissociated near and below its f.p. ($-11·2°$), and is miscible with N_2O_3.

Thus liquid N_2O_3, made up from equimolar proportions of NO and NO_2 in a sealed tube, contains a concentration of the tetroxide that depends on the volume of the dead space above the liquid, since this volume determines the pressure of NO, which behaves as a permanent gas at these temperatures. This explains the unexpected observation (*e.g.*, in the electronic spectra of dilute solutions of the trioxide at low temperatures[1]) that the concentration of the tetroxide is relatively insensitive to temperature.[5]

The ^{14}N n.m.r. spectrum for pure liquid N_2O_3, therefore, was obtained from a sample under a fairly high pressure of NO, about 17 atmospheres, generated by a 1·2 : 1 mixture of NO and NO_2 in a tube containing gas and liquid in a volume ratio 4·8 : 1. Measurements were made with a Varian WL-9 wide-line spectrometer operating at 4 Mc./sec., with an r.f. field of about half a gauss and a modulation frequency typically of 40 c./sec., using the absorption mode; with temperatures down to $-140°$ or so, since these liquids can supercool. All shifts are quoted relative to saturated aqueous nitrite ion at room temperature, which we measured to be at -232 p.p.m. from saturated aqueous nitrate ion. $Me_2N·NO$, with its two resonances, was used as external reference during the measurements. The accuracy is about ± 10 p.p.m.

The spectrum of pure liquid N_2O_3, under excess NO, consisted of two resonances, with chemical shifts of $+165$ and -70 p.p.m. at $-50°$. In a sample made up with equimolar proportions of NO and NO_2 the N_2O_4 signal appeared as well, at $+243$ p.p.m. at $-50°$. When the ratio of NO_2 to NO taken was raised to 1·1 : 1, and then to 3 : 1, the intensity of the N_2O_4 signal increased at the expense of the N_2O_3 signals, in the expected proportions. Thus for the 3 : 1 sample, with roughly equimolar trioxide and tetroxide, the trioxide signals have about half the integrated intensity of the accompanying tetroxide signal, and of the signals for pure N_2O_3 under the same conditions. In a given sample there was no change, within experimental error, in the ratio of the tetroxide to the trioxide intensities, in the range −30° to −80°.

Pure N_2O_4 yielded a single resonance, as expected from its $O_2N{\cdot}NO_2$ structure, with about the same chemical shift as in the mixture with N_2O_3. Some typical spectra are shown in Figure 1.

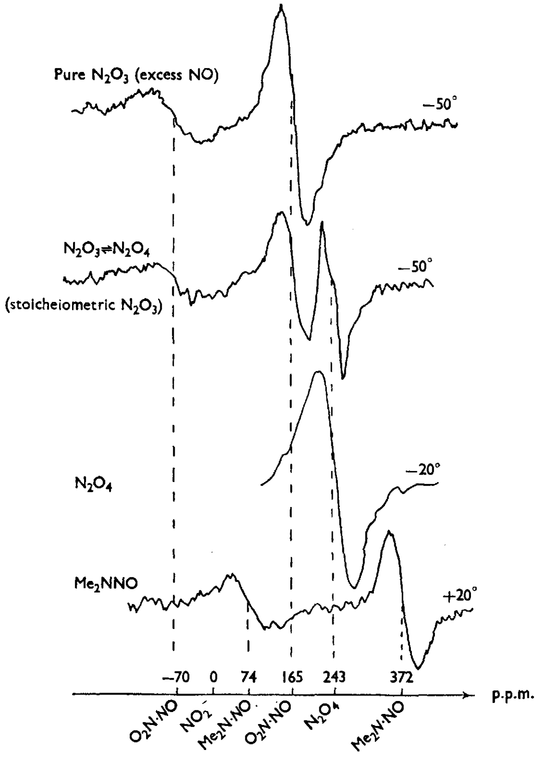

FIGURE 1. *^{14}N resonances, recorded in the absorption mode, presented as derivative curves. The N_2O_4 line, normally narrow in the N_2O_3 solution, is modulation broadened in the second trace.*

The assignment of the $O_2N{\cdot}NO$ resonances is obvious from the N_2O_4 chemical shift. This is sandwiched between those of the *N*-nitro- and *C*-nitro-compounds, $Me_2N{\cdot}\mathit{N}O_2$ and $MeNO_2$, which we found to be at +264 and +232 p.p.m., respectively. Thus the N_2O_3 resonance at +165 p.p.m. is due to the nitro-nitrogen, and the nitroso-nitrogen gives the line at −70 p.p.m. The latter then lies between the resonances of the *N*-nitroso-nitrogen in $Me_2N{\cdot}\mathit{N}O$, at +74 p.p.m. (*cf.*, $Me_2\mathit{N}{\cdot}NO$ at +372 p.p.m.), and of *C*-nitroso-compounds, at very low fields. The values are shown in Figure 2, with some literature values for related molecules.

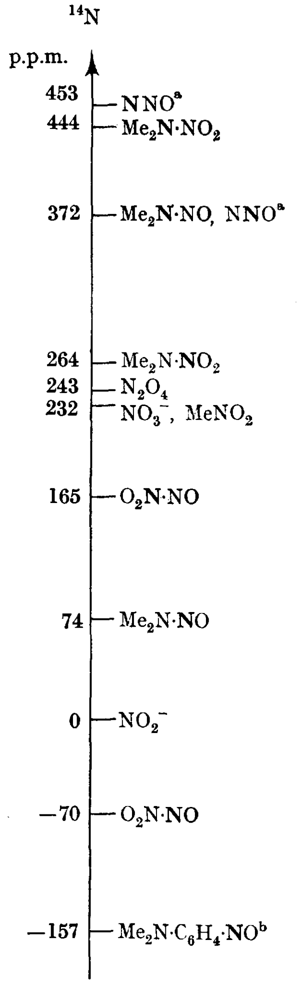

FIGURE 2

^{14}N chemical shifts.

[a] J. E. Kent and E. L. Wagner, *J. Chem. Phys.*, 1966, **44**, 3530; [b] D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 1964, **8**, 19.

These chemical shifts, and those of related compounds, will be interpreted in terms of the theory of nuclear shielding developed by Ramsey, Slichter, Pople, and others. A pleasing correlation is that between the deep blue colour of N_2O_3, as of *C*-nitroso compounds, and the very large shift to low field of the nitroso-nitrogen in each case. This arises because these ^{14}N shifts depend mainly on the paramagnetic contribution to the screening (variations in the diamagnetic contribution being small), and this contains a factor $(\Delta E)^{-1}$, where ΔE is the mean electronic excitation energy of the atom in question.[6] ΔE is strongly influenced by the energy of the lowest $n \rightarrow \pi^*$ (*i.e.*, magnetically allowed) transition, and this energy is very low, and responsible for the blue colour, in *C*-nitroso-compounds, and in this nitro-nitroso-compound, N_2O_3. The mixing of the readily accessible $n_N \rightarrow \pi^*$ excited state with the ground state by the magnetic field de-shields the ^{14}N nucleus and shifts the resonance to low field.

In the variation with temperature of the n.m.r. spectra of liquid N_2O_3 and N_2O_4 several factors may be separated. The spectra confirm that of the various equilibria that can be imagined (*e.g.*, with molecules that have been detected at lower temperatures, such as the nitrito-forms $O:N{\cdot}O{\cdot}N:O$ and $O:N{\cdot}O{\cdot}NO_2$, or the nitric oxide dimer $O:N{\cdot}N:O$) only the ones mentioned initially are significant. Broadening due to paramagnetic relaxation by dissolved NO_2 becomes important above $-5°$ or so in N_2O_4, and possibly down to $-20°$ in N_2O_3. At these higher temperatures part of the line broadening is due to chemical exchange, which is to be expected from the isotopic evidence[7] and from the thermal parameters for N–N bond breaking and re-making. At lower temperatures, below $-60°$ or so, the lines broaden because of quadrupole relaxation as the liquid becomes more viscous, but they are still discernible in liquids at $-120°$.

The chemical exchange, the comparison with a range of related molecules, and the theoretical and spectroscopic correlations, will be described more fully in due course.

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