Dinitrogen Trioxide. Part 14.[1] Adduct Formation between Dinitrogen Trioxide and Aromatic Donors

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The phase diagrams for some binary systems containing N_2O_3 and aromatic compounds have been determined and demonstrate the existence of 1 : 1 solid adducts. In contrast, NOCl and probably NOBr do not form adducts with aromatic donors.

THERE are several reasons for suspecting some specific interaction between N_2O_3 and aromatic compounds and possibly the formation of adducts. It has been observed that N_2O_3 is immiscible with simple alkanes and alkenes but is miscible in all proportions with a wide range of aromatic solvents.[2] This suggests some interaction with aromatic compounds which is not present with the other hydrocarbons.

The electronic-absorption spectra of N_2O_3, N_2O_4, and NOX (X = Cl or Br) in aromatic solvents show an additional band in the u.v. region. This can be assigned to an intermolecular charge-transfer band which is displaced to lower energy with increasing donor ability of the aromatic compound.[3-5]

The existence of solid adducts of N_2O_4 and aromatic compounds is well known.[6] Shaw[7] has previously observed that certain mixtures of N_2O_3 with mesitylene melted at a higher temperature than either of the pure components suggesting an adduct was probably formed. We have therefore determined the phase diagrams for both N_2O_3 and NOCl with simple aromatic compounds and now present the results.

EXPERIMENTAL

The phase diagrams were obtained using the classical method of determining melting points or freezing points of various mixtures of the two components. The following difficulties were encountered with these systems. Both N_2O_3 and NOX (X = Cl or Br) are readily oxidised and/or hydrolysed so that all the measurements were conducted in an all-glass high-vacuum system fitted with greaseless stopcocks and joints. At > -20 °C the dissociation of N_2O_3 and NOBr with loss of NO into the gas phase may be significant. This was minimised by maintaining an elevated pressure of NO above the liquid. Chemical reaction between the two components was minimised by storing the mixtures at low temperatures and for as short a time as possible. Chemical reaction was a major difficulty for NOBr systems.

Commercial NO and N_2O_4 were purified as previously described.[8] Nitrosyl chloride and Br_2 were fractionated *in vacuo*. The aromatic compounds were purified by conventional means[9] and dried over molecular sieves followed by bright sodium wire. The N_2O_4 or Br_2 was distilled into the cryoscope or melting-point tube from a weighed ampoule and was then quantitatively converted into N_2O_3 or NOBr

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[1] Part 13, A. J. Vosper, *J.C.S. Dalton*, 1976, 135.

[2] A. J. Vosper, unpublished work.

[3] A. W. Shaw and A. J. Vosper, *J.C.S. Dalton*, 1972, 961.

[4] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1958, 3142.

[5] E. Niciecki and A. J. Vosper, unpublished work.

[6] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1956, 1941.

[7] A. W. Shaw, Ph.D. Thesis, University of Southampton, 1972.

[8] I. R. Beattie and S. W. Bell, *J. Chem. Soc.*, 1957, 1681.

[9] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, 'Technique of Organic Chemistry,' Interscience, New York, 1955, vol. 7.

by reaction with NO under appropriate conditions.[5,10] The NOCl could be directly distilled from a weighed ampoule. The compound was cooled and an appropriate amount of the aromatic compound was distilled into the apparatus also from a weighed ampoule.

Freezing points were determined using a cryoscope similar in design to that previously described.[11] These were more reliable at the lower temperatures although difficulties due to excessive supercooling were sometimes experienced. The melting points were determined by slowly warming the two components sealed in a capillary tube and noting the temperature at which the last trace amount of solid disappeared. The N_2O_3–mesitylene system was particularly difficult due to the high melting point of the adduct. The two components were condensed in a thick-walled tube, cooled with liquid nitrogen, and a controlled volume of NO was condensed into the tube which was then sealed. On warming, the elevated pressure of NO above the liquid minimised dissociation. **CAUTION**: Care was needed and a number of such tubes exploded.

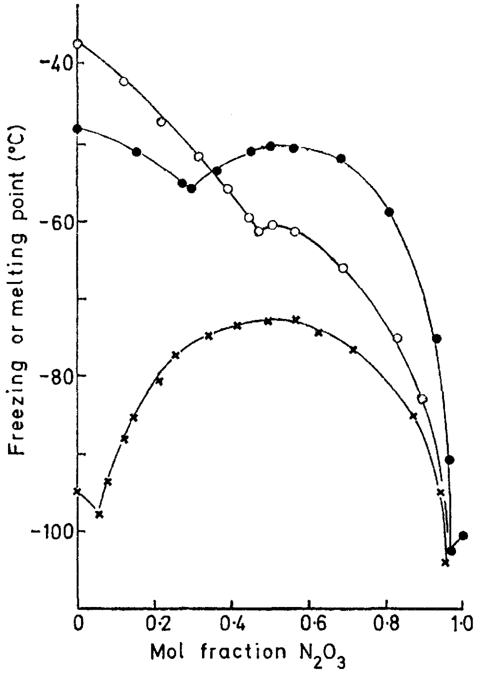

FIGURE 1 Phase diagrams for the N_2O_3–anisole (○), –*m*-xylene (●), and –toluene (×) systems

Temperatures were measured using either calibrated copper–constantan thermocouples or mercury-in-glass or alcohol-in-glass thermometers.

RESULTS AND DISCUSSION

The various phase diagrams are shown in Figures 1—3. There is little doubt that N_2O_3 forms 1 : 1 solid adducts with toluene, *m*-xylene, mesitylene, and anisole. In the case of mesitylene the freezing-point determinations gave low values due to dissociation of N_2O_3 at the higher temperatures. The N_2O_3–benzene system showed a slight inflexion at the composition corresponding to a 1 : 1 adduct (see Figure 2). This could be due to an incongruent melting point but this is uncertain.

In contrast, NOCl formed no adducts with benzene, *o*- and *m*-xylene, or mesitylene (see Figures 2 and 3). In all cases simple phase diagrams with a single eutectic were obtained. Attempts to obtain phase diagrams for NOBr and aromatic compounds were thwarted by

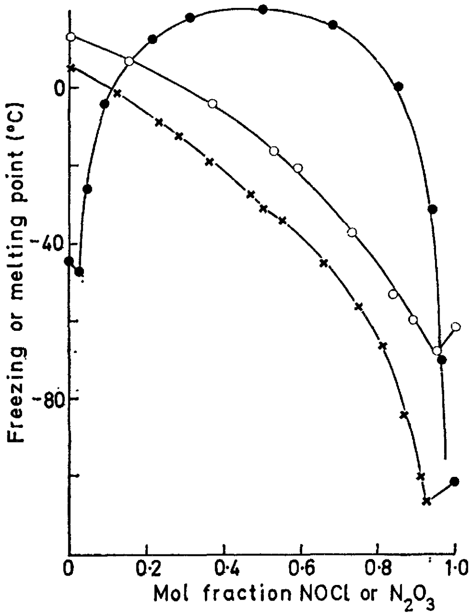

FIGURE 2 Phase diagrams for the NOCl–*p*-xylene (○), N_2O_3–mesitylene (●), and N_2O_3–benzene (×) systems

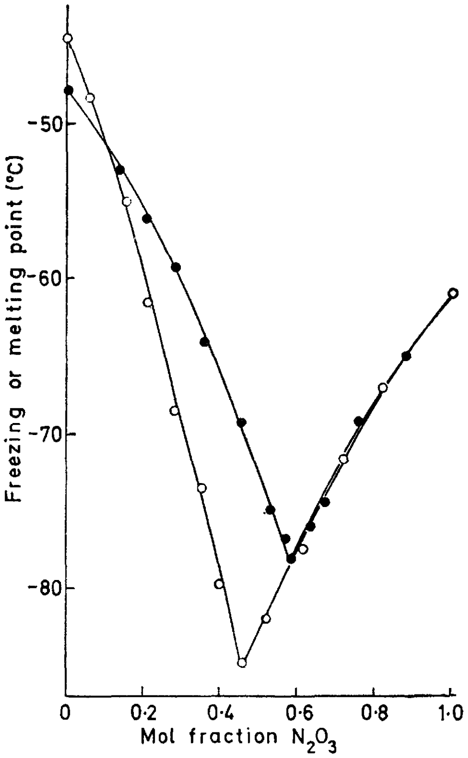

FIGURE 3 Phase diagrams for the NOCl–mesitylene (○) and –*m*-xylene (●) systems

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[10] A. W. Shaw and A. J. Vosper, *J. Chem. Soc. (A)*, 1970, 2193.

[11] I. R. Beattie, S. W. Bell, and A. J. Vosper, *J. Chem. Soc.*, 1960, 4796.

reaction between the two components and so no quantitative results are presented. The limited results obtained gave no evidence for adduct formation.

Since N_2O_3 and N_2O_4 are structurally closed related[12,13] and both form adducts with aromatic compounds, it seems likely that these adducts are of the same general type. The structure of the N_2O_4–benzene adduct is known[14] and consists of infinite chains of alternate N_2O_4 and benzene molecules arranged with the molecular planes perpendicular to the chain axis. The detailed structure suggests the donation of electron density from the aromatic molecule to N_2O_4. The interaction must be fairly weak since the distance between the two molecules is similar to the value calculated from the appropriate van der Waals radii. This is not unexpected since aromatic compounds are relatively weak donors and N_2O_4 is unlikely to be a powerful acceptor molecule.

The complexes between N_2O_3 and aromatic compounds are likely to be similar, *i.e.* plane-to-plane packing of alternate donor and acceptor molecules to allow partial electron transfer. Since N_2O_3, unlike N_2O_4, has a permanent dipole moment[12] then dipole–dipole interactions may be significant in some cases.

Although the adduct can be formulated as an ionic compound, *i.e.* $[NO{\cdot}R]^+[NO_2]^-$, this seems unlikely for the following reasons. The electrolytic conductivity of N_2O_3 is decreased by dilution with an aromatic solvent,[15] whereas if the adduct was ionic one would expect an increased conductivity. The solid adducts are pale blue in colour like N_2O_3, suggesting no major electronic rearrangement occurs on forming the adduct. The i.r. spectrum of N_2O_3 in an aromatic solvent shows bands characteristic of molecular N_2O_3 rather than the ions $[NO]^+$ and $[NO_2]^-$. The three strongest bands of N_2O_3 which correspond approximately to ν(NO) of the NO and NO_2 groups are visible although displaced to some extent compared to their gas-phase values.[16] In contrast, no band was observed in the 2 000—2 200 cm^{-1} region that could be assigned to ν(NO) of an $[NO]^+$ complex.

In general, N_2O_4 appears to form adducts with weaker donor molecules than N_2O_3.[6] The lack of an adduct between N_2O_4 and *p*-xylene may be for steric reasons. It appears that the acceptor properties decrease in the order $N_2O_4 > N_2O_3 > NOX$ (X = Cl or Br).

Although 1 : 1 adducts are formed in the solid state it is probable that these are extensively dissociated on melting. Low-temperature i.r. studies of liquid mixtures of N_2O_3 and aromatic compounds gave no evidence for additional bands although they would only be expected to occur at low frequencies. Low-temperature ^1H n.m.r. studies of the aromatic compounds were not greatly affected by the presence of N_2O_3 except at the higher temperatures when the paramagnetic NO and NO_2 are present. It seems likely that the additional absorption observed in the u.v. region when N_2O_3,[3] N_2O_4,[4] or NOX[5] are dissolved in an aromatic solvent is due to a contact charge-transfer band rather than a discrete molecular complex.

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