534. *Double Melting of Molecular Addition Compounds of Dinitrogen Tetroxide with Organic Donors.*

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Phase diagrams for binary systems of dinitrogen tetroxide with certain organic donors show two distinct liquidus curves over the same concentration range; the addition compounds separate from the mixtures in two forms, having different melting points. With ethyl acetate and *p*-tolyl cyanide the two solid compounds have the same component ratio (2 : 1 and 1 : 1 respectively) but with benzophenone a 1 : 1 or a 2 : 1 compound may crystallise from the same liquid mixture. Thermal analysis of the acetic anhydride–dinitrogen tetroxide systems is also reported.

THE existence of solid molecular addition compounds between dinitrogen tetroxide and 'onium or π donors is readily recognised by thermal analysis of the binary systems. With the donor molecules already reported,[1, 2] clear phase diagrams were obtained, but very occasionally the solid formed by partial freezing of the liquid mixture was found to melt at a temperature quite different from that indicated by the established phase diagram. A search was therefore made for organic donors showing this effect to a greater extent, and full thermal analysis of mixtures with ethyl acetate, benzophenone, and *p*-tolyl cyanide has led to the surprising observation that over the concentration range representing crystallisation of the addition compound, two distinct liquidus curves are obtained which can be separated by as much as 10°. For a given donor, the two melting-point maxima may occur at the same ratio (2 : 1 for ethyl acetate, 1 : 1 for *p*-tolyl cyanide) or at different ratios (1 : 1 and 2 : 1 for benzophenone). In this paper the phenomenon is discussed in the light of the alternative solid compounds which are possible.

This type of double crystallisation and melting appears to be almost unique. A phase diagram for mixtures of ethylene glycol diethyl ether with dinitrogen tetroxide reported by Whanger and Sisler[3] suggests the presence of this effect also, though no reference is made to it in the text. There is also an early observation[4] that, when an equimolecular mixture of phenol and *p*-toluidine cools, crystalline plates melting at 28·5° separate first, and that these can be converted into needles melting at 30°, but examples of such behaviour are rare.

RESULTS and DISCUSSION

Some present and past observations on the crystallisation of mixtures of dinitrogen tetroxide with a second liquid will first be correlated by reference to Fig. 1, in which $AE_3E_2E_1$ represents the liquidus curve, and E_1 the ultimate eutectic in the absence of compound formation. In all cases in which the crystals from tetroxide-rich solutions have been examined, they have been found to be solid solutions, so that a solidus curve such as $AF_3F_2F_1$ exists also. With some liquids (*e.g.*, nitromethane,[5] nitrosyl chloride,[6] and some halogeno-hydrocarbons[7]) the simple eutectic diagram AE_1B is obtained. With the many liquids which give addition compounds, the liquidus curve is represented by AE_2C_1; if cooling is slow, it has been observed (*e.g.*, with diethylnitrosamine mixtures[8]) that crystallisation can proceed beyond E_2 along E_2E_1 for several degrees, and if the mixture is then warmed, no eutectic arrest corresponding to E_2 occurs. Cooling along E_2E_1 may therefore be regarded as normal cooling with respect to the simple eutectic system, or as supercooling with respect to compound C_1. With tetroxide mixtures, cooling beyond about 10° below E_2 usually causes crystallisation of compound C_1. In the same way,

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[1] Addison and Sheldon, *J.*, 1956, 1941.
[2] *Idem*, preceding paper.
[3] Whanger and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 5188.
[4] Philip, *J.*, 1903, **83**, 814.
[5] Addison, Hodge, and Lewis, *J.*, 1953, 2631.
[6] Addison and Thompson, *J.*, 1949, S 218.
[7] Pascal, *Bull. Soc. chim. France*, 1923, **33**, 539.
[8] Addison, Conduit, and Thompson, *J.*, 1951, 1303.

when a second solid compound C_2 is possible, cooling along E_3E_2 may be regarded either as normal cooling with respect to compound C_1 or as supercooling with respect to C_2; it is consistent with this general picture that compound C_2 is obtained on strong supercooling of the liquid. When the molecular ratio in the two compounds C_1 and C_2 is the same, cooling of C_1 often produces a spontaneous change to C_2, but this does not occur when the two molecular ratios are different (as with benzophenone). We have not yet found any reliable method of ensuring that a particular compound (C_1 or C_2) separates on crystallisation, since the readiness with which C_2 is formed varies with the donor molecule used, but the results in Figs. 2 and 3 show that all melting points lie on one of two distinct curves. The fact that curve AE_1 is not varied, whatever compound may separate, indicates in itself that the two components are not strongly associated in the liquid state.

Ethyl Acetate Compounds.—The phase diagram in Fig. 2 shows two solid 2 : 1 compounds, m. p.s —64·5° and —71·5°, and illustrates the general points mentioned above. The two compounds no doubt result from two different arrangements of the components in the crystal lattice. Ethyl acetate is a weak donor, and until crystallographic evidence is available it is not possible to determine whether electron transfer to the dinitrogen tetroxide acceptor molecule makes a major contribution to the lattice energy. If this should be the case, the same addition-compound unit may be packed in different ways in the crystal, or the compound itself may have more than one structure; *e.g.*, electron donation is possible from either the carbonyl- or the ether-oxygen atom in ethyl acetate. No colour was produced on cooling the solid compounds.

FIG. 1.

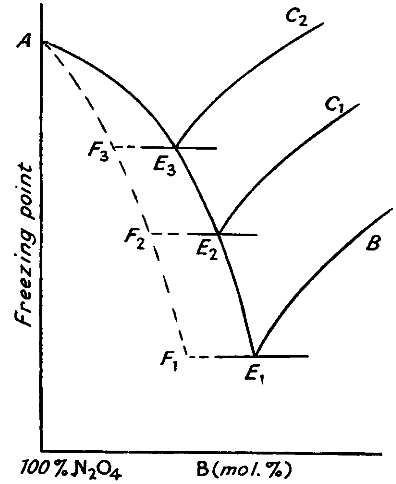
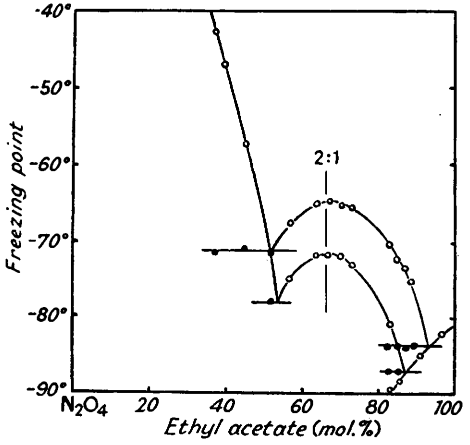


FIG. 2.



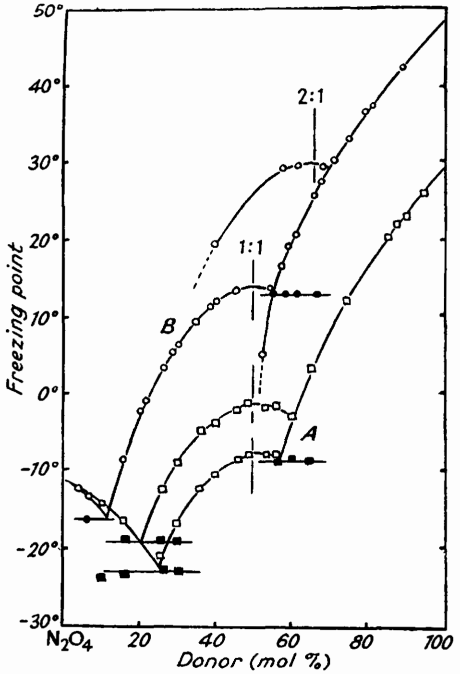
p-*Tolyl Cyanide Compounds.*—The phase diagram (Fig. 3) shows two solid 1 : 1 compounds, m. p.s —1° and —7·5°. On strong cooling, the solid phases developed yellow or grey-purple colours. The colour which formed varied with the relative concentrations of the components used, and any one colour was not a property of a particular 1 : 1 compound. The development of colour was reversible, and could be diminished or intensified at will by variation in temperature. This, and the component ratio, indicate that compound formation is by orbital overlap, the *p*-tolyl cyanide acting as a π-electron donor. It has been suggested[1] that such solid compounds have the components arranged plane-to-plane in column form; the two solid compounds now observed may therefore result from different relative arrangements of the tetroxide and tolyl cyanide molecules in the column, or from different modes of packing of the columns themselves.

Benzophenone Compounds.—These represent a third type of double melting system, since the two melting-point maxima (Fig. 3) represent different component ratios (1 : 1, m. p. 13·5°; 2 : 1, m. p. 29·5°). The 1 : 1 compound is well characterised by experimental values, and is regarded as a π-compound involving the aromatic orbitals of benzophenone.

This compound undergoes some curious colour changes. Immediately after crystallisation it was yellow, but the colour was lost on warming and was not re-formed on cooling. When the yellow solid was cooled below −10°, a phase change occurred; colourless patches developed which spread throughout the solid, and the colour was not restored by change in temperature.

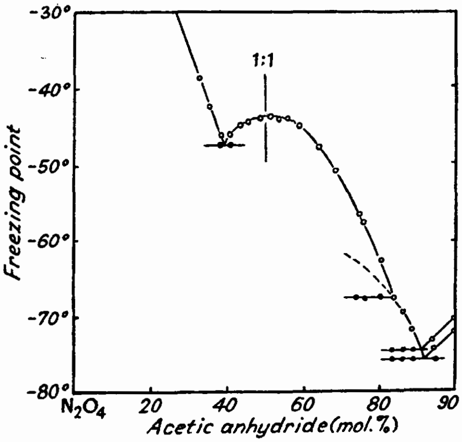
The 2 : 1 compound is not easily formed, and is made more difficult to obtain by the readiness with which the 1 : 1 compound separates from solution. Only four points have been obtained on the liquidus curve, but there is no doubt as to the existence of the 2 : 1 compound. In a typical preparation, a 62 mol. % solution of benzophenone was cooled; at 20°, needles of benzophenone (or solid solution) began to separate. On further cooling, a new solid phase grew from nuclei at various points on the vessel walls, and within a few seconds the whole mixture was transformed into a solid which melted over a very narrow temperature range at 29°. This solid was almost colourless at 0°; at −30° it was appreciably yellow, and there was no further colour change on cooling to −80°. Colour changes between 0° and −30° were reversible (in contrast to the 1 : 1 compound). On the basis of the 2 : 1 ratio the compound might be regarded as an 'onium complex. However, electron donation from the oxygen atom of benzophenone will be appreciably reduced by the deactivating property of the two phenyl groups. Since reversible colour changes are also observed, molecular association in this compound may again occur through π-orbital overlap, and a more complicated solid structure would reduce the probability of its formation. The wider range of solid compounds formed between benzophenone and dinitrogen tetroxide may not be unrelated to the fact that pure benzophenone exists in two solid modifications (m. p.s 49° and 26°).

FIG. 3.



A, p-*Tolyl cyanide.* *B*, *Benzophenone.*

FIG. 4.



Acetic Anhydride Compounds.—There appear to be two modes of crystal packing in solid acetic anhydride, possessing similar lattice energies, since the pure solid has two melting points 2° apart (Fig. 4). This is reflected in the existence of two eutectic temperatures similarly separated, and two liquidus curves on the acetic anhydride side of the eutectic composition. On the dinitrogen tetroxide side, no double melting occurs; there is pronounced evidence for a 1 : 1 compound (m. p. −43·5°) and a compound of higher ratio (probably 2 : 1) melting incongruently. Reference has already been made[9] to the formulation of the 1 : 1 compound as an 'onium complex involving electron donation from two of the oxygen atoms in acetic anhydride.

Experimental.—Benzophenone and *p*-tolyl cyanide (British Drug Houses Limited) proved sufficiently pure for use without further treatment; recrystallisation did not improve the sharpness of their m. p.s. Ethyl acetate was washed successively with sodium carbonate solution, water, calcium chloride solution, and water. It was dried ($CaCl_2$) and fractionated over phosphoric oxide. Acetic anhydride was fractionated. All compounds were anhydrous, and were stable in contact with dinitrogen tetroxide for several days. Melting points were determined from warming curves as already described.[6, 8]

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[9] Addison, *Rec. Trav. chim.*, 1956 : Proceedings of International Conference on Co-ordination Compounds, Amsterdam, 1955; Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.