380. *Molecular Addition Compounds of Dinitrogen Tetroxide with Nitrogen, Oxygen, and Aromatic Hydrocarbon Donors.*

By C. C. ADDISON and J. C. SHELDON.

Dinitrogen tetroxide forms molecular addition complexes with a wide range of organic compounds. Compound formation is considered to result from electron acceptance by the electron-deficient dinitrogen tetroxide molecule. The electron donors are subdivided into 'onium donors (*e.g.*, carboxylic acids, esters, ketones, and nitriles) which generally give 2 : 1 compounds, and π donors (aromatic hydrocarbons and some simple derivatives) which give 1 : 1 compounds. This paper is primarily concerned with compound formation in the solid state, as shown by thermal analysis.

THE chemical reactivity of liquid dinitrogen tetroxide is modified profoundly in the presence of certain organic compounds. Addition of diethylnitrosamine gives a mixture which reacts vigorously with a number of metals.[1] Levy and Scaife [2] found that the oxidising properties of the tetroxide were modified by certain organic solvents (notably ethers and esters), and Sisler *et al.* have shown, by thermal analysis of binary systems of dinitrogen tetroxide with a range of ethers, that compound formation occurs in the solid state.[3, 4] Compounds are formed with amines in both solid and liquid phases,[5, 6] with camphor,[7] and with *o*-nitrotoluene,[8] but not with halogeno-hydrocarbons.[9] It is unlikely that these addition compounds conform to any single structural type; although many appear to be molecular addition compounds, some show properties which suggest an ionic formulation.

The evidence in the literature is fragmentary, and in view of their significance in the dinitrogen tetroxide solvent system, we have undertaken a broader survey of these addition compounds.

DISCUSSION AND RESULTS

Classification of Donors.—Molecular-compound formation occurs as a result of electron deficiency in the dinitrogen tetroxide molecule, which therefore acts as an electron acceptor. Compounds with which the tetroxide combines are treated throughout as electron donors. They are of two types: (1) 'Onium donors, *i.e.*, compounds containing an atom which has one or more lone pairs of electrons available in *s* and *p* orbitals; (2) π donors, *i.e.*, aromatic hydrocarbons and their derivatives, which have electrons available in molecular π orbitals, and can form molecular addition compounds by orbital overlap.

Molecular or Ionic Formulation for Addition Compounds.—The structure of the addition compound will be determined by the mode of electron acceptance by dinitrogen tetroxide, which has structure (I).[10] Each atom possesses a *p* atomic orbital perpendicular to the plane of the molecule, and these combine to give a system of π molecular orbitals. The existence of orbitals embracing the whole molecule is a possibility, the nitro-group orbitals

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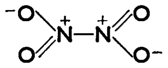
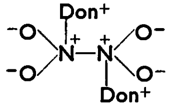
[1] Addison and Conduit, *J.*, 1952, 1399.
[2] Levy and Scaife, *J.*, 1946, 1093.
[3] Rubin, Shechter, and Sisler, *J. Amer. Chem. Soc.*, 1952, **74**, 877.
[4] Whanger and Sisler, *ibid.*, 1953, **75**, 5188.
[5] Davenport, Burkhardt, and Sisler, *ibid.*, p. 4175.
[6] Comyns, *Nature*, 1953, **172**, 491; *J.*, 1955, 1557.
[7] Pascal and Garnier, *Compt. rend.*, 1923, **176**, 450.
[8] Breithaupt, Thesis, Genève, 38, Nr. 446; Landolt-Börnstein " Tabellen," Band 3, Teil 1, 1935, p. 550.
[9] Pascal, *Bull. Soc. chim. France*, 1923, **33**, 539.
[10] Broadley and Robertson, *Nature*, 1949, **164**, 915.

not necessarily being completely separate. The six molecular orbitals can together possess a maximum of twelve electrons. The N_2O_4 molecule is considered as having eight electrons in the molecular-orbital system, and hence two pairs of electrons may be accepted.

(I)



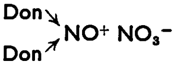


(II)

The NO_2 groups being regarded as the site for combination, 2 : 1 compounds with onium donors are generally to be expected. Complete transfer of two electron pairs to an N_2O_4 molecule involves a large charge separation in that molecule, as shown in (II). This tends to inhibit acceptance, which is therefore weakened.

As an alternative, the compounds may be considered as ionic in character. The equilibrium $N_2O_4 \rightleftharpoons NO^+NO_3^-$ is well established in the liquid state, and the NO^+ ion (like the analogous diazonium ion) is also electron deficient. The saturated NO unit contains 14 valency electrons, whereas the NO^+ ion has only ten. In the form of an ion pair, dinitrogen tetroxide may be regarded as accepting up to two electron pairs to give the compounds (III) and (IV). (Don is a donor compound.) It is to be expected, however, that (III) will be more stable than (IV), since the ion $Don^+—N{=}O$ is electrostatically more favourable than $(Don^+)_2NO^-$. As with molecular compound (II), the donation-acceptance processes are weakened by charge separation, and the 1 : 1 is more likely than the 2 : 1 ratio in ionic compounds.

(III) $\mathrm{Don} \rightarrow NO^+\ NO_3^-$



$$\begin{matrix}\mathrm{Don}\searrow \\ \mathrm{Don}\nearrow\end{matrix} NO^+\ NO_3^-$$

(IV)

Classification of Addition Compounds.—Since there are two types of donors ('onium and π) and two modes of electron acceptance (by N_2O_4 or NO^+), the following four classes of compounds are possible: (1) molecular compounds with 'onium donors, (2) molecular compounds with π donors, (3) ionic compounds with 'onium donors, (4) ionic compounds with π donors. There is no evidence for the existence of compounds of class (4). Conductometric titrations by Comyns[6] demonstrated the existence of ionic complexes (class 3) between liquid dinitrogen tetroxide and the tertiary amines. In the liquid phase the electron-deficient species N_2O_4 and NO^+ exist together, and any added donor has the opportunity of combining with either (or both) of these species. The liquid phase may therefore be represented in terms of the two equilibria

$$(\mathrm{Don})_n,NO^+,NO_3^- \rightleftharpoons n(\mathrm{Don}) + N_2O_4 \rightleftharpoons (\mathrm{Don})_n,N_2O_4$$

The relative positions of these equilibria depend on the donor, and particularly on its basic strength. Formation of an ionic compound involves preliminary ionisation of the tetroxide, and more energy is therefore required for the formation of an ionic than a molecular compound. The tertiary amines are amongst the strongest donors known, and it is probable that their solid compounds with dinitrogen tetroxide are also ionic in character. The amine : N_2O_4 ratio found was 1 : 1, which is again consistent with an ionic formulation. A general ratio of 2 : 1 was found by Sisler *et al.*[5] for compounds of the tetroxide with heterocyclic amines. The latter are weaker electron donors than the tertiary amines, and the compounds may well be molecular (class 1) as the ratio suggests. The solid compounds described in this paper involve relatively weak donors, and are all believed to fall into classes (1) and (2). Even so, in the liquid state the equilibrium is not entirely on the side of the molecular compounds $(\mathrm{Don})_n,N_2O_4$; reaction rates of these mixtures with metals indicate the presence of a (probably small) proportion of ionic complex, and these will be discussed in a later paper. The variation in type of addition compound with electron donor strength may be summarised as follows:

	Liquid phase	Solid phase
Strong donors (R_3N)	$(\mathrm{Don})_n,NO^+\ NO_3^-$	$(\mathrm{Don})_n,NO^+\ NO_3^-$
Medium-strength donors (C_5H_5N, R_2O, RCN)	$(\mathrm{Don})_n,NO^+\ NO_3^-$ and $(\mathrm{Don})_n,N_2O_4$	$(\mathrm{Don})_n,N_2O_4$
Weak donors (C_6H_6, $C_6H_5{\cdot}NO_2$)	$(\mathrm{Don})_n,N_2O_4$	$(\mathrm{Don})_n,N_2O_4$

Nitrogen Donor System.—The phase diagram for dinitrogen tetroxide with dimethylnitrosamine is compared in Fig. 1 with that for diethylnitrosamine.[16b] Both compounds give a 2 : 1 ratio only, but the melting point of the dimethylnitrosamine compound is much higher. However, the m. p.s of dimethyl- and diethyl-nitrosamine are —22° and —81° respectively, and the fact that the change in m. p. of the compound is a reflection of a change of a similar order in that of one component is in itself some support for the belief that the solid compounds are molecular and not ionic in character. In these compounds, and those mentioned below, the m. p. of the compound seldom lies more than about 20° from the mean of the m. p.s of the components. Those factors which determine the lattice bonding of the components, and thus their melting points (van der Waals forces, dipole interactions, and steric effects), thus determine also the melting of the compound. Since dinitrogen tetroxide is a weak electron acceptor, compound formation will make only a small contribution to the lattice energy in these systems.

The phase diagrams for ethylphenyl- and methylphenyl-nitrosamines (Fig. 2) again show 2 : 1 compound formation only, though the compound with the latter melts incongruently. The nitrosamines are sufficiently strong donors to give rise to some ionic complex formation in the liquid phase; [11] electron donation, which is considered to occur at the amine nitrogen atoms, will be weakened by the presence of the phenyl group, but the consistent 2 : 1 ratio indicates that the crystals are molecular compounds with 'onium donors, and that the phenyl group takes no direct part in addition-compound formation. *N*-Nitrosopiperidine (Fig. 2) gives compounds of the unusual ratios 1 : 1 and 3 : 1. Although few such compounds have yet been studied, there appear to be exceptional steric factors associated with alicyclic compounds. For example, camphor [7] gives the unusual ratios 4 : 5 and 3 : 2, so that addition compound formation is not the only factor determining the composition of the solid. (Although most alicyclic ethers appear to give the expected 2 : 1 ratio, the phase diagram for tetrahydrofuran shows a pronounced 1 : 1 compound.[3]) *N*-Nitrosopiperidine probably forms, with dinitrogen tetroxide, lattice complexes of addition compounds of normal ratio, together with uncombined molecules of one of the components.

The alkyl cyanides provide further examples of nitrogen donors (Fig. 3). 1-Chloro-2-cyanoethane gives a 2 : 1 compound only, and the small maximum and limited composition range indicate very weak association with dinitrogen tetroxide. Substitution of a chlorine atom has a similar effect in the ethers; [3] diethyl ether gives a pronounced compound, whereas 2 : 2'-dichlorodiethyl ether shows no compound formation. Benzyl cyanide gives a 2 : 1 compound only, but methyl cyanide shows clear evidence of a 1 : 1 compound also. (Many experimental points have been omitted from Fig. 3 in the region of the 2 : 1 maxima for methyl and benzyl cyanides for the sake of clarity.) Though not in conflict with the general picture outlined above, this 1 : 1 ratio is unusual, since methyl cyanide can only act as an 'onium donor; the question of stable orientation in the lattice may become as important here as the orbital requirements of the electron donor and acceptor.

Oxygen Donor Systems.—Four such systems are shown in Fig. 4. All curves show 2 : 1 compounds only, the acetophenone compound having an incongruent melting point. The dialkyl ethers give similar curves.[3,4] Ethyl acetate also gives a 2 : 1 compound, but this system shows double melting and will be discussed in a later paper. There is therefore much justification for the general rule that molecular compounds of dinitrogen tetroxide with 'onium donors have 2 : 1 ratio. Some molecules containing two donor atoms give 1 : 1 compounds with dinitrogen tetroxide, but are not exceptions to this rule. If the donor atoms are at an appropriate distance apart (as may well be the case with ethylene glycol diethyl ether,[4] 1 : 4- and 1 : 3-dioxan [3,4,12] and acetic anhydride [13]), the donors behave as chelate groups, donating two pairs of electrons.

The importance of structure and physical dimensions of the donor molecule in determining the shape and position of the phase diagram may be seen by comparison of certain of the systems in Figs. 1—4. The carbonyl and *N*-nitroso-groups seem able to replace

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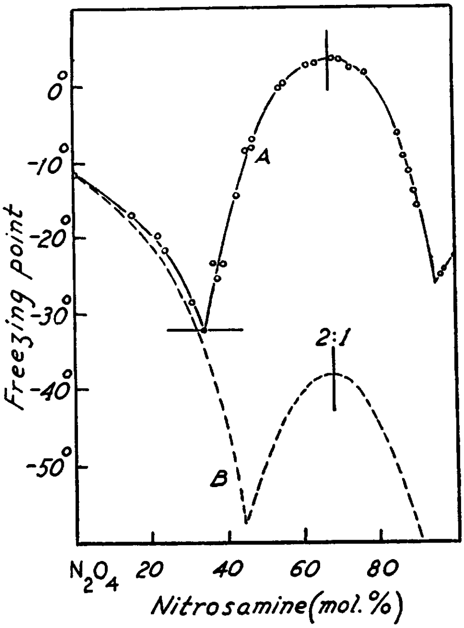
[11] Addison and Conduit, *J.*, 1952, 1390.

[12] Ling and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 5191.

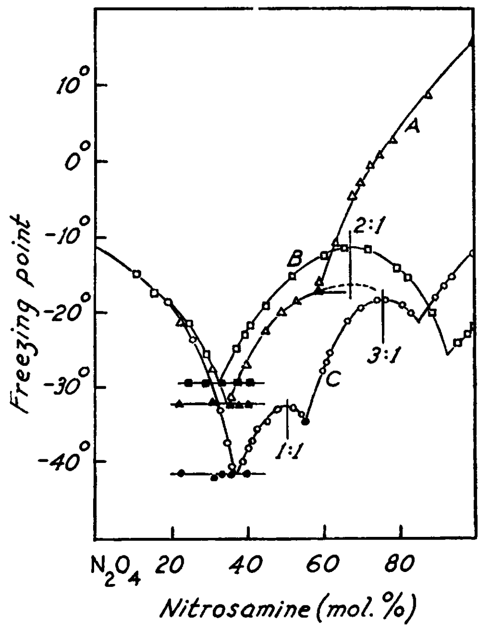
[13] Addison and Sheldon, unpublished results.

FIG. 1.



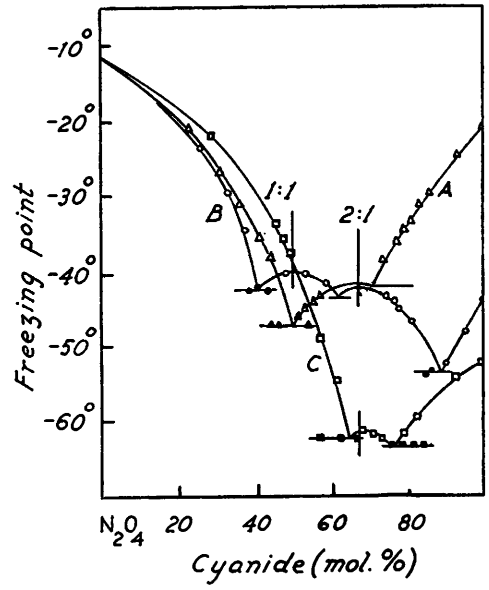
A, $Me_2N{\cdot}NO$; *B*, $Et_2N{\cdot}NO$.

FIG. 2.



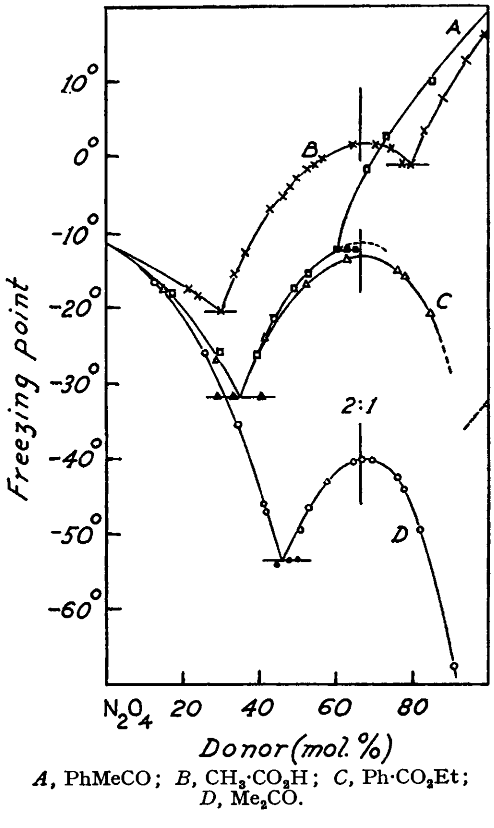
A, $PhMeN{\cdot}NO$; *B*, $PhEtN{\cdot}NO$; $C_5H_{10}N{\cdot}NO$.

FIG. 3.



A, $Ph{\cdot}CH_2{\cdot}CN$; *B*, MeCN; *C*, $CH_2Cl{\cdot}CH_2{\cdot}CN$.

FIG. 4.

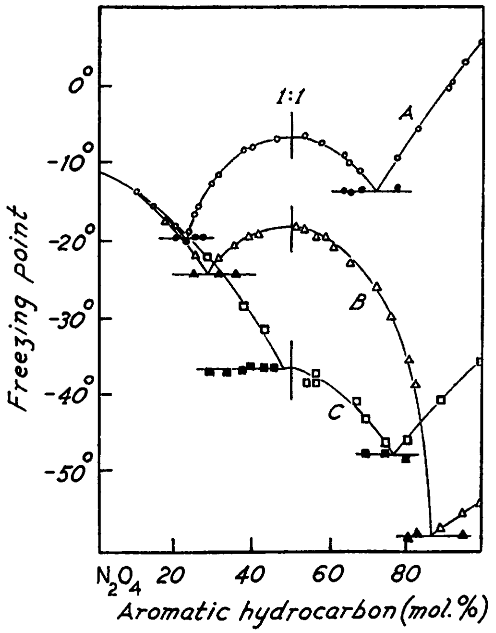


A, PhMeCO; *B*, $CH_3{\cdot}CO_2H$; *C*, $Ph{\cdot}CO_2Et$; *D*, Me_2CO.

one another without appreciable modification in the system. Acetophenone and methylphenylnitrosamine give very similar systems; the eutectic temperatures and compositions, and the incongruent melting points, are closely similar. The same is true for systems with ethyl benzoate and ethylphenylnitrosamine, and the 2 : 1 compounds formed by these four donors all melt within 5°. The acetone system also closely resembles that for diethylnitrosamine.

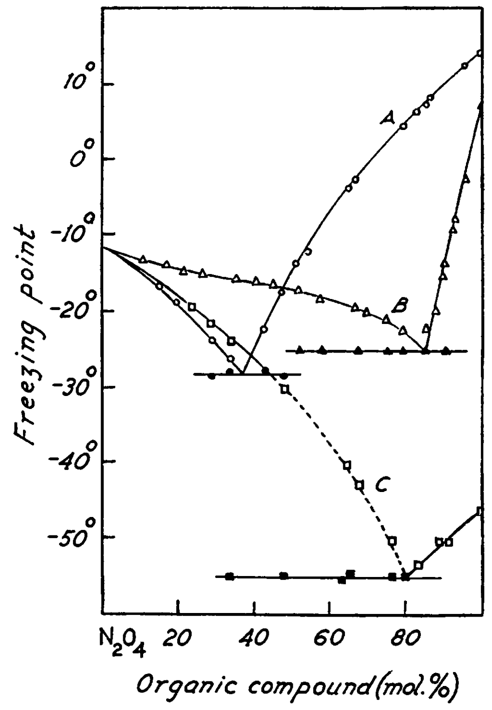
In most cases the viscosity of the liquid mixture from which crystallisation occurs is appreciably higher than that of the components. This increase in viscosity is particularly obvious with the esters because of the considerable supercooling which occurs. With ethyl benzoate (Fig. 4) this renders determination of crystallisation temperatures inaccurate in high concentrations of the ester.

FIG. 5.



A, C_6H_6; *B*, $C_6H_3Me_3$; *C*, $C_{10}H_{12}$.

FIG. 6.



A, $C_6H_4Me_2$; *B*, C_6H_{12}; *C*, PhCl.

Aromatic Hydrocarbon Donors.—Dinitrogen tetroxide forms addition compounds with aromatic hydrocarbons, and three phase diagrams are shown in Fig. 5. The uniform 1 : 1 ratio is in sharp contrast to the 2 : 1 compounds obtained with 'onium donors. These compounds have not previously been observed, and they are of special interest when compared with the addition compounds between aromatic hydrocarbons and nitro-compounds which are in common use in the characterisation of organic compounds. In this general class of solid compound (which includes addition compounds of aromatic hydrocarbons, amines, and phenols with nitro-compounds and quinones) crystallographic studies[14] have shown that the significant structural feature is plane-to-plane packing of the donor and acceptor molecules, arranged alternately. The pronounced colour of these compounds, and the frequent examples of pleochroism, suggest greater electron mobility along the plane-to-plane axis than perpendicular to it. Provided that the structure of the molecules will permit sufficiently close approach, partial electron transfer can occur by overlap of orbitals. In the addition of aromatic hydrocarbons to nitro-compounds, the former act as donors, and the acceptor properties of nitro-compounds are largely due

[14] Powell, Huse, and Cooke, *J.*, 1943, 153; Harding and Wallwork, *Acta Cryst.*, 1953, **6**, 791.

to the nitro-groups present. Thus hydrocarbon compounds of trinitrobenzene are well known; *p*-dinitrobenzene forms a similar but more restricted range of hydrocarbon compounds,[15] and the data in Fig. 5 show that if the aromatic ring is removed completely from dinitrobenzene, compound formation with aromatic hydrocarbons by the two remaining nitro-groups can still occur.

Since N_2O_4 is a flat molecule, it can approach the aromatic ring most closely by a plane-to-plane packing in the crystal. The molecules may be arranged in a column, but on geometric grounds alone the closest orbital overlap seems most likely to occur if the molecules are " staggered " somewhat. The compound is therefore to be considered as having an $n : n$ rather than a 1 : 1 ratio. The fact that these compounds result from electron donation and acceptance is supported by comparison of the benzene system (Fig. 5) with that for *cyclo*hexane (Fig. 6), which shows a simple eutectic system.

It is probable that, whenever dinitrogen tetroxide is mixed with an aromatic compound in the liquid state, some molecular interaction takes place. For example, the absorption spectrum of the tetroxide is modified in the presence of benzene. However, whether a solid compound can be crystallised from the liquid mixture depends on the structure of the aromatic compound, since this will determine whether the tetroxide can approach sufficiently closely to the aromatic ring for π orbital overlap to occur. Thus mesitylene and tetrahydronaphthalene give $n : n$ compounds (Fig. 5), but *p*-xylene and chlorobenzene show no evidence of solid compound formation (Fig. 6). Bromobenzene also gives a simple eutectic system with dinitrogen tetroxide.[9] However, the behaviour of mixtures with chlorobenzene was unusual in the concentration range covered by the eutectic line (Fig. 6) on the N_2O_4 side of the eutectic concentration. On melting the solid, there was a prolonged arrest at the eutectic temperature while almost all of the solid melted; when the temperature increased again, the liquid phase contained only a small quantity of semi-solid particles which gave no more than a turbidity to the liquid. The liquidus curve (shown as a broken line in Fig. 6) represents clearing of this turbidity, since there was no detectable break in the warming curve on disappearance of turbidity.

The slope of the liquidus curve for *cyclo*hexane-rich mixtures (Fig. 6) is higher than in the other systems examined. This is not abnormal, and reflects the unusually large molecular depression of freezing point of *cyclo*hexane (cf. benzene 49°, acetic acid 39°, *cyclo*hexane 200° per mole of solute/100 g. of solvent). The molar heat of fusion (L_f) is correspondingly small (compare benzene 2·36 kcal., acetic acid 2·80 kcal., *cyclo*hexane 0·65 kcal.). The freezing point depressions (T_0–T) as shown in the phase diagrams, compared with the values (in parentheses) calculated from the equation $\ln x = -L_f(1/T - 1/T_0)/\mathbf{R}$ for solutions in which the mole fraction x of N_2O_4 is 0·1, are: Benzene, 6·8° (6·8°); Acetic acid, 7·0° (6·1°); *cyclo*Hexane, 21° (23°).

*cyclo*Hexane is therefore showing normal behaviour. Solid-solution formation is not uncommon in these systems[9,16] and probably accounts for the small freezing-point depression in *cyclo*hexane mixtures rich in dinitrogen tetroxide.

Molecules Capable of Both 'Onium and π Donation.—Several of the compounds mentioned above possess both an aromatic ring and an 'onium donor atom. The molecular ratio involved in the compound may be used as a general guide to distinguish 'onium (2 : 1) from π (1 : 1) complexes. When the 'onium donor is sufficiently strong, combination through the donor atom is usually preferred. With a very weak 'onium donor, π complexes are generally preferred; this is probably because compact plane-to-plane packing with 1 : 1 compounds leads to higher lattice energies than in the case of the more open and angular 2 : 1 'onium compound molecules. Nitrobenzene (Fig. 7) forms a 1 : 1 compound with dinitrogen tetroxide; since the nitro-group has no donor properties towards the tetroxide, this is clearly a π donor compound. Of particular interest, however, is the fact that phenyl cyanide and benzaldehyde also form 1 : 1 compounds, whereas benzyl cyanide (Fig. 3) and acetophenone (Fig. 4) give 2 : 1 compounds. In both phenyl cyanide and benzaldehyde the donor atoms will be appreciably deactivated by conjugation with the phenyl

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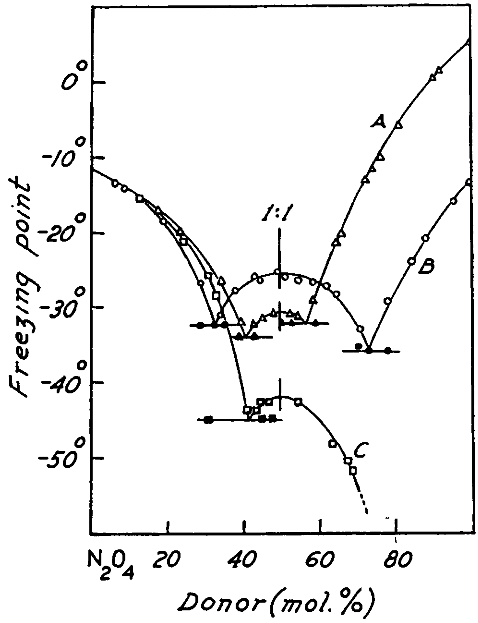
[15] Kremann, *Monatsh.*, 1908, **29**, 863; Kremann and Rodinis, *ibid.*, 1906, **27**, 125.

[16] (*a*) Addison and Thompson, *J.*, 1949, S 218; (*b*) Addison, Conduit, and Thompson, *J.*, 1951, 1303; (*c*) Addison, Hodge, and Lewis, *J.*, 1953, 2631.

group, leading to weak electron-pair donation; in benzyl cyanide the phenyl group is not in direct conjugation, and in acetophenone it is compensated by an activating methyl group.

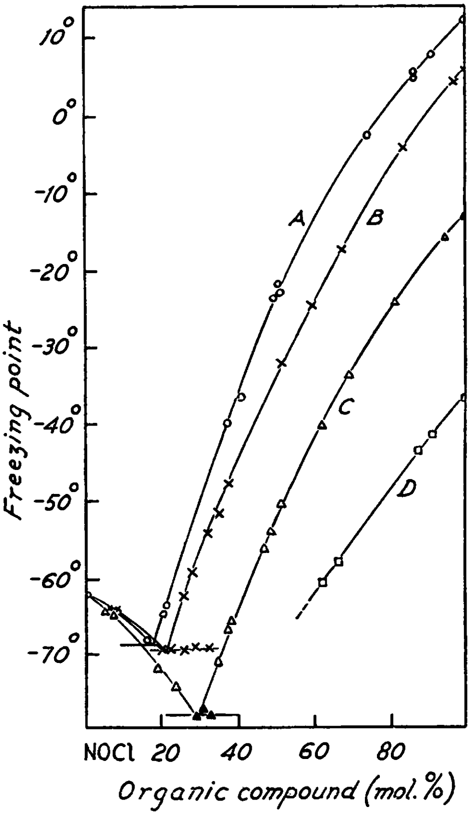
Colour in Aromatic Hydrocarbon–Dinitrogen Tetroxide Mixtures.—These mixtures are often strongly coloured, thus giving further evidence for electronic interaction between the hydrocarbons and the tetroxide. Liquid mixtures with benzene show no colour (apart from that due to nitrogen dioxide). The solid compound at its m. p. (−7°) is colourless, but becomes pale orange at −50°; this colour fades on warming and the change is reversible. Liquid mixtures with toluene show no colour, but the solid phase which crystallises from an approximately equimolar mixture with dinitrogen tetroxide at −100° is bright red. *p*-Xylene solutions are colourless at room temperature, but become deep red-brown at −20°. Mesitylene and tetrahydronaphthalene solutions show this colour at room temperature, and at −20° are almost black. However, the fact that it is not possible to deduce the properties of the solid from those of the liquid (or *vice versa*) is well illustrated by the observation that the solids crystallising from deeply coloured solutions of mesitylene and tetrahydronaphthalene are without appreciable colour. Not all the addition compounds formed by the aromatic hydrocarbons and their derivatives absorb in the visible range, so that no clear scheme emerges from observations of colour. The benzaldehyde and nitrobenzene mixtures are colourless, whereas mixtures containing chlorobenzene, benzophenone, phenyl cyanide, or *p*-tolyl cyanide give yellow or orange solids.

FIG. 7.



A, $PhNO_2$; *B*, PhCN; *C*, Ph·CHO

FIG. 8.

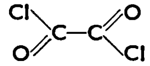


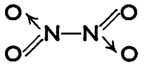
A, $C_4H_8O_2$; *B*, C_6H_6; *C*, PhCN; *D*, C_5H_5N.

Comparison with Nitrosyl Chloride Systems.—Some confirmation of the molecular character of these compounds is obtained by comparison with corresponding systems formed by nitrosyl chloride, which can undergo the self-ionisation $NOCl \rightleftharpoons NO^+ + Cl^-$.[17] Nitrosyl chloride does not possess a π orbital system comparable with dinitrogen tetroxide, and will not therefore form similar molecular compounds. The ability to give the NO^+ ion is, however, common to each molecule, so that if any particular donor forms a compound of similar ratio with both nitrosyl chloride and dinitrogen tetroxide, there may be some justification for regarding compounds with the latter as being ionic in the solid state. Three phase diagrams are given in Fig. 8. Neither benzene nor phenyl cyanide shows compound formation with nitrosyl chloride; 1 : 4-dioxan gives a 1 : 1 compound with dinitrogen tetroxide,[3] but no compound with nitrosyl chloride. The high viscosity of the mixtures rendered determination of the pyridine–nitrosyl chloride phase diagram inaccurate below −60°, yet the pyridine–dinitrogen tetroxide compound melts above 0°.[5] The absence of compound formation with nitrosyl chloride therefore gives positive evidence that the solid compounds with dinitrogen tetroxide are not ionic in character.

Comparison with Other Electron Acceptors.—Two other electron acceptors, oxalyl chloride and iodine, give molecular addition compounds with typical 'onium and π donors

(V)





(VI)

which resemble those described in this paper. The two molecules (V) and (VI) are electronically analogous, and will show some similarity in the orbitals formed and in their electron deficiency. A 1 : 1 compound between 1 : 4-dioxan and oxalyl chloride is known.[18] This compound, separated by mixing the components in light petroleum at −5°, is stable in a closed system and melts at 68°. The m. p. of the N_2O_4 compound, 45°, is also unusually high. No compounds with diethyl or di*iso*pentyl ether were observed, but may be found at sufficiently low temperatures. Infrared, ultraviolet, and Raman spectra also suggest the existence of a 1 : 1 benzene–oxalyl chloride complex.[19] Iodine forms addition compounds with 'onium and with π donors such as the heterocyclic amines, esters, ketones, ethers, and aromatic hydrocarbons. The type of bonding in these compounds has been discussed in detail by Mulliken,[20, 21] and the concept of charge-transfer bonding forces is as applicable to dinitrogen tetroxide as to iodine. There are also features in the ultraviolet absorption spectra of dinitrogen tetroxide–donor mixtures (to be discussed in a later paper) which resemble the corresponding iodine systems. Other broad similarities should be noted; each is capable of dissociating either into two identical uncharged units or into an anion and an electron-deficient cation :

$$I_2 \longrightarrow 2I \text{ or } (I^+ + I^-) \qquad N_2O_4 \longrightarrow 2NO_2 \text{ or } (NO^+ + NO_3^-)$$

The addition compounds in each case are mostly molecular, but a small concentration of the ions ($PyI^+ + I^-$) is thought to exist in solutions of iodine in pyridine,[21] just as a small quantity of ionic dinitrogen tetroxide complex almost certainly exists in mixtures with strong 'onium donors.

EXPERIMENTAL

Liquidus Curves.—Supercooling is common in these systems, and the f. p.s recorded in Figs. 1—8 were therefore determined from breaks in warming curves. The solution (about 5 g.) was contained in a 3″ × ½″ tube; the components were weighed directly into the tube, care being taken to minimise contact with the atmosphere. The tube was closed by a Silicone rubber plug carrying a mercury or alcohol (depending on the temperature) thermometer, and the solution stirred by movement of the thermometer. The thermometers were calibrated with pure liquids of known f. p. The solution was partially frozen (with constant stirring) by immersing the tube in alcohol cooled by solid carbon dioxide, or in liquid air. The tube was then transferred to an air-bath surrounded by a liquid (water, or alcohol–solid carbon dioxide) at such a temperature (a little above the expected f. p.) that melting was sufficiently slow to

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[17] Lewis and Wilkins, *J.*, 1955, 56.
[18] Varvoglis, *Ber.*, 1938, **71**, 32.
[19] Saksena and Kagarise, *J. Chem. Phys.*, 1951, **19**, 994.
[20] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.
[21] Mulliken and Reid, *J. Amer. Chem. Soc.*, 1954, **76**, 3869.

give accurate warming curves. When decomposition of the solution was negligible its concentration was then altered by addition of one of the components; whenever slight decomposition occurred, each f. p. was determined on a fresh mixture.

Purification.—The compounds used as electron donors are readily available liquids having known physical constants. Each liquid was scrupulously purified immediately before use. As water on mixing with dinitrogen tetroxide gives nitric acid, which accelerates decomposition of the mixtures, liquids were carefully dried.

Stability of Mixtures.—Most organic compounds are attacked by dinitrogen tetroxide given sufficient time, and certain liquids (*e.g.*, olefins, amines, phenols) which would have been of interest as donors could not be studied because of rapid reaction even at low temperatures. Reaction with the following liquids was not detectable at room temperature during several hours : acetic acid, dimethylnitrosamine, *N*-nitrosopiperidine, methyl cyanide, phenyl cyanide, nitrobenzene, 1-chloro-2-cyanoethane, ethyl benzoate, *cyclo*hexane, benzene, and chlorobenzene. The other donors used showed some attack (oxidative degradation of aliphatic compounds, and nitration of aromatic compounds) at room temperature. In each case nitric acid is produced, and the rate of reaction increases with time. Pure acetone, for example, mixes with dinitrogen tetroxide to give a red-brown solution at room temperature. Within a few minutes a green colour develops, nitric oxide is evolved, and the temperature rises at an increasing rate; eventually the solution boils.

Chemical reaction between such donor liquids and dinitrogen tetroxide is highly dependent on temperature, and can be almost entirely inhibited by reducing the temperature. The solids appear to be stable indefinitely. At the low temperatures at which the freezing points (Figs. 1—8) were obtained, chemical reaction was always negligible; this was confirmed by the fact that f. p.s did not change with time provided the solutions were kept cold. Freezing points of acetone mixtures (for example) were obtained by adding approximately the required amount of the tetroxide to a weighed quantity of cold acetone. The mixture was rapidly cooled, and the f. p. determined. The mixture was then allowed to warm to room temperature, weighed, and discarded.

At room temperature acetophenone and benzaldehyde were slowly attacked. Reaction with benzyl cyanide, to produce nitrobenzoic acids, is apparent after a few days. Methyl- and ethyl-phenylnitrosamines are attacked rapidly, and the *p*-nitro-compound has been isolated in large yield. *p*-Xylene, mesitylene, and tetrahydronaphthalene show some reaction after several minutes, and a dark lower liquid layer separates. Reaction with these three donors can be prevented by immediately cooling the fresh solutions, so that the observations made earlier on colour at low temperatures are not complicated by chemical reaction.

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