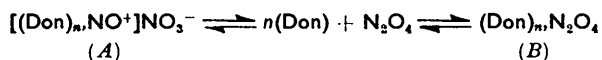


373. Vapour Pressures of Mixtures of Dinitrogen Tetroxide with Donor and with Non-donor Organic Solvents : Comparison with Some Nitrosyl Chloride Systems.

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

Vapour pressures are recorded for mixtures of dinitrogen tetroxide with the following solvents over the full concentration range at 0°: carbon tetrachloride, chlorobenzene, benzene, toluene, nitrobenzene, benzyl cyanide, methyl cyanide, and acetic acid. Vapour pressures of mixtures with *n*-heptane, chloroform, nitromethane, acetic anhydride, and ethyl acetate are recorded from -10° to +10°, and a few measurements are reported for mixtures with *cyclohexane*, dioxan, and diethylnitrosamine. Deviations from ideal behaviour are correlated with the polar nature and donor properties of the solvents, and the degree of addition-compound formation in the liquid. For comparison, vapour pressures of mixtures of nitrosyl chloride with chloroform, pyridine, and ethyl acetate have been measured over the range -50° to -20°.

LIQUID dinitrogen tetroxide, when used as a reactant, is frequently diluted with organic solvents. Previous papers¹ have illustrated the wide range of organic compounds capable of forming addition compounds in the solid state, and addition compounds are present in the liquid mixtures also. In some reactions the presence of the tetroxide-solvent complex may not influence the course of a reaction; Sisler and his co-workers, studying compound formation between heterocyclic amines and dinitrogen tetroxide in ether, found the dissociation of the ether-tetroxide complex to be so far advanced above its melting point that the amine-tetroxide reaction was not affected.² In contrast, propene and the butenes with liquid dinitrogen tetroxide give oxidation products which contain little or no nitro-paraffin, whereas in a 50% (w/w) solution of the tetroxide in diethyl ether, oxidations are almost entirely prevented.³ Again, nitration of the benzene ring by dinitrogen tetroxide is promoted by addition of acetic anhydride.⁴ Our study of the molecular addition compounds has therefore been extended to the liquid state, which is represented by the equilibrium



(Don) is the donor solvent; the small proportion of complex (A) influences profoundly the reaction of the mixtures with metals.⁵ The value of *n* cannot be determined in the liquid as readily as in the solid, but with weak donor solvents it is unlikely that *n* differs from unity. The presence of molecular addition complexes (B) is not usually obvious in the liquid, since in rare cases only (*e.g.*, with dimethyl sulphoxide,^{1a} 1:4-dioxan,^{3b, 6} and ethyl phenylpropionate⁷) does an addition compound crystallise on mixing solvent and tetroxide at room temperature. The colours which some mixtures develop indicate electron transfer,^{1a, 1c} but in general such electron transfer provides only an additional (and not necessarily the predominant) type of molecular attraction, so that its influence on the physical properties of tetroxide mixtures cannot be deduced from measurements with any one solvent; a range of solvents having differing structure and polar character has therefore been employed.

¹ Addison and Sheldon, *J.*, 1956, (a) 1941, (b) 2705, (c) 2709.

² Davenport, Burkhardt, and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 4175.

³ Levy and Scaife, *J.*, 1946, (a) 1093, (b) 1096, (c) 1100.

⁴ Valynashko, Bliznyukov, and Lutskii, *Trudy Khar'kov Khim.—Tekhnol. Inst. im S.M. Kirova*, 1944, No. 4, 48 (*Chem. Abs.*, 1948, **42**, 1218 f).

⁵ Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

⁶ Rubin, Sisler, and Shechter, *J. Amer. Chem. Soc.*, 1952, **74**, 877.

⁷ Wieland, Schamberg, and Wagner, *Ber.*, 1920, **53**, 1343; Wieland and Blümich, *Annalen*, 1921, **424**, 100.

Because of the high volatility of dinitrogen tetroxide compared with that of the solvents used, the vapour pressure of the mixtures reflects the behaviour of the tetroxide in the liquid, and can be interpreted in terms of the degree of association between dinitrogen tetroxide and the organic component. Comparison of the deviations from Raoult's law for a range of solvents provides a measure of the relative significance of the various types of molecular interaction occurring in the mixtures. The theory of the liquid state is not sufficiently developed to permit quantitative assessment of the separate interactions when the components possess one or more polar, donor, or acceptor groups, so that the deductions are at present largely qualitative. There are clear correlations between vapour pressure, heats of mixing, and dipolar character of the solvent which will be discussed in a later paper.⁸

RESULTS AND DISCUSSION

The vapour pressures of mixtures with the organic compounds listed in Table 1 are given in Figs. 1—3. The compounds are arranged in order of percentage deviation, which is defined as $100(P_{\text{observed}} - P_{\text{ideal}})/P_{\text{ideal}}$, for equimolecular mixtures, P_{ideal} being the vapour pressure which the system would possess if Raoult's law were obeyed. Vapour pressures

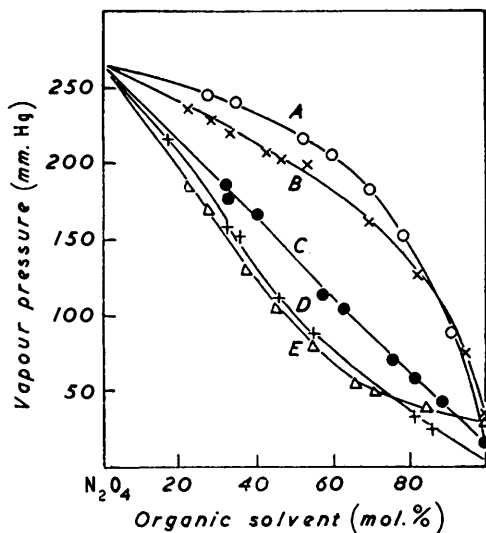


FIG. 1. Vapour pressures of N_2O_4 -organic solvent mixtures at 0° .

A, *n*-Heptane; B, carbon tetrachloride;
C, nitromethane; D, acetic anhydride;
E, ethyl acetate.

for all thirteen systems in Figs. 1—3 have been measured at 0° and for five systems (Table 2) measurements are recorded over a range of temperature.

Tables 1 and 2 and Figs. 1—3 show that by varying the organic component it is possible to obtain vapour-pressure systems covering the full range from strongly positive, through zero, to strongly negative deviations. Compounds marked by an asterisk in Table 1 are known to form addition compounds with dinitrogen tetroxide in the solid state.

Vapour-pressure data for three systems, which have not been fully examined, are given in Table 3. The results for diethylnitrosamine indicate a deviation of approximately -30% , which supports previous evidence^{8a} of well-developed compound formation in the liquid state. Crystallisation of the addition compound from dioxan-tetroxide mixtures⁶ restricted the concentration range available, and the melting point of dioxan (11.7°) limited the temperature range for this system. No firm estimate of the percentage deviation at the equimolecular point can therefore be made for comparison with the values in Table 1, but the deviations from P_{ideal} for dioxan-rich mixtures are as large as for other oxygen donors (*e.g.*, ethyl acetate) at similar concentrations.

⁸ Addison, Sheldon, and Smith, *J.*, 1957, in the press.

^{8a} Addison and Conduit, *J.*, 1952, 1390.

TABLE I.

Organic component	Deviation at 0° (%)	Dipole moment of organic component (D)	Fig. No.
<i>n</i> -Heptane	55.5	0	1 (Table 2)
Carbon tetrachloride	33	0	1 (Table 2)
Chloroform	21	1.15	2
Chlorobenzene	18.5	1.56	3
*Benzene	9.5	0	3
Toluene	6	0.39	2
Nitromethane	0	3.17	1 (Table 2)
*Nitrobenzene	- 6	3.99	3
*Benzyl cyanide	-15.5	3.50	2
*Methyl cyanide	-16	3.37	2
*Acetic anhydride	-28	2.80	1 (Table 2)
*Acetic acid	-34	0.83 ^a	3
		1.75 ^b	
*Ethyl acetate	-34	1.81	1 (Table 2)

^a Dimer. ^b Monomer (Potapenko and Wheeler, *Rev. Mod. Phys.*, 1948, **20**, 143; Pohl, Hobbs, and Gross, *Ann. New York Acad. Sci.*, 1940, **40**, 389).

TABLE 2. Vapour pressures (mm.) of N₂O₄-organic solvent mixtures at various temperatures.

Temp.	0	25.0	33.5	51.8	59.5	69.5	76.5	91.4	100
<i>n</i> -C ₇ H ₁₆ (mol. %)									
10°	444	400	392	340	322	280	228	138	20
5	343	315	307	270	358	228	185	112	15
- 5	201	187	185	169	160	142	120	70	9
-10	151	143	140	129	125	112	93	54	7
CCl ₄ (mol. %)									
10°	390	377	366	345	322	264	207	122	56
5	305	296	285	270	252	205	160	95	43
- 5	180	174	169	160	151	127	97	55	25
-10	136	132	128	123	116	98	74	42	18
Me·NO ₂ (mol. %)									
10°	348	313	280	200	179	120	103	77	16
5	269	241	214	153	136	93	77	56	11
- 5	155	137	123	85	75	50	42	31	6
-10	118	104	92	63	55	37	31	23	4
(Me·CO) ₂ O (mol. %)									
10°		17.2	30.8	35.0	45.0	54.2	81.5	85.0	100
5		355	270	242	183	145	60	50	<3
-10		117	87	81	62	49	19	16	~0
-20		60	47	43	32	27	12	10	~0
Me·CO ₂ Et (mol. %)									
10°	22.8	28.0	37.6	44.5	55.2	67.0	70.6	84.0	100
5	312	287	226	197	148	104	92	70	43
- 5	241	225	168	146	111	78	70	53	33
-10	137	126	96	84	62	43	39	29	18
-20	103	92	73	62	45	31	28	21	13

TABLE 3.

Compn. of mixture (mol. % of solvent)	Vapour pressure (mm.) at					Compn. of mixture (mol. % of solvent)	Vapour pressure (mm.) at		
	-10°	0°	10°	15°	20°		10°	15°	20°
Diethylnitrosamine						1 : 4-Dioxan			
0.0	151	263	444	564	720 ^a	7.0	409	523	650
31	89	160	—	—	—	8.1	401	511.5	633
56	36	66.5	120.5	—	—	89.6	32.5	44	57
72	14.5	29	55	—	—	90.5	32.5	44	55.5
100	~0	~0	~0	—	—	95.7	24	32.5	43
						96.5	24	32	41.5
						100	—	21.5	27
<i>cyclo</i> Hexane									
58	124.5	207	325						
100	—	—	48.5						

^a Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

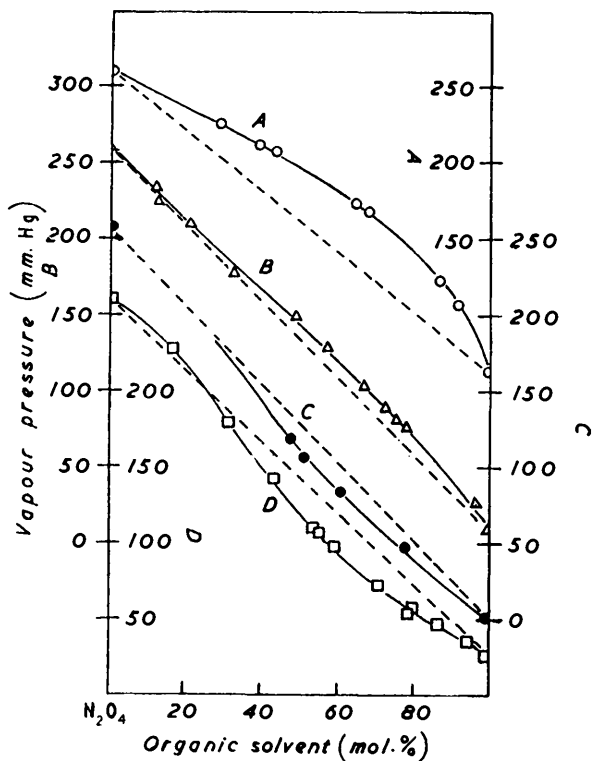
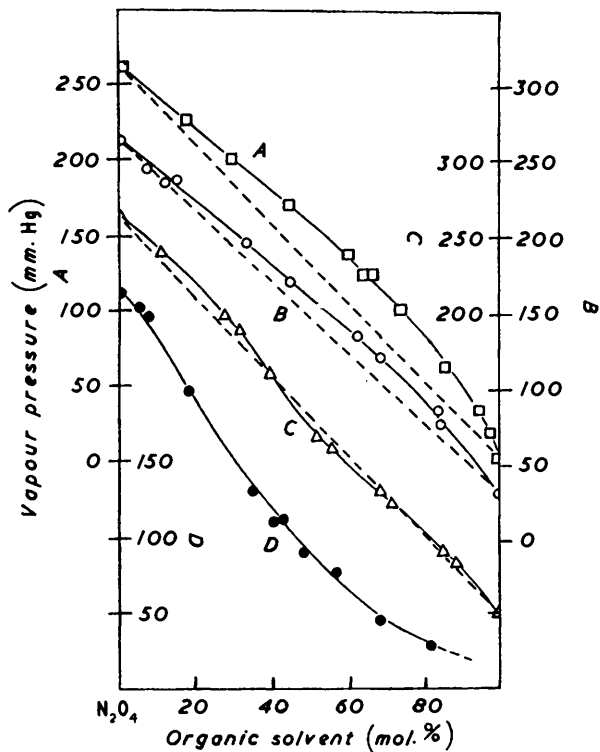


FIG. 2. Vapour pressures (mm.) of N_2O_4 -solvent mixtures.

N_2O_4 with: A, chloroform; B, toluene; C, benzyl cyanide; D, methyl cyanide.

FIG. 3. Vapour pressures (mm.) of N_2O_4 -solvent mixtures.

N_2O_4 with: A, chlorobenzene; B, benzene; C, nitrobenzene; D, acetic acid.



Vapour Pressure of Non-donor Solvent-Dinitrogen Tetroxide Systems.—The *n*-heptane system shows the largest positive deviation observed in dinitrogen tetroxide systems, and probably represents a limiting case. Any attraction between the two molecules involves dispersion and induction effects, and in this instance is clearly small. The behaviour of the cycloparaffins is similar to that of the straight-chain hydrocarbons (cf. cyclohexane, Table 3). Carbon tetrachloride, chloroform,⁹ and nitromethane are also non-donors; the positive deviation diminishes with increase in dipole moment (Table 1), indicating increasing molecular attraction by dipole interaction. Carbon tetrachloride has no dipole moment but can be considered as having polar character, since the carbon-chlorine bond is dipolar.

Autocomplex-formation in Dinitrogen Tetroxide.—In the tetroxide molecule the two polar nitro-groups are opposed, giving a non-polar molecule. However, as observed above for carbon tetrachloride, the cancellation of identical opposed dipoles is not completely effective at distances of the order of molecular dimensions, and some dipole attraction probably exists between tetroxide molecules. It is suggested that some electron-exchange forces also exist in the pure liquid tetroxide; the "autocomplexes" so formed resemble the benzene-benzene autocomplexes postulated by Mulliken,¹⁰ in which it is assumed that some π - π bonding exists between the aromatic molecules. Whereas mixtures of saturated hydrocarbons behave almost ideally (the *n*-heptane-*n*-hexane system gives an almost zero vapour-pressure deviation¹¹ at 30°), systems containing benzene show pronounced positive deviations (the *n*-heptane-benzene and cyclohexane-benzene systems give deviations of +10.4% at 80°¹² and +12.2% at 40°¹³ respectively). There is a general similarity in the spacial distribution of the π orbitals of benzene and dinitrogen tetroxide, and some π - π bonding between tetroxide molecules could also readily account for the positive deviations shown by its mixtures with saturated hydrocarbons.

Aromatic Hydrocarbon Systems.—Measurements have been restricted to benzene and toluene, since other aromatic hydrocarbons were too rapidly attacked by the tetroxide. These two compounds give much smaller positive deviations than does carbon tetrachloride or chloroform; this alone indicates some form of aromatic hydrocarbon-dinitrogen tetroxide bonding other than those of dispersion, orientation, or induction. Thermal analysis shows that aromatic hydrocarbons are π donors with respect to the tetroxide,¹⁴ and this is sufficient to reduce the deviation from 55.5% for a paraffin to 9.5% for benzene. Since the deviation is still positive, the aromatic hydrocarbon-tetroxide bonding is weaker than the sum of polar and π - π bonding between tetroxide molecules.

Aliphatic 'Onium Donor Systems.—Methyl cyanide (an 'onium donor) and nitromethane have similar dipole moments (Table 1) and their dipole interaction with dinitrogen tetroxide should be similar in the two cases. The deviation of -16% for methyl cyanide demonstrates the presence of compound formation in the liquid mixture. However, when the deviations for methyl cyanide and nitromethane are compared with the limiting deviation given by *n*-heptane, it is seen that the proportion of the deviation change which can be ascribed to compound formation with methyl cyanide is much smaller than that to be attributed to polar association. The larger negative deviations observed for the oxygen donors acetic anhydride and ethyl acetate indicate a greater degree of compound formation, but for all the 'onium donor solvents examined here compound formation involving the tetroxide molecule as an electron acceptor makes a smaller contribution to molecular association than does dipole-dipole interaction.

The Acetic Acid System.—Frankland and Farmer¹⁴ have shown from ebullioscopic measurements that some carboxylic acids are dimerised in solution in dinitrogen tetroxide,

⁹ Musil and Breitenhuber, *Z. Electrochem.*, 1953, **57**, 423.

¹⁰ Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

¹¹ Smyth and Engel, *ibid.*, 1929, **51**, 2646.

¹² Brown, *Austral. J. Res.*, 1952, **A**, **5**, 530.

¹³ Scatchard, Wood, and Mochel, *J. Phys. Chem.*, 1939, **43**, 119.

¹⁴ Frankland and Farmer, *J.*, 1901, **79**, 1356.

and this is now shown to be true for acetic acid. The dinitrogen tetroxide-acetic acid phase diagram,^{1a} when plotted with respect to molecular percentage of acetic acid, gives an N₂O₄-rich liquidus curve having smaller slope than corresponding curves for acetic anhydride or ethyl acetate. When composition is plotted as mol. % of the acetic anhydride dimer, the liquidus curve comes into close agreement. Because the acid has m. p. 16°, the full vapour-pressure curve at 0° is not available, and percentage deviations can only be estimated. When vapour pressure is plotted against mol. % of monomer, a slight positive deviation results, which is not in accord with similar systems. Plotted in terms of mol. % of dimer, the deviation is approximately -34%, which is near that for similar oxygen donors.

Systems containing Aromatic Hydrocarbon Derivatives.—Chlorobenzene forms no solid compound with dinitrogen tetroxide,^{1a} but this may be a steric effect and does not preclude consideration of electron exchange in the liquid state as contributing to molecular association. However, the chlorobenzene deviation is appreciably greater than that for benzene; it is slightly less (and the dipole moment slightly greater) than for chloroform, indicating that polar association is the only major interaction between chlorobenzene and dinitrogen tetroxide, π bonding being insignificant. This is consistent with the well known deactivating effect which a substituted chlorine atom has on an aromatic nucleus. (Compare also the influence of the chlorine atom on ether-dinitrogen tetroxide compound formation.^{1a})

The deviations for nitrobenzene and benzyl cyanide are similar to those for their aliphatic relatives nitromethane and methyl cyanide. It appears to be a general rule that when an aromatic compound has a near-zero dipole moment, π - π bonding can make a significant contribution to molecular association in the liquid, but that when the aromatic compound has a large dipole moment, the properties of the liquid are determined much more by polar association than by π - π bonding.

Inflexions in Vapour-pressure Curves.—The curves for nitrobenzene, methyl cyanide, and (to a less extent) nitromethane show one or more inflexions, an unusual feature in vapour-pressure studies. The forces which make up the total molecular attraction will depend in different ways on the molecular structure and molecular arrangements of the components in the liquid. Not all these forces will vary similarly with intermolecular distance and thus with relative concentration of the components. Results indicate that such variation in these forces with concentration is small compared with their total magnitude; they are not readily apparent when super-imposed on curves showing pronounced positive or negative deviations, but become apparent when the behaviour of the system approximates to Raoult's law.

The three solvents referred to above have dipole moments between 3 and 4 D, and molecular attraction is due largely to polar forces. Benzene and toluene, which have similarly small vapour-pressure deviations, show no inflexion. It is assumed, therefore, that inflexion in these curves is the result of variation in polar interactions with solvent concentration.

Influence of Temperature on Deviation.—Deviations at various temperatures are given in Table 4 for six solvents.

TABLE 4. Deviation (%) for equimolecular mixtures at six temperatures.

Solvent	-20°	-10°	-5°	0°	5°	10°	Solvent	-20°	-10°	-5°	0°	5°	10°
<i>n</i> -C ₇ H ₁₆ ...	—	62.5	59.5	55.5	51.5	48.5	Me·NO ₂ ...	—	6	—	~0	—	1.5
CCl ₄	—	39	38	35	32	31	(Me·CO ₂)O	-32	-30	—	-28	—	-27
C ₆ H ₆	—	—	11	9.5	8.5	—	Me·CO ₂ Et	—	-37	-35	-34	-32	-30

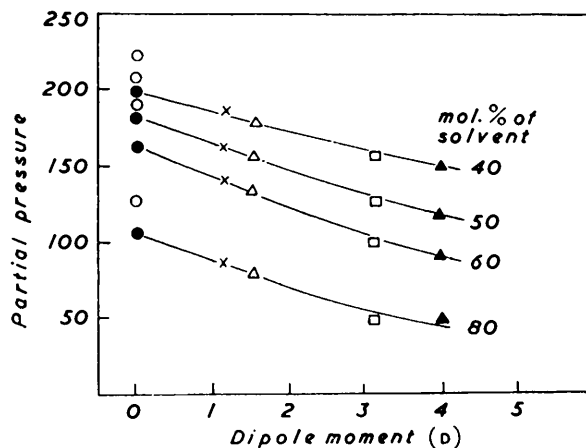
Both negative and positive deviations diminish, *i.e.*, the systems move towards ideal, with increasing temperature. The change in deviation with temperature for acetic anhydride and ethyl acetate, though detectable, is small compared with the magnitude of the deviation, indicating that the energy of compound formation with dinitrogen tetroxide is small in the liquid state.

Dipole Moment-Vapour Pressure Correlation for Non-donors.—In determining the pressures in Fig. 4, the partial pressure of the solvent was assumed to be that proportion of its vapour pressure indicated by the mol. fraction of solvent. This was subtracted from the total observed pressure, and since the vapour pressures of the solvents used are small compared with that of dinitrogen tetroxide the difference gives the partial pressure of the tetroxide without appreciable error. The values so obtained (for 0°) are plotted in Fig. 4 against the dipole moment of the solvent. Five polar solvents of widely differing molecular structures show a correlation which is very close to linear, suggesting that for polar non-donor solvents the only forces of molecular attraction which have significance in tetroxide systems are those which can be expressed quantitatively in terms of dipole moment of the solvent. Values for the non-polar heptane do not correspond with those for the polar solvents.

Degree of Compound Formation with Donor Solvents.—Since compound formation rarely plays the predominant rôle in determining the physical properties of these mixtures, it is not at present possible to derive with accuracy from the vapour-pressure data the proportion of the molecules taking part in compound formation; the difficulties

FIG. 4. Correlation of dipole moment of solvent with partial pressure of N_2O_4 (mm. Hg) at 0°.

● CCl_4 , ○ $n-C_7H_{16}$, × $CHCl_3$,
 △ $PhCl$, □ $MeNO_2$, ▲ $PhNO_2$.



encountered in a quantitative approach are defined briefly below. With certain assumptions, however, an estimate can be made. Thus, we may compare the observed partial pressure of the tetroxide ($P_{obs.}$) with that corresponding to a mixture containing a non-donor solvent whose molecule has an equal dipole moment (P_{dipole} , interpolated from Fig. 4). If the polar and electron-transfer forces are treated as additive (*i.e.*, if it is assumed that partial electron transfer to the tetroxide does not in itself seriously modify the dipole moment of the solvent molecule) then the ratio of the two pressures is a measure of the

TABLE 5.

Solvent	N	$P_{obs.}$ (mm.)	P_{dipole} (mm.)	N_2O_4 molecules combined * (%)
$MeCO_2Et$	0.6	113	178	59
	0.5	82	153	62
	0.4	56	131	69
$(MeCO)_2O$	0.6	126	166	44
	0.5	96	137	46
	0.4	74	113	47

* From $100x/N$ where $x = N(1 - P_{obs.}/P_{dipole})/(1 - NP_{obs.}/P_{dipole})$.

degree of compound formation, and in a mixture in which the initial mol. fraction of dinitrogen tetroxide is N , the mol. fraction of uncombined tetroxide is given by $N \times P_{obs.}/P_{dipole}$. It is clear, however, from the appearance of inflexion in some of the vapour-pressure curves that dipolar forces vary with concentration. These variations,

though small, are sufficiently large to prevent even an approximate assessment of compound formation when the deviation is small (as with methyl cyanide), and these effects also complicate any attempt to derive equilibrium constants over a concentration range. However, with donor solvents showing large negative deviations, these variations are relatively small, and some picture of the order of compound formation at 0° may be derived from the ratio $P_{\text{obs.}}/P_{\text{dipole}}$. Some typical observations are collected in Table 5.

In deriving these values the further assumption is made that with weak donors in the liquid state, the component ratio in the addition compound does not differ from unity.

The various assumptions mentioned are probably sufficiently correct to justify the general conclusion that with the strongest donor solvents used in this work, an equimolar mixture may be considered as equivalent to one in which approximately half the molecules present form addition compounds. In fact, since the environment of each tetroxide molecule will be the same, partial transfer of charge from each solvent to each tetroxide molecule occurs. If the maximum charge transfer corresponding to a stable addition compound be defined by a coefficient (resembling Mulliken's "charge-transfer reaction co-ordinate"¹⁵) of unity, then the state of the liquid mixtures discussed here is represented

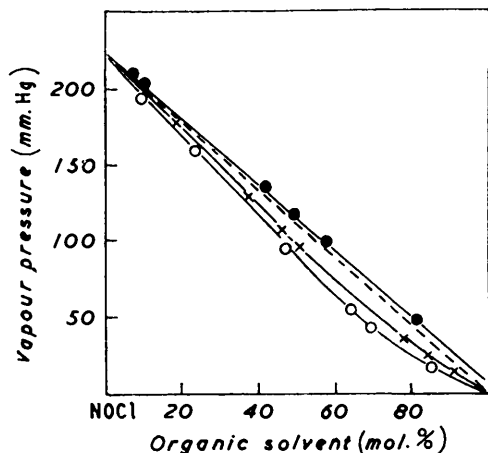


FIG. 5. Vapour pressures of NOCl-organic solvent mixtures at -30.8° .

● CHCl_3 , × pyridine, ○ $\text{Me-CO}_2\text{Et}$.
The broken line represents ideality.

by charge-transfer coefficients up to about 0.5, a degree of charge transfer which is apparently adequate to modify the chemical reactivity of the tetroxide.

Comparison with Nitrosyl Chloride Systems.—In view of its zero dipole moment, dinitrogen tetroxide is particularly convenient for the study of molecular interactions in the liquid state; vapour-pressure deviations can be considered in terms of the dipole moment of the solvent only, and negative deviations are only given by those solvents known to be capable of addition-compound formation. This is not the case in nitrosyl chloride systems, where the polar nature of nitrosyl chloride ($\mu = 1.83$ D) gives rise to negative deviations in the absence of compound formation. Vapour pressures of three organic solvent-nitrosyl chloride mixtures are shown in Fig. 5, and values at other temperatures are collected in Table 6. The influence of this dipole is shown clearly in the mixtures with the non-donor chloroform. With dinitrogen tetroxide there is a positive deviation of 21% at 0° , whereas with nitrosyl chloride the system obeys Raoult's law almost exactly. Ethyl acetate (Fig. 5) shows a deviation of -18% with nitrosyl chloride at -30.8° , compared with -37% for dinitrogen tetroxide mixtures at -10° . The influence of the nitrosyl chloride dipole being allowed for, the vapour-pressure data provide no evidence for compound formation between ethyl acetate and nitrosyl chloride in the liquid state. The solid state has not been studied, but phase diagrams for another oxygen donor compound, dioxan, with nitrosyl chloride show no evidence for compound formation

¹⁵ Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

in the solid state.^{1a} The pyridine system shows only a small negative deviation (12% at -30.8°); this indicates negligible compound formation in the liquid state, though pyridine forms a solid compound with dinitrogen tetroxide at low temperatures.² This is consistent

TABLE 6. Vapour pressures (mm.) of nitrosyl chloride-organic solvent mixtures.

Chloroform (mol. %)	0	7.5	9.0	41.0	42.8	48.5	57.8	80.5	100
Temp.									
-21.2°	363	342	—	223	—	197	167	83	18
-40.7	131	125	120	80	77	69	59	30	4.5
-50.7	71.5	68	66	44	42	40	34	20	2.0
Ethyl acetate (mol. %)	9.0	23.0	47.5	64.0	68.8	85.0	100		
-21.2	332	266	156	94	72	34	6		
-40.7	118	92	55	32	24	11	3		
-50.7	64	53	29	17	13	6	~1		
Pyridine (mol. %)	7.4	18.0	37.2	45.6	50.0	77.4	84.2	90.8	100
-21.2	342	295	215	182	161	64	43	26	1
-40.7	122	103	76	63	58	23	15	10	~0

with other evidence that only the strongest donors (*e.g.*, some simple tertiary amines^{1b}) show evidence of compound formation with nitrosyl chloride in the liquid state.

EXPERIMENTAL

The mixtures (about 25 ml.) were made by direct weighing (with precautions against contact with atmosphere) into a glass bulb of about 25 ml. capacity. This was connected to a glass spiral gauge, and a side arm for evacuation, the vapour volume being about 25 ml. The spiral gauge was used with an optical lever with calibrated scale. The possible error in reading the scale corresponded to a pressure of ± 0.5 mm. Hg. The gauge was employed mainly as a null-point instrument; the air pressure outside the spiral was adjusted, by a fine air-leak, until it approximately balanced the vapour pressure, and was measured by a mercury manometer. The vapour pressures were determined from the manometer reading with a correction for the slight deviation of the gauge scale reading from zero. The liquid mixture was degassed by successive freezing in liquid air, evacuation of the containing vessel to 0.002 mm. Hg, and warming to the temperature of the experiment. This was repeated until the vapour-pressure values were reproducible; two such operations were normally adequate. Ground-glass joints in the apparatus were lubricated with a little Silicone grease. Temperature was controlled by immersing that part of the bulb and leads which contained the liquid mixture and vapour phase in a 2-l. silvered Dewar vessel containing melting ice or solvent maintained at the correct temperature. Temperatures above -20° were measured by a calibrated mercury thermometer; below -20° an alcohol thermometer was used, calibrated with nitrosyl chloride by employing the vapour pressure values accurately determined by Partington and Whynes.¹⁷

The organic liquids used were carefully purified immediately before use, particular care being taken with the drying of the liquids. There was no visible evidence of chemical reaction between the tetroxide and the solvents during the experiments, but slight increases in pressure with time were observed in a few cases. With acetic acid and benzyl cyanide the change in pressure was negligible at -10° and below; at 10° the drift in pressure was of the order of 1 to 5 mm. Hg in 15 min. The accuracy of the vapour-pressure values reported is estimated as ± 1 mm. Hg, and it was not necessary to apply a correction for the gaseous dissociation of the tetroxide into nitrogen dioxide at the low temperatures employed.

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^{1a} Comyns, *Nature*, 1953, **172**, 491; *J.*, 1955, 1557.

¹⁷ Partington and Whynes, *J. Phys. Chem.*, 1949, **53**, 500.