637. *The Ultraviolet Absorption Spectrum of Dinitrogen Tetroxide in Organic Solvents.*

By C. C. Addison and J. C. Sheldon.

The ultraviolet absorption spectrum of dinitrogen tetroxide in *n*- or *cyclo*hexane closely resembles the spectrum of the vapour ($\lambda_{max.}$ 343 mμ; ε 233) with no evidence of fine structure. In non-aromatic solvents (*n*- or *cyclo*hexane, carbon tetrachloride, 1 : 4-dioxan, diethyl ether, chloroform, acetic acid, ethyl acetate, acetic anhydride, methyl cyanide) the extinction coefficient decreases in a regular manner with increase in dipole moment of the solvent, whereas decrease in $\lambda_{max.}$ is determined largely by donor properties of the solvent. The results suggest that in mixtures of dinitrogen tetroxide with donor solvents, discrete molecules of addition complex are not present, but that partial electron-transfer occurs. In aromatic (π-donor) solvents (benzene, toluene, *p*-xylene, chlorobenzene) $\lambda_{max.}$ is unchanged, but the ε values now increase with π-donor strength, confirming that the type of electronic interaction in π- and 'onium donor solvents is different. The contribution of nitrogen dioxide to absorption by dinitrogen tetroxide is discussed.

It has been shown in previous papers that the chemical reactivity of liquid dinitrogen tetroxide is considerably modified in the presence of electron-donor solvents. Addition compounds are formed in the solid state,[1] and vapour-pressure studies give evidence of pronounced interaction between the tetroxide and organic donor molecules (Don) in the liquid state also.[2] Reactions of the mixtures with metals are most readily interpreted on the assumption that ionic species $(Don)_n{\cdot}NO^+$ and NO_3^- are present,[3] but the conductivity of the solutions is not high and it is unlikely that this is the form in which most of the molecules are present. The negative deviations of vapour pressure which occur with strong donor solvents such as ethyl acetate [2] indicate that in equimolar mixtures approximately half the molecules present form addition compounds. An alternative view is that partial charge-transfer from each solvent to each tetroxide molecule occurs. The ultraviolet absorption spectra of mixtures has therefore been examined; if a high proportion of the tetroxide molecules present form ionic species or discrete molecules of addition compound, then pronounced changes in the form of the spectrum are to be expected, whereas partial charge-transfer may not modify the spectrum to the same extent. The spectrum of dinitrogen tetroxide in the vapour phase has been well characterised over

[1] Addison and Sheldon, *J.*, 1956, 1941, 2705, 2709.
[2] *Idem*, *J.*, 1957, 1937.
[3] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

the 240—500 mμ range by Hall and Blacet,[4] who resolved the spectrum of the gaseous N_2O_4–NO_2 mixture at 25° by obtaining the absorption at several vapour pressures, and employing a mechanical analogue differential analyser.

RESULTS AND DISCUSSION

Spectrum of N_2O_4 *in* n- *or* cyclo-*Hexane.*—These solvents show inert solvent behaviour so far as vapour pressures are concerned.[2] Because of the absorption density of the tetroxide at the wavelengths used, approximately centimolar solutions were employed The spectrum is shown in Fig. 1. Identical results were obtained in *n*- or *cyclo*-hexane provided that solvent absorption was negligible (*cyclo*hexane was not used at wavelengths shorter than 260 mμ). The spectrum in hexane is very similar to that in the vapour; significant details of each spectrum are given in Table 1.

The general agreement in the two phases confirms the view that saturated hydrocarbons are inert with respect to dinitrogen tetroxide. The ε values for the solution show some increase over the vapour values, and the 340 mμ maximum undergoes a very slight red shift. Bayliss and McRae [5] suggest that all solutes should suffer a red shift in the spectrum on passing from vapour to solution, though solvation may mask this with a greater blue shift. Although changes in ε cannot be predicted, it is apparent from their data that ε increases for many substances from vapour to liquid phase. In view of the general agreement shown in Table 1, there is interest in Whittaker's observation [6] that the optical absorption coefficient of nitrogen dioxide is the same in both the liquid and the gas phase.

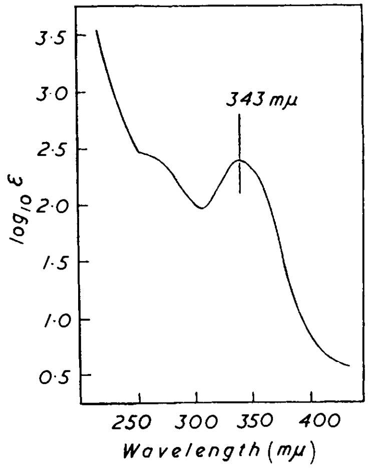


FIG. 1. *Spectrum of* N_2O_4 *in* n- *or* cyclo-*hexane.*

There is a complete absence of fine structure in the spectrum in both phases; reasons for this with respect to the gas phase have been discussed.[4] The small absorption by hexane solutions at 400 mμ (at which wavelength absorption by tetroxide in the vapour is zero) arises from the presence of small quantities of nitrogen dioxide unavoidably present in the solutions. The contribution of nitrogen dioxide to absorption by the tetroxide solutions is discussed later.

TABLE 1.

	Hexane solution (18°)		Vapour phase (25°)	
	λ (mμ)	ε	λ (mμ)	ε
Inflexion	270	240	260	210
Minimum	308	96	306	112
Maximum	343	233	340	179
	400	8	400	0

* Deduced from the results of Hall and Blacet, on the assumption that tetroxide vapour behaves as an ideal gas.

Interpretation of the Tetroxide Spectrum.—Possible assignment of the bands in the spectrum can be made on the basis of resemblances between the carbonyl and the nitro-group, to which attention has been drawn by Bayliss and McRae.[5] Similar weak absorption bands at 280 mμ are observed with each group (cf. acetone, $\lambda_{max.}$ 279, ε 13 in heptane;

---

[4] Hall and Blacet, *J. Chem. Phys.*, 1952, **20**, 1745.
[5] Bayliss and McRae, *J. Phys. Chem.*, 1954, **58**, 1002, 1006.
[6] Whittaker, *J. Chem. Phys.*, 1956, **24**, 780; Steese and Whittaker, *ibid.*, p. 776.

nitromethane, $\lambda_{max.}$ 278, ε 18 in heptane). McMurry[7] has suggested that in the carbonyl group this bond is due to excitation of an electron of the oxygen lone pair to an antibonding π-orbital of the C–O bond. This is a forbidden transition, thus ε is small. The nitro-group is probably capable of a similar transition, a non-bonding electron from the oxygen atoms passing to the lowest vacant π-orbital of the group. The submerged maximum (*i.e.*, inflexion) in the absorption curve at about 270 mμ might reasonably be assigned to this transition. αβ-Dicarbonyl compounds possess two weak absorption maxima, one near 280 mμ and one at longer wavelength (*e.g.*, diacetyl, 286 and 416 mμ). This is interpreted [7] in terms of the conjugated π-orbitals of the two carbonyl groups, the antibonding π-orbitals of the isolated groups being replaced by two different antibonding π-orbitals in the conjugated system. The two bands are then due to excitation of the oxygen lone-pair electron to one or other of these orbitals. A band at 340 mμ is not a general property of a single nitro-group, and from the analogy with conjugated diketones the second absorption maximum for dinitrogen tetroxide at 340 mμ may be the result of conjugation of the two nitro-groups. In this connexion it is relevant that these two groups do not rotate with respect to one another.[8] The fact that the wavelength separation of the two tetroxide bands is smaller than for diacetyl would then indicate that conjugation between the two nitro-groups is less pronounced.

Fig. 2.

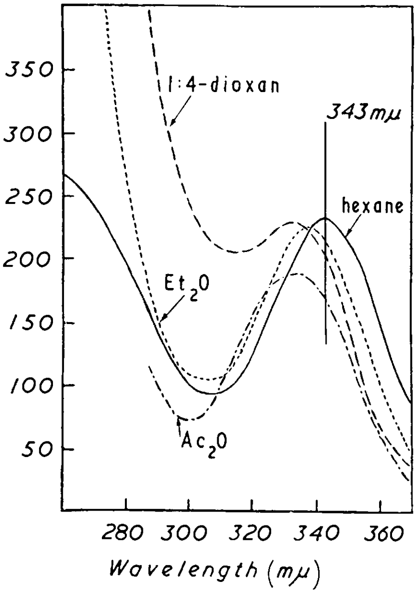
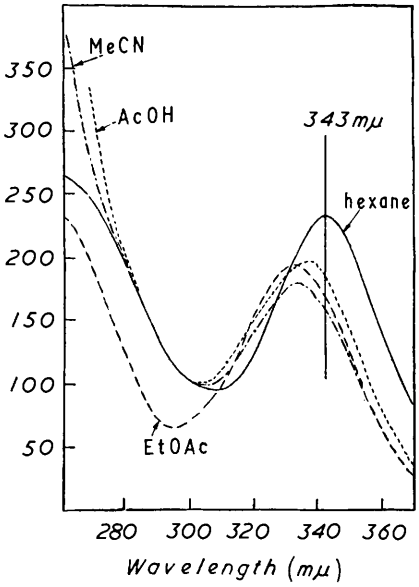


Fig. 3.



Figs. 2 and 3. *Spectrum of* N_2O_4 *in various non-aromatic solvents.*

Absorption Spectra in Other Aliphatic Solvents.—Though the spectrum of the tetroxide in *n*-hexane could be studied down to 220 mμ, it was not usually possible to measure the spectrum in other solvents below about 280 mμ. The 343 mμ band could still be characterised with all the solvents employed; $\lambda_{max.}$ and ε values for this band in aliphatic solvents are shown in Table 2 in order of dipole moment, and the spectra are shown in Figs. 2 and 3.

The C–Cl bond in carbon tetrachloride has dipolar character and, in spite of the resultant zero dipole moment of the molecule, dipole interaction with dinitrogen tetroxide was apparent

---

[7] McMurry, *J. Chem. Phys.*, 1941, **9**, 231, 241.

[8] Giauque and Kemp, *ibid.*, 1938, **6**, 40; Chalvet and Daudel, *J. Chim. phys.*, 1952, **49**, 77.

in vapour-pressure measurements.[2] However, the absorption of dinitrogen tetroxide in carbon tetrachloride was found to be identical with that in hexane (Fig. 4), so that it is the permanent dipole of the solvent which is significant in considering modifications of the spectrum. The non-donor chloroform molecule has a permanent dipole, and interaction with the tetroxide is revealed clearly in a variation in ε, though not in wavelength.

TABLE 2.

Solvent	Dipole moment of solvent	$\lambda_{max.}$ (mμ)	ε
n-Hexane	0	343	233
Carbon tetrachloride	0	343	233
* 1 : 4-Dioxan	0·45	332	230
* Diethyl ether	1·15	337	225
Chloroform	1·15	342	200
* Acetic acid	1·75	336	197
* Ethyl acetate	1·81	333	195
* Acetic anhydride	2·8	333	190
* Methyl cyanide	3·37	333	177

* Donor solvents with respect to dinitrogen tetroxide.

The data in Table 2 indicate that the donor properties of the solvent, and its dipole moment, influence the spectrum in different ways which can be clearly distinguished. Thus, the ε value decreases regularly with increase in the dipole moment of the solvent, irrespective of whether the solvent possesses donor properties. On the other hand, decrease in $\lambda_{max.}$ is determined largely by the donor properties of the solvent. The position of acetic acid in Table 2 has special interest. In phase studies,[1] and vapour-pressure studies,[2] where solutions of acetic acid in dinitrogen tetroxide were involved, the acid fell into place in the list of solvents when it was assumed to exist as the dimer and the corresponding dipole moment (0·83) employed. In the solutions used for spectra the position is reversed. Acetic acid becomes the solvent; it shows anomalous behaviour if regarded as dimeric, but falls into place with other donor solvents if the dipole moment of the monomer (1·75) is regarded as operative.

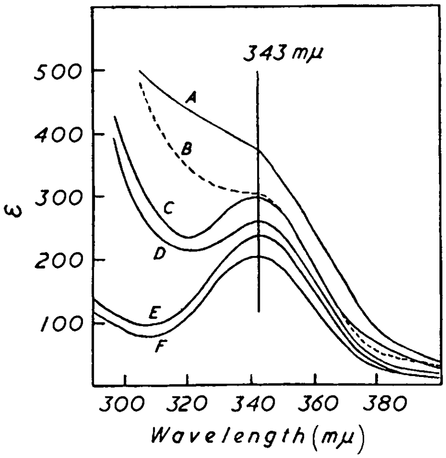


FIG. 4. *Spectrum of* N_2O_4 *in aromatic solvents: (A)* p-*xylene, (B) toluene, (C) benzene, (D) chlorobenzene; also (E) carbon tetrachloride or* n- *or* cyclo-*hexane and (F) chloroform.*

Since the wavelength shift occurs only with donor solvents, it is clearly due to partial electron-donation and not dipole interaction. The electrons from the organic donor may be regarded as entering the lowest vacant orbital of the tetroxide, and it is to this orbital that electrons are excited by ultraviolet absorption by the tetroxide at 343 mμ. The weakly donated electrons are easily expelled from the tetroxide π-orbital by the excitation process, the extra energy required appearing as a decrease in $\lambda_{max.}$. This decrease (10 mμ) is equivalent to a change in the excitation energy of about 2 kcal. mole^{-1}, which is of the same order as the energy of interaction determined from heats of mixing. This apparently small solvent–tetroxide interaction is nevertheless sufficient to alter markedly the nature as well as the degree of chemical reactivity of the tetroxide with change of solvent.

The general similarity of the absorption curves in donor and non-donor solvents suggests that discrete molecules of addition complex are not present in solutions of dinitrogen tetroxide in donor solvents, and therefore the question as to whether the molecular ratios formed in the solid complexes persist in the liquid state does not arise. The concept of partial electron-transfer, with each tetroxide molecule having similar environment in solution, adequately explains physical properties such as vapour pressure, viscosity, and thermal properties of mixtures. (It should be noted that tetroxide absorption is influenced by solvents to a greater extent at wavelengths below the 343 mμ band. It is possible that molecular association of the kind envisaged gives rise to absorption bands at wavelengths below the range experimentally available.) It is also easy to accept the fact that after partial electron-transfer from a solvent molecule the tetroxide molecule should follow a different mechanism in its reactions with organic compounds.[9] Reactions of tetroxide–donor solvent mixtures with metals is less readily understood. To explain these observations (*e.g.*, that copper does not react with either dinitrogen tetroxide or ethyl acetate, but reacts vigorously with the mixture) it is still necessary to postulate the presence of ionic species $(\mathrm{Don})_n\mathrm{NO}^+\cdot\mathrm{NO}_3^-$, which are present in too small a concentration to modify the ultraviolet absorption spectrum. In such species the question of a value for *n* is not irrelevant, and there is evidence from conductivity measurements that it may exceed unity.[10, 11] The only evidence that the ionic concentration is very high is from spectroscopic measurements on diethylnitrosamine–dinitrogen tetroxide mixtures.[11] On re-examination, however, it appears that absorption by the nitrosamine, which was used in the compensating cell, was so high at 415 mμ as to render spurious the absorption band at this wavelength believed to be due to the co-ordinated NO^+ ion.

FIG. 5. *Influence of* NO_2 *on optical density of* $\mathrm{N}_2\mathrm{O}_4$ *solutions in* n- *or* cyclo-*hexane.*

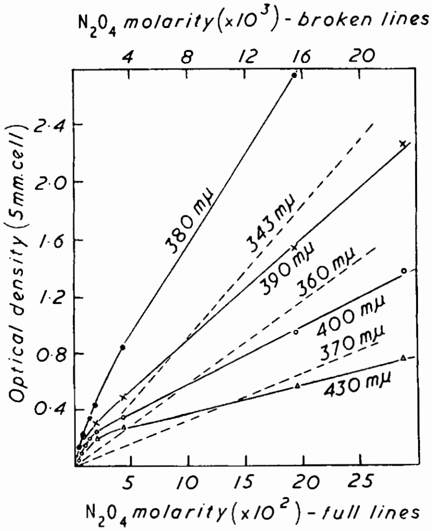
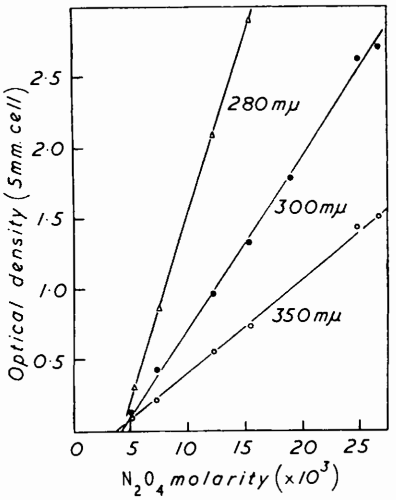


FIG. 6. *Optical density of* $\mathrm{N}_2\mathrm{O}_4$ *solutions in* 1 : 4-*dioxan.*



In connection with measurements on the ultraviolet absorption spectrum of nitroparaffins, alkyl nitrates, and alkyl nitrates, Ungnade and Smiley[12] report that solutions of " nitrogen dioxide " in ether (obtained by direct dissolution of dinitrogen tetroxide in ether, and consequent dilution with ether) absorb in the same region as the nitrites, and that there are five pronounced vibrational fine-structure bands. Their curve is similar to that for nitrous acid in strongly acid aqueous solutions,[13] but resembles even more closely the curve obtained when solutions of dinitrogen tetroxide in organic solvents are contaminated with water. We therefore consider that the curve in Fig. 2, which shows

---

[9] Levy and Scaife, *J.*, 1946, 1093, 1096, 1100.

[10] Addison, Conduit, and Thompson, *J.*, 1951, 1303.

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

[12] Ungnade and Smiley, *J. Org. Chem.*, 1956, **21**, 993.

[13] Singer and Vamplew, *J.*, 1956, 3971; Bayliss and Watts, *Chem. and Ind.*, 1955, 1353; *Austral. J. Chem.*, 1956, **9**, 319.

no apparent fine-structure, is characteristic of dinitrogen tetroxide under fully anhydrous conditions.

Absorption Spectra in Aromatic Solvents.—From a study of solid molecular addition compounds it was possible to identify two types of organic donor. The 'onium donors, of the type discussed above, contain an atom which has one or more lone pairs of electrons available in *s*- and *p*-orbitals, and usually give 2 : 1 compounds with dinitrogen tetroxide. The π-donors, which include aromatic hydrocarbons and their derivatives, give 1 : 1 solid compounds. They have electrons available in molecular orbitals, and form compounds by orbital overlap; this is often evident from reversible colour changes in the solids. The absorption spectra of π-donors (Fig. 4) provide confirmation that the type of electronic interaction differs from that of 'onium donors in the liquid state also. With π-donor solvents, $\lambda_{\text{max.}}$ remains unchanged at 343 mμ, but the ε values increase with the strength of the π-donor: chlorobenzene, benzene, toluene, *p*-xylene. As absorption increases, the curve tails into the visible. *p*-Xylene solutions, though colourless at room temperature, become deep red-brown at $-20°$, and solutions in mesitylene and tetrahydronaphthalene have this colour at room temperature. The last two solvents give dinitrogen tetroxide absorption curves of the *p*-xylene type (Fig. 4), but with much higher ε values; unfortunately a small amount of chemical attack occurs, so that the exact tetroxide concentration in these very dilute tetroxide solutions (and hence the ε values) cannot be determined with accuracy. It is certain, however, that the intense colours arise from orbital overlap rather than chemical decomposition.

Contribution of NO_2 *to Absorption by* N_2O_4 *Solutions.*—The solutions were coloured light brown by the nitrogen dioxide present. Pure liquid dinitrogen tetroxide contains 0·09% by weight of dioxide [6] at 20°, and for ideal solutions this will increase if the tetroxide is diluted by solvents. It was therefore important to determine the extent to which the dioxide present in the solutions might contribute to the absorption. The optical density of solutions has therefore been measured at different molarities (Fig. 5) over a wavelength range covering the 343 mμ band. At wavelengths up to 370 mμ, Beer's law is obeyed closely. The proportion of dioxide in the tetroxide will vary with concentration of the latter, and any significant absorption would result in a deviation from Beer's law. However, absorption by nitrogen dioxide becomes detectable at 380 mμ, and the curvature of the Beer's law plot at low tetroxide concentrations becomes more pronounced with increase in wavelength. In the determination of ε at these higher wavelengths (Figs. 1—4) advantage was taken of the fact that as concentration of dinitrogen tetroxide increases, the relative proportion of nitrogen dioxide decreases, and the curvature of the Beer's law plot ultimately vanishes. The minimum gradient of each curve (Fig. 5) at high tetroxide concentrations was therefore taken to represent the true ε value for dinitrogen tetroxide at that wavelength.

For a given concentration of tetroxide, the depth of the nitrogen dioxide coloration varied widely with the solvent used. It was greatest for paraffins, carbon tetrachloride, and chloroform, and decreased with increasing donor properties of the solvent; ethyl acetate and dioxan solutions were only faintly coloured. The equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is therefore influenced by change in solvent. Cundall [14] first observed this effect. It is reasonable to assume that partial electron-donation to the tetroxide, which is known to influence its chemical reactions, should also restrict its homolytic dissociation, and it is likely that a list of donor solvents, drawn up in reverse order of the intensity of their colour with dinitrogen tetroxide, would coincide with that drawn up on the basis of vapour-pressure deviations.[2]

EXPERIMENTAL

All measurements were made with a Unicam S.P. 500 spectrophotometer, at a temperature close to 18°. The 5 mm. cells used were of fused silica, with ground stoppers, and were optically matched.

[14] Cundall, *J.*, 1891, 1076; 1895, 794.

Materials.—To obtain the appropriate optical density, it was necessary to employ very dilute tetroxide solutions (as low as 0·002M). It was therefore essential that the solvents should be purified with scrupulous care. This was done by usual procedures, particular care being taken to remove water and those impurities likely to react with dinitrogen tetroxide. For example, thiophen reacts readily, and was removed from aromatic hydrocarbons by sulphuric acid. Carbon tetrachloride was washed with alcoholic sodium hydroxide, to remove hydrogen chloride which reacts to give nitrosyl chloride; acetic anhydride did not give consistent results until it had been refluxed for several hours over sodium and fractionated from it.

Dinitrogen tetroxide was prepared by the method already described,[15] and no further purification was necessary.[16]

Preparation of Solutions.—A small weighed bulb was evacuated on a vacuum-line. About 0·1 g. of dinitrogen tetroxide was condensed into the bulb, which was then sealed off and reweighed. The bulb was transferred to a stout 150 ml. glass bottle containing a weighed quantity (about 100 g.) of pure solvent. The bulb was broken under the solvent and a sample of the stirred solution rapidly transferred to the silica cell in a closed system. This procedure allowed the immediate use of the solution, and by suitable choice of tetroxide weights and solvent volumes no dilution adjustments were necessary. This aspect is of great importance in this work because, in spite of the great care taken in purifying solvents, all solutions deteriorated with time, the optical density usually decreasing. For example, after repeated fractionation from phosphoric oxide, paraffins reacted at such a rate that the absorption fell by about 2% in 10 min. Spectra were therefore recorded immediately after mixing. The absorption spectrum is much more sensitive to this slight deterioration than is any other physical property of the solutions so far examined, and was observed in cases where phase studies, viscosity, volume changes, electrical conductivity, and thermal properties showed no evidence of changes with time.

Despite the appropriate and often lengthy purification adopted for each solvent, it was sometimes impossible to remove final traces of impurity which destroyed some part of the small quantity of tetroxide present in the solutions. This led to a corresponding error in evaluating ε, which was not evident however without examination of the optical density–concentration curves. The procedure adopted to obtain the true extinction coefficient is illustrated in Fig. 6 for dioxan solutions. Optical densities at a particular wavelength were plotted against concentration (determined from added weight) of tetroxide for a series of solutions, a fresh solution being made up for each measurement from the same bulk stock of solvent. Part of the tetroxide is seen to have been destroyed, giving a product which was relatively non-absorbing, since the Beer's law plots gave straight lines which intersected the concentration axis at a positive value. The true ε values were obtained from the slopes of these lines, and are thus independent of the intercept on the axis.

The authors are indebted to the Department of Scientific and Industrial Research for a Maintenance Grant (to J. C. S.).

THE UNIVERSITY, NOTTINGHAM.

[*Received, April* 28*th*, 1958.]

---

[15] Addison and Thompson, *J.*, 1949, S 218.

[16] Addison, Allen, Bolton, and Lewis, *J.*, 1951, 1289.