252. *Dinitrogen Trioxide: Some Observations on the Electronic Spectrum and Structure.*

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The visible and near-ultraviolet absorption of dinitrogen trioxide, in toluene and other solvents at low temperatures, has been examined. The blue colour is due to a weak band in the red region, with $f \sim 4{\cdot}5 \times 10^{-4}$, $\lambda_{max.}$ 6620 Å in toluene, which is structureless, but otherwise resembles the nitrosoalkane band, and there is a strong band with $\varepsilon_{max.} > 2500$ below 3500 Å. The visible band shifts towards the blue with increasing polarity of the solvent.

Molecular-orbital, spectroscopic, and thermochemical considerations support the assignment of the trioxide visible band to a nitroso n_N–π^* transition, and the near-ultraviolet band to a π–π^* transition, in a nitro-nitroso-molecule with a π-only N–N bond. A nitrito-structure, or a nitro-nitroso-structure with a $(\sigma + \pi)$ N–N bond, would be more difficult to reconcile with the visible absorption and low heat of dissociation of dinitrogen trioxide.

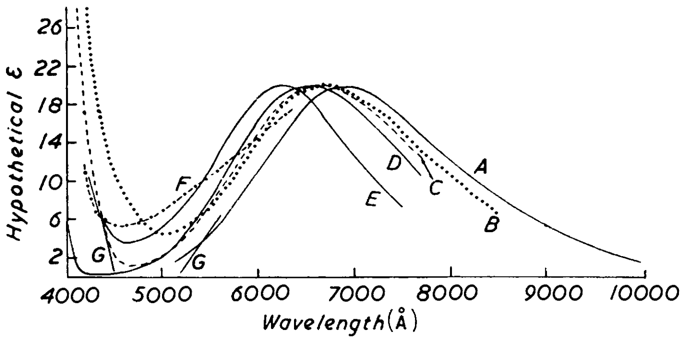
ALTHOUGH dinitrogen trioxide has been known [1] since 1816, and is readily recognised by its deep blue colour, precise knowledge of the molecule is lacking, probably because of its instability; it is 80% dissociated [2] into nitric oxide and nitrogen dioxide–dinitrogen tetroxide at 25° and 1 atm. Its rôle in the chamber process for sulphuric acid, and in

[1] Dulong, *Ann. Chim. Phys.*, 1816, **3**, 240.
[2] Beattie and Bell, *J.*, 1957, 1681.

nitrosation,[3] and its addition to olefins, are still being investigated, and opinions are divided as to the molecular constitution.

The visible and ultraviolet spectra have been examined, mostly at −80°, of standard trioxide solutions in toluene, ethyl ether, or mixed paraffins, made up by vacuum methods. Reproducible results were obtained with toluene as solvent, Beer's law being obeyed over the range studied, 0·007—0·038M. The spectrum is drawn in the Figure, and wavelengths and extinction coefficients are listed in the Table. The oscillator strength of the visible band is $f \sim 4{\cdot}5 \times 10^{-4}$, if the long tail beyond the limit of the Cary spectrophotometer at 7700 Å is estimated from the spectrum[4] of the carbon tetrachloride solution. All the solutions were opaque from about 3500 Å to 2000 Å. The extinction measurements are accurate to 5% or better at the higher densities, but less good at the minima, because of sensitivity there to the presence of impurities, and to misting of the cell windows.

Spectrum of dinitrogen trioxide in various solvents.



Solvents: *A*, Carbon tetrachloride; *B*, acetic anhydride; *C*, toluene; *D*, diethyl ether; *E*, aqueous acid; *F*, liquid nitric oxide; *G*, toluene, plotted from Berl and Winnaker's results.[5]

There is no other quantitative measurement, in any solvent or without, for comparison, except Berl and Winnaker's[5] " transparency maximum " at 4750 Å for a toluene solution of the trioxide at −50°; their results can be plotted as the two straight lines (*G*) in the Figure. They studied only the 4400—5600 Å region, and found Beer's law to be obeyed for 0·32—0·67M concentrations of trioxide.

Solvent	Dielect. const.	Temp.	$\varepsilon_{max.}$	$\lambda_{max.}$ (Å)	ε_{min}	$\lambda_{min.}$ (Å)	Ref.
Alkanes	2·0	−180°	—	~7200	—	—	—
Liq. NO ...	—	−150	0·56 (extrapolated)	~7000	0·14	4600	*a*
CCl_4	2·2	?	12	6960	<2	<5000	4
Toluene	2·4	−80	20·1	6620	1·1	4700	—
,, ...	,,	−50	—	—	<1	4750	5
Et_2O	4·3	−80	~20	6650	<1	4300	—
Ac_2O	20·5	20	—	6700	—	4770	*c*
Aq. acid......	>80	20	—	6250	—	4800	*b*
,, ...	,,	,,	—	—	1	4780	5

[a] Vodar, *Compt. rend.*, 1937, **204**, 1467. [b] Bunton and Stedman, *J.*, 1958, 2440. [c] Deschamps, personal communication.

Quantitative spectra were not obtained with the other solvents (see Experimental section). Dissociation and loss of nitric oxide, which could only be detected in toluene solutions at −45° and above, occurred well below −80° with the aliphatic hydrocarbons,

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[3] Hughes, Ingold, and Ridd, *J.*, 1958, 58.
[4] Seel and Sauer, *Z. anorg. Chem.*, 1957, **292**, 1.
[5] Berl and Winnaker, *ibid.*, 1933, **212**, 113.

in which the trioxide is less soluble, and there was some hydrolysis in the ether solutions. Qualitative curves, for unknown concentrations of trioxide in various solvents, are plotted in the Figure so as to have an arbitrary $\varepsilon_{\text{max.}}$ of 20, although $\varepsilon_{\text{max.}}$ commonly varies with the solvent. These solutions also are described in the Table.

The low-temperature spectra show that nitrogen dioxide is absent, for this would absorb[6] moderately strongly ($\varepsilon \sim 100$) at the minimum of the trioxide's absorption, and its banded spectrum is readily recognised. Dinitrogen tetroxide, however, might be present, for its absorption,[6,7a] which begins at about 3900 Å and reaches $\varepsilon_{\text{max.}}$ 170 (for the vapour) at 3400 Å, would be masked by the intense ultraviolet absorption of the trioxide that begins at about 4500 Å and reaches $\varepsilon_{\text{max.}} > 2500$ below 3500 Å.

Dissociation of the trioxide should be small, however; at −80° and 0·6 atm. (0·038M expressed as a gas pressure), gaseous dinitrogen trioxide is 2% dissociated, according to a rather extended extrapolation of the equilibrium equations[2] for 5°—45°; and it is likely that toluene or ether stabilises the trioxide, as the tetroxide is stabilised relative to nitrogen dioxide by aromatic molecules and Lewis bases.[7] The tetroxide forms complexes[7] with these, but according to the spectra the trioxide does not, under the conditions described; neither does it cleave the ether, although this has been reported[8] as taking place readily. Study of some related solutions (see Experimental) showed that stronger reagents than dinitrogen trioxide, and higher temperatures than −80°, are needed for ether cleavage. If the trioxide were ionised, the absorption of the nitrosyl ion[9] and of the nitrite ion[10] would be hidden by the trioxide's ultraviolet band, but such species would not be stable in these organic solvents.

The spectra appear to be temperature-invariant, except for evidence of dissociation at higher temperatures. In none of the solutions could any trace of vibrational structure be detected in the visible band, and this is in contrast to the visible band of trifluoronitrosomethane,[11] which is very similar in shape, location, and intensity but shows considerable (though not very sharp) structure. This difference may be related to the dissociation energies of the bonds to the nitroso-group, about 50 kcal./mole for the *C*-nitroso-compound[11] as against 10·3 for the trioxide:[2] the energy at the long-wavelength limit of the trioxide band, about 10,000 Å, is over 20 kcal./mole, so that dissociation may well follow absorption. The nitrosoalkane band does not have the trioxide band's long tail in the red region, so that the oscillator strength is slightly larger for the trioxide, and the band origin perhaps 0·3 ev lower, since the trioxide molecule is probably vibrationless at −80° in the electronic ground state.

Nature of the Transitions.—If dinitrogen trioxide is a nitronitroso-compound (see below), we should expect to find in the electronic spectrum a low-energy low-intensity band due to a nitroso n_{N}–π^* transition (where n refers to non-bonding electrons, and π^* to the lowest unfilled π orbital) absorbing near 7000 Å in the nitrosoalkanes.[11,12] Sidman[13] has assigned the nitroso visible band to an n_{O}–π^* transition, on intensity grounds, but the (small) variations of the n–π^* intensities are not yet understood, and the assignment to the n_{N} electrons is preferred here on energetic grounds [cf. the n_{N}–π^* bands of azomethane[14] near 3000 Å ($\varepsilon_{\text{max.}} \sim 5$), and diazomethane[15] near 4000 Å ($\varepsilon_{\text{max.}} \sim 3$)]. The n_{O}–π^* bands are considered to be at shorter wavelengths because of the greater electronegativity of oxygen (though this energy increment may be offset to some extent by a higher p character in the

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[6] Hall and Blacet, *J. Chem. Phys.*, 1952, **20**, 1745.

[7] Addison and Sheldon, *J.*, (*a*) 1958, 3142; (*b*) 1956, 1941, 2705, 2709; Ling and Sisler, *J. Amer. Chem. Soc.*, 1953, **75**, 5191 and earlier papers.

[8] (*a*) Wieland, *Ber.*, 1921, **54**, 1782; (*b*) Reihlen and Hake, *Annalen*, 1927, **452**, 48.

[9] Deschamps, *Compt. rend.*, 1957, **245**, 1432.

[10] Sidman, *J. Amer. Chem. Soc.*, 1957, **79**, 2669.

[11] Mason (Banus), *J.*, 1957, 3904.

[12] Orgel, *J.*, 1953, 1276.

[13] Sidman, *Chem. Rev.*, 1958, 689.

[14] Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 123.

[15] Brinton and Volman, *J. Chem. Phys.*, 1951, **19**, 1395.

n_O than in the n_N electron): *e.g.*, 2700 and 2800 Å ($\varepsilon_{max.}$ ~2 and 10) for the alkyl nitroso- and nitro-compounds respectively[11] and 2800 Å ($\varepsilon_{max.}$ ~10) for aliphatic ketones. There is as yet no certain basis for these assignments.

The trioxide spectrum has not been examined in the near-infrared region, and n–π^* transitions in the near ultraviolet region will be hidden by the intense absorption there, since they are largely overlap-forbidden; the strong ultraviolet band is probably due to a fairly low-energy π–π transition (these are all allowed).

Solvent Shifts.—Blue shifts with increase in polarity of the solvent are characteristic, and occasionally diagnostic, of n–π^* bands,[16] because interaction of the n electrons with polar, perhaps hydrogen-bonding, solvent molecules stabilises the ground state relative to the excited state in the transition. Such blue shifts are found for alkyl *C*-, *N*-, and *O*-nitroso n_N–π^* bands,[11] and may be larger for dinitrogen trioxide than for *C*-nitroso-compounds, since the trioxide molecule is more polar than a nitrosoalkane, and the shifts are very large for the dialkyl *N*-nitrosamine bands. π–π Bands in systems of this sort are usually much less affected by changes in the polarity of the solvent.

From wavelengths listed in the Table, we can estimate a blue shift of 200 cm.$^{-1}$ for ether solutions of the trioxide compared with toluene solution, and 1000 cm.$^{-1}$ for aqueous acid solution compared with toluene; these shifts are increased if an aliphatic hydrocarbon is taken as reference solvent. For trifluoronitrosomethane the blue shift is 100 cm.$^{-1}$ for ether solution, or 350 cm.$^{-1}$ for aqueous solution, each relative to aliphatic hydrocarbon solvent; the corresponding figures for *N*-nitrosamines are 150 and 2500 cm.$^{-1}$, while the blue shifts for alkyl nitrites are small. On the other hand, the blue shifts for the n_O–π^* band of nitromethane[17] are 700 cm.$^{-1}$ for dioxan and 900 cm.$^{-1}$ for aqueous, relative to aliphatic hydrocarbon, solution, and there is a red shift of 600 cm.$^{-1}$ for toluene solution.

The dinitrogen trioxide solvent shifts thus support the assignment of the visible band to an n–π^* transition, and if it is from nitrogen rather than from oxygen, the trioxide is behaving more like an *N*-nitroso- than a *C*- or *O*-nitroso-compound. The sequence of bands for the different solvents follows the order of the dielectric constants, with the exception of the acetic anhydride solution spectrum; however this was observed without special precautions, such as rigorous drying of the solvent, which were found to be necessary before consistent spectra of dinitrogen tetroxide could be obtained in it, and the 3400 Å tetroxide band shifts to the red in acetic acid, as compared with anhydride, solution.[7a]

Structure of Dinitrogen Trioxide.—Direct evidence as to the molecular constitution of the trioxide is lacking. The *X*-ray study[18] of the solid (m. p. *ca.* −103°) at −115° was inconclusive; it is reported[19] to exchange with nitric oxide at −118°. The liquid (b. p. *ca.* 3·5°) is diamagnetic and non-conducting,[8a] and less likely to be ionised than the tetroxide.[20] Tarte,[21] who examined the infrared spectrum in the sodium chloride region of gaseous dinitrogen trioxide (at room temperature in the presence of its dissociation products and a little nitrous acid), found that it could not be assigned in terms of a nitrito-structure $O{:}N{\cdot}O{\cdot}N{:}O$, and that fundamental frequencies for a nitronitroso-molecule $O_2N{\cdot}N{:}O$ could be chosen to fit corresponding ones in nitric oxide, nitrogen dioxide, and dinitrogen tetroxide.

Supporters of a nitronitroso-structure for dinitrogen trioxide include Wieland,[8a] Ingold and Ingold,[22] Walsh[22] (with the dubious argument that the bond is probably N–N since the odd electron in nitric oxide and in nitrogen dioxide is nearer to the nitrogen atom than to oxygen), Addison and Lewis,[22] and Coulson and Duchesne.[23]

[16] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

[17] Bayliss and Brackenridge, *J. Amer. Chem. Soc.*, 1955, **77**, 3959.

[18] Reed and Lipscomb, *Acta Cryst.*, 1953, **6**, 781.

[19] Leifer, *J. Chem. Phys.*, 1940, **8**, 301.

[20] Addison, Lewis, and Thompson, *J.*, 1951, 2838.

[21] Tarte, *Bull. Soc. roy. Sci. Liège*, 1953, 276.

[22] Ingold and Ingold, *Nature*, 1947, **159**, 743; Walsh, *J.*, 1953, 2272; Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.

[23] Coulson and Duchesne, *Bull. acad. roy. Belg.*, 1957, **43**, 522.

A nitrito-structure is preferred by Sidgwick;[24] he and Cartmell and Fowles[25] quote Leifer's opinion[19] that the rapid exchange of ^{14}N in nitric oxide and ^{15}N in nitrogen dioxide at −35° proves the two nitrogen atoms in the trioxide to be equivalent. However there can be other routes to the exchange than the dinitrogen trioxide molecule. Packer and Vaughan[26] consider that the trioxide behaves (in acid nitrite solution) as an equilibrium mixture of the nitrito- and the nitronitroso-form, but such an equilibrium is unlikely in the solutions studied here, since the visible absorption is temperature-invariant and obeys Beer's law within the experimental limits (exact measurement of optical densities above or below −80° was difficult); and the spectrum might be expected to show the nitrite structure below 4000 Å, as do trioxide solutions when partial hydrolysis has occurred.

Nature of the N–N *Bond.*—The presence in the trioxide of a weak bond comparable to the N–N bond in the tetroxide is suggested by the heats of dissociation, respectively[2,27] 10·3 and 12·875 kcal./mole (and it is likely that in the trioxide[21] as in the tetroxide[23] the geometries and bond properties are similar to those of the molecular dissociation products). The N–N single-bond energy term, however, is much higher than this, if somewhat less than the N–N bond dissociation energy for hydrazine,[28] 60 kcal./mole. That the N–N bond type is different in the tetroxide and in the hydride is borne out by the stretching frequencies, respectively[29] 265 and 850 cm.$^{-1}$, and by the lengths, 1·75 Å for the gaseous tetroxide[30] against 1·47 Å for hydrazine.[31] The values are not known for the trioxide, but from the energy of dissociation the analogy between the trioxide and tetroxide, in contrast to the hydride, seems plausible. The nitric oxide dimer, which has a dissociation energy[32a] of 4 kcal./mole and is diamagnetic as a solid[32b] and as a liquid,[32c] is sometimes included in this comparison;[21,23] however the molecule in the crystal[32d] is not ON·NO, but a rectangle of two nitric oxide molecules head-to-tail.

From molecular-orbital calculations on the tetroxide molecule, Chalvet and Daudel[33] derive a total N–N bond order ($\sigma + \pi$) of 1·164, but this is difficult to reconcile with the length and weakness of the bond. A more convincing description[23,30] is that the tetroxide N–N bond is formed by π overlap only, with no (resultant) σ component, for the molecule is planar even in the gas phase, with an N–N bond 0·27 Å longer than the normal single bond. Coulson and Duchesne[23] derive a total bond order of about $\frac{1}{3}$ for this π-only N–N bond; this figure is obtained by use of the normal double-bond value for the resonance integral, and a better approximation is to take the latter as proportional[34] to the overlap (estimated[35] for Slater orbitals, for N–N bond lengths of 1·24 and 1·75 Å); the bond order then reduces to about 0·1. A plot of N–N bond orders against lengths extrapolates readily to a bond order of 0·1 (or $\frac{1}{3}$) for the long N–N bond. The curvature between bond orders 1 and 3 is greater than for C–C bonds, perhaps because the n_N electrons repel more strongly at closer approach.

The nitrogen lone pairs that overlap in the centre of the molecule can be considered to interact to form fully occupied σ and σ^* orbitals, somewhat antibonding in total effect.

Although fewer measurements are available for the trioxide than for the tetroxide

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[24] Sidgwick, " The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, **1**, 688.

[25] Cartmell and Fowles, " Valency and Molecular Structure," Butterworths, London, 1956, 162.

[26] Packer and Vaughan, " Organic Chemistry," Oxford Univ. Press, 1958, 148.

[27] Giauque and Kemp, *J. Chem. Phys.*, 1938, **6**, 40.

[28] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954.

[29] Wiener and Nixon, *J. Chem. Phys.*, 1957, **26**, 906; Fresenius and Karweil, *Z. phys. Chem.*, 1939, *B*, **44**, 1.

[30] Smith and Hedberg, *J. Chem. Phys.*, 1956, **25**, 1282.

[31] Anderson and Kistiakowsky, *ibid.*, 1943, **11**, 6.

[32] (*a*) Rice, *ibid.*, 1936, **4**, 367; Eucken and d'Or, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl.*, 1932, 107; (*b*) Lips, *Helv. Chim. Acta*, 1935, **8**, 247; (*c*) Bizette, and Tsai, *Compt. rend.*, 1938, **206**, 1288; (*d*) Dulmage, Meyers, and Lipscomb, *J. Chem. Phys.*, 1951, **19**, 1432.

[33] Chalvet and Daudel, *J. Chim. phys.*, 1952, **49**, 77.

[34] Mulliken, *ibid.*, 1949, **46**, 712.

[35] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

molecule, two criteria for a π-only N–N bond, a low dissociation energy and similar bond properties in the compound molecule and in its molecular dissociation products,[21] appear to be fulfilled.

A consequence of a π-only N–N bond is that the n–π^* (and π–π^*) transitions should require less energy than if the trioxide molecule had a ($\sigma + \pi$) N–N bond, or a nitrito-structure; the numbers of π electrons in the three forms are respectively 4, 6, and 6, so that in the π-only N–N bonded molecule transitions can be made to the non-bonding molecular orbital, which is some way below the lowest anti-bonding orbital. Thus for the π-only form it is likely, and for the other structures less likely, that the extension of the delocalisation to cover five nuclei, instead of two in the nitrosoalkane, brings down the π^* orbital, to compensate for the shrinkage of the nitroso n_N orbital by the nitro-group. This would explain the similar energies of the nitrosoalkane and trioxide visible bands, for the n_N–π^* absorption of alkyl *N*-nitroso(and *O*-nitroso)-compounds is in the near ultra-violet region.

The charge in the non-bonding molecular orbital of the nitronitroso-molecule is very largely on the nitro-oxygen atoms, and in the higher bonding orbital much of the charge is on the nitroso-oxygen. Because of the reduced overlap, the lowest-energy π–π transition may absorb less strongly than the others. This charge distribution in the non-bonding molecular orbital might also be expected to reduce the n_N–π^* transition probability compared with that of a nitrosoalkane (the antibonding orbital is more evenly distributed over the nuclei), but the oscillator strengths are similar; a higher s component in the trioxide nitroso n_N electrons would be a compensating factor.

A nitrito-structure has a higher delocalisation energy than a nitronitroso-structure (as is usual for a branched system compared with its straight-chain isomer), and this, together with the extra σ bond, might be expected to give the nitrito-form the advantage in stability over the π-only N–N-bonded form. The balance could be restored, however, if, as seems likely, the energy term is much lower for a " single " than for a " double " N–O bond, as is the case for N–N and O–O bonds.[28,36]

Justification for the π-only bond in the trioxide (and in the tetroxide) can be found in the higher s–p promotion energy [37] of nitrogen (11 ev) and oxygen (nearly 16 ev) than of carbon (4 ev), which has a lower nuclear charge and in which the s electron goes into an empty p orbital. The large promotion energy outweighs the fairly low further energies to form valence states [38] (3·3 for nitrogen, 2 for oxygen, against 4 ev for carbon). This favours the π-only N–N bonded structure, which has more n electrons (12 n_O, 6 n_N) than either the ($\sigma + \pi$) N–N-bonded form (12 n_O, 2 n_N), or the nitrito-form (10 n_O, 4 n_N), since n electrons usually are largely s in character, unless they can delocalise; the economy in promotion energy more than offsets any weakening of the bonds due to higher-valence shell repulsions.

A really high s component in the n_N orbitals that overlap in the π-only N–N bond would reduce the repulsion, for at 1·75 Å the $2s\sigma$–$2s\sigma$ overlap [35] ($S_\sigma = 0{\cdot}15$) for nitrogen is less than half the sp, sp^2, or sp^3 overlap ($S_\sigma = 0{\cdot}37$). However the repulsion of the n_O electrons in the nitro-group sets a lower limit to the ONO angle, 133° in the tetroxide (134° in the dioxide), so that the tetroxide's nitrogen atoms are roughly sp^2 hybridised, with a rather higher p component in the N–N σ bond-plus-antibond than in the bonds to oxygen. The bonding π overlap [35] is low ($S_\pi = 0{\cdot}07$), but can outweigh a larger repulsive S_σ overlap: according to Mulliken's magic formula [39] the energy terms are respectively proportional to $S_\pi/(1 + S_\pi)$ and to $S_\sigma^2/2$.

The overlap between adjacent n_N and n_O orbitals in the nitroso-group is not negligible (it is [35] 0·1 for sp^2, or 0·4 for pure s orbitals, for a bond distance of 1·2 Å) and will split

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[36] Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367; Samuel, *Rev. Mod. Phys.*, 1946, **18**, 103.

[37] Atomic Energy Levels, Nat. Bur. Stand., Washington, circular no. 467, 1949, **1**, 22, 32, 46.

[38] Skinner and Pritchard, *Trans. Faraday Soc.*, 1953, **49**, 1254.

[39] Mulliken, *J. Phys. Chem.*, 1952, **56**, 295.

the n_N and n_O energy levels further apart, lowering the " n_N–π* " and raising the " n_O–π* " transition energies. This factor should be taken into account in a comparison of nitroso *n*–π* energies with those of carbonyl or (*trans*-)azo-groups, for example, where this *n*-orbital overlap is absent.

Attempts to find the maximum of the intense trioxide absorption in the near ultraviolet region were unsuccessful, possibly because of dissociation of the trioxide in solutions that were weak enough for the absorption to be measurable. This problem could perhaps be attacked by a low-temperature study of a trioxide film, or of a solution with a very small absorbing path, which should also be examined in the near infrared region.

EXPERIMENTAL

The spectra were measured with a Cary recording spectrophotometer. A doubly-jacketed metal cell[40] (with some modifications) was used at −183°, −80°, and at −45° (melting chlorobenzene), the outer jacket being filled with dry nitrogen (since it was not vacuum-tight at low temperatures) and hot air blown on the outer windows.

The ether and toluene solvents were dried over sodium wire and distilled through a very efficient column; middle fractions were taken, and kept over bright sodium wire. The mixed hydrocarbon solvent, 6 : 1 *iso*pentane–methyl*cyclo*hexane, was purified for ultraviolet transmission by prolonged shaking with sulphuric acid, then with potassium hydroxide pellets to remove sulphur dioxide. Nitric oxide was prepared by reduction of nitrite by ferrous ion, the method[41] having been adapted for use with a vacuum system.

Solutions of dinitrogen trioxide and nitrogen dioxide were made up by vacuum methods to exclude moisture or air, and where vacuum grease was unavoidable, Silicone grease was used. The dioxide or trioxide was made from measured amounts of nitric oxide and dry oxygen, and distilled *in vacuo* into the frozen solvent in a Carius tube, which was sealed and kept frozen until required. The Carius tubes and metal cell were dried and flushed out with dry nitrogen before use, and a dry-nitrogen train was attached to the cell in use. The spectra were measured as quickly as possible because of misting of the cell windows.

Dinitrogen Trioxide in Toluene.—Twelve solutions, 0·007—0·038M in trioxide, were examined, and the absorption found to obey Beer's law. There was no trace of nitrous acid structure in any of the toluene spectra, although these were examined with the same technique as for the ether spectra.

Dinitrogen Trioxide in Ether.—While the spectra were being recorded, the visible and ultraviolet bands of the trioxide became fainter as the banded spectrum of nitrous acid[42] emerged. By comparison with a standard solution of nitrous acid in ether it was found that the formation of acid by a trioxide solution left in the low-temperature cell until colourless was almost quantitative, according to the equation $N_2O_3 + H_2O \rightleftharpoons 2HO{\cdot}NO$, so that no dissociation had occurred. Hydrolysis of the trioxide, and the reverse reaction, are known to be slow. If the visible band of the ether trioxide solution is assumed to have $\varepsilon_{max.} \sim 20$, the nitrous acid coexisting with trioxide is equivalent to the trioxide missing. This points to the absence of any ether–trioxide complex, nitrito-trioxide molecules, or products of ether cleavage.

The only other solvent besides ether to give some (slight) nitrous acid structure in the spectrum was the hydrocarbon mixture, despite the purification procedure. In acetic anhydride the solvent could act as scavenger. Quantitative spectra of the trioxide, as of the tetroxide,[7a] should be obtainable with ether.

Dinitrogen Trioxide in Aliphatic Hydrocarbons.—The trioxide's visible band could only be roughly estimated, because of low solubility at temperatures just above −183°, and misting of the cell windows. In the most dilute solutions studied, about 0·001M, the ultraviolet absorption was too strong to be measured, so that $\varepsilon_{max.}$ was probably above 2500.

Other Solutes.—Solutions of nitrogen dioxide and of nitrosyl perchlorate in dry ether or dioxan at −80° and at room temperature were examined. The nitrosyl perchlorate solution at room temperature developed a little ethyl nitrite with time, as if the ether was slowly cleaved

[40] Passerini and Ross, *J. Sci. Instr.*, 1953, **30**, 274.

[41] *Inorg. Synth.*, 1946, **2**, 126.

[42] Tarte, *Bull. Soc. chim. belges*, 1950, **59**, 365; Deschamps, personal communication; Ungnade and Smiley, *J. Org. Chem.*, 1956, **21**, 993.

(the spectrum was compared with that of ethyl nitrite in ether). There was some hydrolysis. An ethyl nitrite spectrum was also obtained from a solution of nitronium hydrogen pyrosulphate in dry ether or dioxan at room temperature. It seems, then, that stronger reagents than dinitrogen trioxide, and temperatures above −80°, are required to cleave ethyl ether.

The intense near-ultraviolet absorption was shown by all the trioxide solutions, and by no others. In many of the other solutions studied, the alkyl nitrite or nitrous acid spectra overlaid an absorption rising gently from 4000 to 3000 Å, due perhaps to dinitrogen tetroxide.

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