295. *Thermal Stability and Solution Properties of Copper Nitrate–Dinitrogen Tetroxide.*

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The preparation of the addition compound $Cu(NO_3)_2,N_2O_4$ from copper in organic solvent–dinitrogen tetroxide mixtures is described. Dissociation vapour pressures have been measured in the temperature range 20—80°. The Clausius–Clapeyron plot shows a break at 60°; heats of dissociation are 15·1 and 16·2 kcal./mole above and below 60° respectively. An absorption band in the NO^+ region in the infrared spectrum of the solid indicates that the ionic form $NO^+[Cu(NO_3)_3]^-$ may make some contribution to the structure of the solid. The visible and the ultraviolet absorption spectra of solutions of the addition compound, and of anhydrous copper nitrate, in various non-aqueous solvents are compared. Electrical conductivities in nitromethane solution are compared. These properties indicate that the compound dissociates completely into its components in solution.

THE 1 : 1 addition compound of copper nitrate with dinitrogen tetroxide, $Cu(NO_3)_2,N_2O_4$,[1] is the parent compound from which anhydrous copper nitrate is obtained. Prepared as described below, the compound is obtained as blue needles, strongly deliquescent in moist air. The stability of such compounds varies widely with the metal employed, and in general 1 : 2 compounds appear to be much less stable than 1 : 1 compounds. The compounds $Zn(NO_3)_2,2N_2O_4$ and $Co(NO_3)_2,2N_2O_4$ have an obvious vapour pressure of dinitrogen tetroxide at room temperature, but the uranyl compound $UO_2(NO_3)_2,N_2O_4$ is highly stable.[2] The iron compound $Fe(NO_3)_3,N_2O_4$ sublimes without decomposition;[3] in the solid state it has the structure $NO^+[Fe(NO_3)_4]^-$ and gives conducting solutions in non-aqueous solvents.[15] The utility of these compounds as solid oxidants depends upon thermal stability and structure. Copper nitrate–dinitrogen tetroxide has a thermal stability lying between the extremes mentioned above, and there are three possible structures, (I), (II), (III). The first represents a lattice compound; in bonding to copper

$Cu(NO_3)_2,N_2O_4$	$NO^+[Cu(NO_3)_3]^-$	$NO,Cu(NO_3)_3$
(I)	(II)	(III)

nitrate the identity of the dinitrogen tetroxide molecules is retained. The ionic structure (II) is analogous to that of the iron compound above, and would be expected to possess

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[1] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19; *J.*, 1958, 3099.
[2] Gibson and Katz, *J. Amer. Chem. Soc.*, 1954, **76**, 4668.
[3] Addison, Hathaway, and Logan, *Proc. Chem. Soc.*, 1958, 51.

high thermal stability. Structure (III) involves co-ordination of the nitrosonium ion to the copper ion. In this paper, some properties of the compound are discussed in the light of these structures.

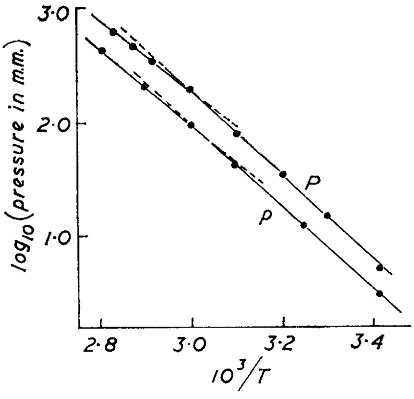
Dissociation Vapour Pressure.—In a closed tube at room temperature the crystals develop a slight atmosphere of dinitrogen tetroxide. Because of thermal decomposition a normal m. p. cannot be obtained, but if the sample is heated rapidly, transient melting to a green oil occurs before decomposition. Under these conditions the m. p. is approximately 120°.

Thermal decomposition has been studied by measuring the dinitrogen tetroxide vapour pressure. Results are shown in Table 1. P is the total vapour pressure observed, and p the equivalent pressure on the assumption that no dissociation into nitrogen dioxide occurred in the gas phase; p was calculated by using the equilibrium constants recorded by Bodenstein and Boes [4] and Verhoek and Daniels.[5] The results give smooth curves, and the temperature of 83·5° at which the vapour pressure reaches 1 atm. is obtained by extrapolation. The vapour pressure falls below 1 mm. at 6°. The decomposition is completely reversible, and at these temperatures the vapour pressure of copper nitrate is not significant. The plot of $\log_{10} P$ against $10^3/T$ is shown as the upper graph in Fig. 1. It consists of two straight lines intersecting near 60°. Some rearrangement in the solid structure probably takes place at this temperature, and it may be relevant that the specific heat and the thermal conductivity curves of the dinitrogen tetroxide–nitrogen dioxide equilibrium mixture pass through a maximum at this temperature.[6] From the slopes of these lines, the heats of dissociation ΔH of copper nitrate–dinitrogen tetroxide is 17·0 kcal./mole below and 14·2 kcal./mole above 60°. The lower plot (Fig. 1) is based on the equivalent dinitrogen tetroxide pressures p; the break in the line is only just apparent, the ΔH values being 16·2 kcal./mole below and 15·1 kcal./mole above 60°.

TABLE 1. *Thermal dissociation of* $Cu(NO_3)_2,N_2O_4$.

Temp.	20°	30°	40°	50°	60°	70°	75°	80°	[83·5°]
P (mm. Hg)	5	15	34	77	190	349	484	638	760
p (mm. Hg)	3	9	19	43	98	198	268	362	429

FIG. 1.



The partial pressure of dinitrogen tetroxide in the gas mixture over the low-temperature range was also calculated by using the known equilibrium constants, and plotted similarly. This gave $\Delta H = 16{\cdot}4$ kcal./mole for the reaction $Cu(NO_3)_2,N_2O_4 \rightleftharpoons Cu(NO_3)_2 + N_2O_4$.

The breaking of the bonds between copper nitrate and dinitrogen tetroxide in the solid is only one of several terms making up the heat of dissociation. Further consideration will be deferred until ΔH values for related compounds are available, but it seems unlikely that the bonding is entirely of the type which the fully ionic structure $NO^+[Cu(NO_3)_3]^-$ would require.

In view of the existence of the 1 : 2 compounds $Co(NO_3)_2,2N_2O_4$ and $Zn(NO_3)_2,2N_2O_4$, it appeared possible that a corresponding copper compound might exist. The ionic formulation $(NO^+)_2[Cu(NO_3)_4]^{2-}$ for such a compound also involves the more acceptable

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[4] Bodenstein and Boes, *Z. phys. Chem.*, 1922, **100**, 75.
[5] Verhoek and Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250.
[6] Gray, *Chem. Rev.*, 1955, **55**, 1069.

4-co-ordination of the copper ion. However, vapour-pressure measurements on the compound $Cu(NO_3)_2,N_2O_4$ in the presence of excess of dinitrogen tetroxide gave no indication of the existence of a 1 : 2 compound.

Infrared Spectrum.—The absorption bands are compared in Table 2 with those for the NO^+ and N_2O_4 species, and with the bands (col. 2) assignable to the covalently bonded nitrate group, as observed in anhydrous copper nitrate.[9] The results indicate that: (1) There is no absorption at the 1360 cm.$^{-1}$ region which is the characteristic vibration ν_3 for the nitrate ion, so that all nitrate groups are covalently bonded. (2) Bands occur at frequencies expected for dinitrogen tetroxide, but in each case these coincide with covalent nitrate absorption; the results are therefore consistent with the presence of dinitrogen tetroxide molecules, but do not confirm this. (3) A sharp peak is observed at 2294 cm.$^{-1}$, which is much more pronounced than the weak absorption which is observed for copper nitrate in this region. This must be taken as indicating the presence of the NO^+ ion in the crystals. (4) Absorption in the 1730 cm.$^{-1}$ region is observed for many compounds in which the nitrosonium ion is co-ordinated to a metal.[10] However, this band is weak, and as absorption in this region also occurs with copper nitrate and with dinitrogen tetroxide, it provides no direct evidence for the structure $NO,Cu(NO_3)_3$.

The relatively low heat of dissociation, taken together with the infrared spectrum, leads to the conclusion that the solid has properties of both the lattice compound $Cu(NO_3)_2,N_2O_4$ and the ionic compound $NO^+[Cu(NO_3)_3]^-$. The solid, as isolated, is not regarded as a mechanical mixture of these two species. The crystal structure of anhydrous copper nitrate recently determined[11] shows that the nitrate groups already exist in two different environments, and the introduction of dinitrogen tetroxide into the crystal increases the variety of N–O bonds present. Molecular interaction will distort these bonds, and a relatively small distortion may be sufficient to produce NO^+ absorption by the crystal. In consequence, the application of infrared spectra to the study of nitrosyl complexes becomes much more limited in compounds which already contain covalent nitrate groups.

Action of Solvents.—In aqueous solution, complete dissociation occurs. The compound has an appreciable solubility in dry diethyl ether and in ethyl alcohol, giving clear green solutions. These solutions are unstable, and gassing occurs; oxidation of the solvents appears to occur more rapidly than with dinitrogen tetroxide alone. [This effect has been observed also with the compound $Zn(NO_3)_2,2N_2O_4$.[12]] Copper nitrate–dinitrogen tetroxide is readily soluble in a number of oxygen- and nitrogen-containing solvents, *e.g.*, ethyl acetate, nitromethane, nitrobenzene, dioxan, acetone, tetrahydrofuran, and methyl, benzyl, and phenyl cyanides. Solubilities are frequently high, but in no case do they

TABLE 2. *Infrared absorption bands* (*cm.*$^{-1}$).

$Cu(NO_3)_2,N_2O_4$	$Cu(NO_3)_2$	NO^+	N_2O_4	$Cu(NO_3)_2,N_2O_4$	$Cu(NO_3)_2$	NO^+	N_2O_4
2294 m sp	2381 w	2300 [a]	—	1289 v s	1289 v s	—	1265
	2299 w	2252 [b]	—	1264 v s	1264 v s		
1730 w	1792 m	—	1749 [c]	1042 sh	1038 m	—	—
	1733 m sh	—	—	1026 s	1016 s		
1520 sh	1592 v s	—	—	814	795 s	—	—
1490 v s	1565 v s			802 s	787 s		
1464 w	1546 v s			765 w	770 s	—	752
	1504 v s			740 w sh	—	—	—

[a] NO^+ in nitrosyl perchlorate.[7] [b] NO^+ in $NO^+[Fe(NO_3)_4]^-$ (Addison, Gatehouse, and Logan, unpublished results). [c] See ref. 8.

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[7] Millen and Watson, *J.*, 1957, 1369.

[8] Sutherland, *Proc. Roy. Soc.*, 1933, **141**, *A*, 342.

[9] Addison and Gatehouse, *Chem. and Ind.*, 1958, 464; *J.*, 1960, in the press.

[10] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32; Griffith, Lewis, and Wilkinson, *ibid.*, p. 38.

[11] Wallwork, *Proc. Chem. Soc.*, 1959, 311.

[12] Addison, Lewis, and Thompson, *J.*, 1951, 2829.

exceed that of anhydrous copper nitrate. For example, the solubilities of copper nitrate and its tetroxide addition compound in ethyl acetate at 25° are 150 g. and 163 g. (0·80 and 0·58 mole) per 100 g. of solvent, respectively. Solutions of the addition compound in these solvents are emerald green and stable, but in a closed tube a visible atmosphere of dinitrogen tetroxide slowly develops above the solutions. These preliminary observations indicate that the simple dissociation $Cu(NO_3)_2,N_2O_4 \longrightarrow Cu(NO_3)_2 + N_2O_4$ occurs at least partially in solution. Both copper nitrate [13] and dinitrogen tetroxide [14] can form addition compounds with these solvents, which will also encourage this form of dissociation. Metal nitrates are insoluble in pure dinitrogen tetroxide, and the lower solubility of the addition compound, compared in mole units, is therefore attributed to the introduction of free dinitrogen tetroxide into the solvent.

Copper nitrate–dinitrogen tetroxide is quite insoluble in non-polar solvents such as carbon tetrachloride, chloroform, benzene, and n- and cyclo-hexane.

Absorption Spectra of Solutions.—Solutions in a number of solvents show a single broad absorption band in the visible region. Table 3 shows values for the maximum extinction coefficient $\varepsilon_{max.}$ at the wavelength $\lambda_{max.}$ for solutions of copper nitrate–dinitrogen tetroxide, together with corresponding data for anhydrous copper nitrate. All solutions show $\lambda_{max.}$ values near 800 mμ, but $\varepsilon_{max.}$ values are much greater in non-aqueous solvents than in water.

TABLE 3.

Solvent	H_2O	EtOH	EtOAc	$C_4H_8O_2$	NO_2Me
$Cu(NO_3)_2$: $\lambda_{max.}$ ($\varepsilon_{max.}$)	800 (12)	780 (32)	820 (50)	785 (34)	800 (64)
$Cu(NO_3)_2,N_2O_4$: $\lambda_{max.}$ ($\varepsilon_{max.}$)	810 (13)	770 (32)	840 (59)	770 (34)	800 (65)

The high extinction coefficients observed for solutions of copper nitrate in non-aqueous solvents, in both the visible and the ultraviolet range, will be discussed elsewhere. Table 3 shows, however, that visible-range absorption by the addition compound closely resembles that of the anhydrous nitrate, and is consistent with complete dissociation into copper nitrate and dinitrogen tetroxide. Only with the ethyl acetate solutions is an appreciable difference observed. The very high solubility of copper nitrate in ethyl acetate [15] implies unusually strong solvation, but the tetroxide appears to have some influence on this process. The ultraviolet spectra of these solutions were therefore compared (Fig. 2). The curve (*A*) for the addition compound has $\lambda_{max.}$ at 295 mμ, the displacement from the nitrate peak in aqueous solution (302·5 mμ) being a solvent effect. Curve *B* for copper nitrate in ethyl acetate is very similar; the difference between the two curves (curve *E*) is close to the absorption curve for dinitrogen tetroxide in ethyl acetate [16] (curve *F*), so that the ultraviolet spectrum of the addition compound in ethyl acetate may be regarded as the sum of the absorption spectra of its components. Curve *C*, obtained with 1,4-dioxan, is similar to that for ethyl acetate. For fresh solutions in ethyl alcohol (curve *D*) the absorption at 295 mμ is again very high compared with nitrate absorption in water ($\varepsilon =$ 7·0 at 302·5 mμ), but the appearance of an inflexion at 357 mμ, characteristic of nitrite, indicates some reaction with the solvent.

Conductivity of Solutions.—The absorption spectra of solutions in non-aqueous solvents leave no doubt that a large proportion of the addition compound must undergo the simple dissociation $Cu(NO_3)_2,N_2O_4 \longrightarrow Cu(NO_3)_2 + N_2O_4$ in solution. The presence of NO^+ and $[Cu(NO_3)_3]^-$ ions should, however, be revealed in the electrical conductivity of solutions in a solvent of high dielectric constant. Fig. 3 shows molar conductivities in nitromethane. The maximum molar conductivity is 6·5 ohm^{-1} $cm.^2$, so that neither copper nitrate nor the addition compound gives rise to an appreciable number of ions (the compound

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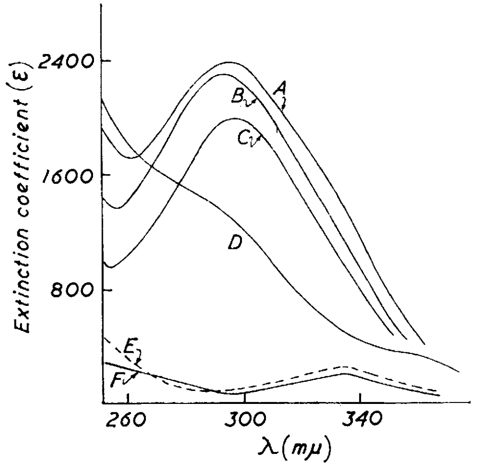
[13] Addison, Hathaway, and Logan, unpublished results.
[14] Addison and Sheldon, *J.*, 1956, 1941.
[15] Addison and Logan, unpublished results.
[16] Addison and Sheldon, *J.*, 1958, 3142.

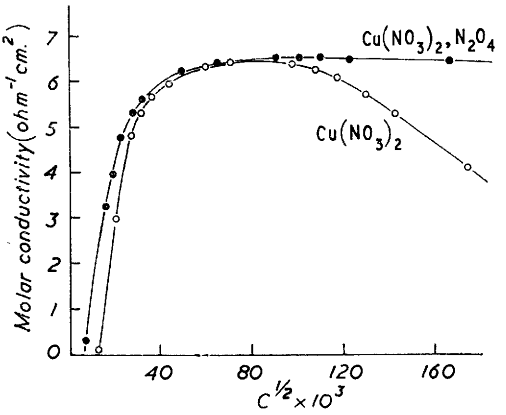
$NO^+[Fe(NO_3)_4]^-$ has a maximum molar conductivity of 45 ohm^{-1} cm.^{2} at 25° in nitromethane[15]). Copper nitrate is known[17] to exist as the un-ionised monomer in ethyl acetate (dielectric constant 6·1). In nitromethane medium of dielectric constant 37 slight ionisation may occur, so that the decrease in molar conductivity with increasing concentration, in the high concentration range, is normal. The increase in molar conductivity which occurs at low concentrations is quite unusual. This effect has been observed with some other anhydrous transition-metal nitrates, and will be discussed elsewhere. The conductivity curve for the addition compound follows closely that for copper nitrate. A significant difference is observed only at high concentrations. Dinitrogen tetroxide alone, when added to nitromethane, undergoes self-ionisation,[18] the specific conductivity increasing from 10^{-7} to 10^{-5} ohm^{-1} cm.$^{-1}$, and the difference between the two curves (Fig. 3) may be attributed to this effect rather than to the direct ionisation of the $Cu(NO_3)_2,N_2O_4$ molecule.

FIG. 2.



A. $Cu(NO_3)_2,N_2O_4$ in ethyl acetate.
B. $Cu(NO_3)_2$ in ethyl acetate.
C. $Cu(NO_3)_2,N_2O_4$ in 1,4-dioxan.
D. $Cu(NO_3)_2,N_2O_4$ in ethyl alcohol (fresh solution) (the curve is raised 200 units on the ε scale for clarity).
E. Difference between curves *A* and *B*.
F. Absorption spectrum of N_2O_4.

FIG. 3. *Electrical conductivities in nitromethane at 25°.*



We conclude, therefore, that, although the ionic form $NO^+[Cu(NO_3)_3]^-$ may make some contribution to the structure of the solid, there is no evidence for the formation of ionic species when the compound is dissolved in non-aqueous solvents.

EXPERIMENTAL

Copper nitrate–dinitrogen tetroxide was prepared by reaction between copper metal and mixtures of dinitrogen tetroxide with ethyl acetate or nitromethane. The rates of reaction of copper with these mixtures have been reported.[19] However, these data are of little assistance in selecting optimum conditions for isolation of products, since solution properties of the mixtures, as well as their reactivity, vary considerably with composition.

Mixtures with Ethyl Acetate.—The rate of reaction with copper is greatest at 20 mol. % of ethyl acetate. Mixtures containing up to 50% of ethyl acetate could be used; with larger proportions of ethyl acetate, the green colour of copper salts was only evident in the solution

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[17] Addison and Hathaway, unpublished results.
[18] Addison, Hodge, and Lewis, *J.*, 1953, 2631.
[19] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

after several days. Over the 10—30 mol. % range, the initial rapid reaction quickly subsided owing to the coating of the metal surface with fine blue crystals. When these were removed mechanically the reaction proceeded again. The product was filtered off and washed with dinitrogen tetroxide, excess of the latter being removed in a stream of dry air in the apparatus described below. Copper was determined gravimetrically as the ethylenediamine–mercury iodide complex; total nitrogen was obtained by hydrolysing the complex in sodium hydroxide solution, reducing with Devarda's alloy, and determining the ammonia evolved; the sodium hydroxide solution of the complex was titrated directly for nitrite content, from which the N_2O_4 content of the complex was determined [Found: Cu, 22·7; N, 19·9; N_2O_4, 32·9. $Cu(NO_3)_2,N_2O_4$ requires Cu, 22·75; N, 20·0; N_2O_4, 32·9%].

Mixtures containing 30—50 mol. % of ethyl acetate reacted steadily with copper for some hours at room temperature. The mixture became a dark green viscous oil, but no product was precipitated. Addition of excess of dinitrogen tetroxide to this oil precipitated copper nitrate–dinitrogen tetroxide as a pale blue amorphous powder. However, if the viscous oil was warmed slightly and the tetroxide added until solid just appeared, a high yield of crystalline copper nitrate–dinitrogen tetroxide was obtained within an hour. This procedure was used to prepare the compound in quantity. No evidence of solid complexes between copper nitrate and ethyl acetate was obtained in this work; it is noteworthy that when alkyl or aryl cyanides are employed in place of ethyl acetate, the reaction product almost invariably contains combined cyanide.[17]

Mixtures with Nitromethane.—The reaction rate with copper is maximum at 90 mol. % of nitromethane. Below 75%, reaction was slight and quickly subsided. Above 90%, reaction was vigorous but again quickly subsided. Between 75 and 90 mol. % of nitromethane, reaction was maintained, and blue crystals were deposited within a few minutes (Found: Cu, 22·7; N, 20·0%). The product described here is no doubt the same as the jade-green microcrystalline solid obtained by Ferraro and Gibson,[20] who heated dinitrogen tetroxide with cupric oxide in a sealed tube at 87° and 14·7 atm. for 7·5 hr., but the present method of crystallisation from solution gives the product in a more crystalline form.

Filtration and Washing of Product.—The apparatus used is shown in Fig. 4, and has found general application where it is necessary to separate crystalline products from dinitrogen tetroxide media with the minimum of contact with the air. The apparatus is thoroughly dried, and flushed with dry air through connection *D*. The flow of dry air being maintained, the tube attached to the B.24 joint *A* is rapidly replaced by the flask containing the crystals and liquid. Entry of air into the flask is avoided by the simple expedient of warming it with the hand immediately before transfer. Tetroxide vapour then gushes from the mouth of the flask during transfer. The apparatus is then inverted; the crystals then collect on the sintered plate *P* (porosity 3) and are freed from supernatant liquor by gentle suction at *D*. Washing is effected by replacing the empty flask at *A* by one containing dinitrogen tetroxide, connected to joint *A* through a short bent tube so that the tetroxide can be poured by turning on the joint. If dry gas is now passed in at *C* or *D*, the vessels attached to *A* and *B* can be replaced by dry tubes. The apparatus is then again inverted, and the product shaken into the tube at *A*. From this stage, the manipulations can be carried out in a dry box.

Thermal Dissociation.—Vapour pressures were measured in the apparatus shown in Fig. 5, which incorporates a glass spiral gauge, sensitivity 90° deflection per atm. Pressure changes were recorded by reflection on to a scale at a distance of 3 m. The sample was placed in tube *A* at room temperature, the apparatus evacuated, and the zero of the gauge recorded with tap *T* open to vacuum; *T* was then closed, and the apparatus immersed in an oil-bath to the level *L*. The time required to reach pressure equilibrium was between 3 and 6 hr., depending on temperature. Pressures were first determined by heating the bath to the required temperature $t°$, which was then maintained until equilibrium was established. The bath was then heated, and allowed to cool again to $t°$. The pressures obtained by the two methods were in close agreement, indicating that the decomposition is a reversible process.

Possible Existence of the Compound $Cu(NO_3)_2,2N_2O_4$.—A sample of the 1 : 1 compound was placed in tube *A* (Fig. 5) together with liquid dinitrogen tetroxide, and the temperature was kept at 0°. The equilibrium vapour pressure was the value (242 mm. Hg) for the liquid tetroxide. Successive known quantities of the tetroxide were then removed; the vapour pressure remained constant, until it dropped suddenly to zero when all excess of liquid

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[20] Ferraro and Gibson, *J. Amer. Chem. Soc.*, 1953, **75**, 5747.

tetroxide had been removed. Analysis of the solid remaining at this stage showed it to be the 1 : 1 compound.

Measurement of Spectra.—Ultraviolet spectra were determined with the Unicam S.P. 500 spectrophotometer. The solutions were contained in matched fused silica cells with ground-glass stoppers. The infrared spectrum was determined by using a Parsons double-beam spectrometer; and cell windows were of sodium chloride coated with polystyrene. Nujol and hexachlorobutadiene were used as mulling agents.

FIG. 4.

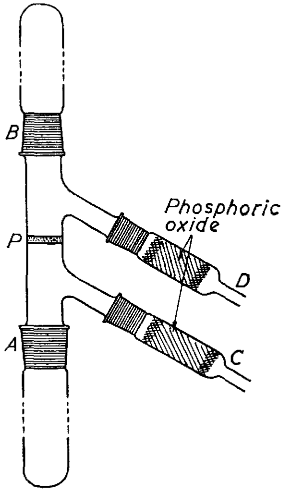
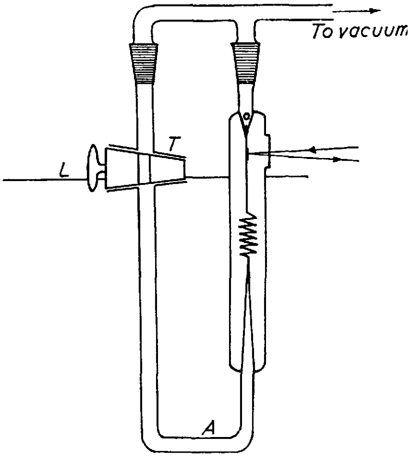


FIG. 5.



Electrical Conductivities.—Nitromethane was purified as already described,[18] and had specific conductivity 1×10^{-7} ohm^{-1} cm.$^{-1}$. The conductivity cell was of the type designed by Groeneveld and Zuur.[21] Resistances were measured at 1000 cycles/sec., the circuit described by Greenwood and Worrall [22] being used.

The authors thank Dr. B. M. Gatehouse (University College, London) and Dr. Dagleish (Reckitts and Colman Ltd., Hull) for infrared spectra, and Dr. N. Logan for measurement of electrical conductivities.

THE UNIVERSITY, NOTTINGHAM. [*Received, October 12th*, 1959.]

[21] Groeneveld and Zuur, *Rec. Trav. chim.*, 1953, **72**, 617.
[22] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.