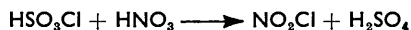


78. Nitryl Chloride. Part I. Its Preparation and the Properties of its Solutions in Some Organic Solvents.*

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Nitryl chloride, NO_2Cl , was prepared by Dachlaucher's method as a pale yellow liquid, b. p. -14.3° , m. p. $-141^\circ \pm 2^\circ$. Gaseous nitryl chloride decomposes at room temperature very slowly. The alkaline hydrolysis of nitryl chloride to hypochlorite and nitrite was confirmed. The nature of nitryl chloride in various organic solvents was studied as a preliminary to examining its reactions with organic compounds. Its solutions in less polar solvents are colourless, and those in polar solvents are yellow, the latter owing their colour to nitrosyl chloride and chlorine, formed by the hydrolysis of nitryl chloride by traces of moisture in these solvents. It also reacts with hydrogen chloride.

Preparation, Purification, and Physical Properties.—Although nitryl chloride was prepared¹ in 1929 by oxidation of nitrosyl chloride with ozone, its physical constants and the colour of the pure liquid are not yet accurately known. The more convenient method of preparation used here is the addition of chlorosulphuric acid to nitric acid at or just below room temperature:²



It was purified by passing ozonised oxygen through the liquefied gas to oxidise any nitrosyl chloride, then fractionally distilled to remove nitrogen dioxide and chlorine. Nitryl chloride condensed as a pale yellow liquid, b. p. -14.3° , and solidified to a pale yellow solid, m. p. $-141^\circ \pm 2^\circ$ (see Table 1).

Schumacher and Sprenger¹ and, later, Petri³ reported that nitryl chloride condensed to a colourless liquid, but although the main impurities, chlorine, nitrogen dioxide, and nitrosyl chloride do colour the product, we found that the most careful refractionation does not remove its pale yellow colour. Its b. p. was constant within 0.2° , at any given atmospheric pressure, and its composition indicated that it was pure.

Ogg,⁴ Seel,⁵ and Volpe⁶ and their co-workers purified nitryl chloride by vacuum distillation, but only Himel⁷ used a low-temperature fractionating column which seemed

* For a summary of this work see *Chem. and Ind.*, 1955, 1742.

¹ Schumacher and Sprenger, *Z. anorg. Chem.*, 1929, **182**, 139.

² Dachlaucher, D.P. 509,405.

³ Petri, *Z. anorg. Chem.*, 1948, **257**, 180.

⁴ Ogg, Freiling, and Johnston, *J. Chem. Phys.*, 1952, **20**, 327.

⁵ Seel and Nogradi, *Z. anorg. Chem.*, 1952, **269**, 188.

⁶ Volpe and Johnston, *J. Amer. Chem. Soc.*, 1956, **78**, 3903.

⁷ Himel, U.S.P. 2,511,915.

essential to remove chlorine. Dachlaucher² and Ville⁸ both bubbled the gas through concentrated sulphuric acid to remove the oxides of nitrogen although we found that removal was not complete.

TABLE 1. *Physical constants of nitryl chloride; comparison with earlier work.*

Name	Method of Prepn.	Purifn.*	M. p.	B. p.	Analyses, etc.†
Schumacher and Sprenger ^a	NOCl + O ₃	None	-145°	-15°	d_4^{20} 1.37, d_4^{16} 1.33
Petri ^b	HNO ₃ + HSO ₃ Cl	None	-149	-15 to -14	d_4^{20} 1.46
Batey and Sisler ^c	"	None	-145	—	—
Seel and Nogradi ^d	"	V.D.	-116	—	—
Shechter <i>et al.</i> ^e	"	None	-145 ± 2	-17 to -15	44.9% Cl
Ville ^f	"	None	—	-15	44—45% Cl
Present authors ...	"	O ₃ and F.D.	-141 ± 2	-14.3	17.07% N 43.6% Cl

* V.D., vacuum distillation; F.D., fractional distillation.

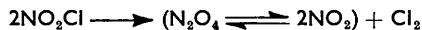
† Calc. for NO₂Cl: Cl, 43.52; N, 17.18%.

^a Ref. 1; ^b ref. 3; ^c Batey and Sisler, *J. Amer. Chem. Soc.*, 1952, **74**, 3048; ^d ref. 5; ^e Shechter, Conrad, Daulton, and Kaplan, *J. Amer. Chem. Soc.*, 1952, **74**, 3052; ^f ref. 8.

Stability of Nitryl Chloride.—The kinetics of the thermal decomposition of nitryl chloride were studied by Schumacher and Sprenger,⁹ who found that it decomposed at a measurable rate between 100° and 150°:

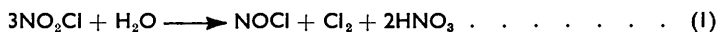


Ogg and Wilson¹⁰ showed that at room temperature chlorine and nitrogen dioxide interact slowly with the partial formation of nitryl chloride, an equilibrium being established. They gave no exact data for the extent or the rate of decomposition at room temperature except that nitryl chloride is considerably more stable than previously supposed. As we needed a clearer idea of its stability, we made some approximate measurements of the rate of decomposition of the gas at 25° by measuring the rate of increase of pressure. At room temperature one product of decomposition, nitrogen dioxide, is partially in the form of dinitrogen tetroxide, but it should be sufficiently dissociated to cause an appreciable rise in pressure with the decomposition of the nitryl chloride:



We concluded that dry nitryl chloride decomposes at approximately ½% per day, that moisture increases the rate, and that the decomposition is probably not photochemical. Despite the slow rate of decomposition, the initially colourless gas became distinctly brown in a few hours, presumably owing to traces of nitrogen dioxide.

Solutions of Nitryl Chloride in Organic Solvents.—Dilute solutions of nitryl chloride in polar solvents such as nitromethane, acetonitrile, and acetic acid were yellow whereas those in less polar solvents such as benzene, carbon tetrachloride, and methylene dichloride were colourless. The formation of colour was not always immediate, there often being an induction period of the order of minutes. The absorption spectra and distillation of these solutions showed that whereas colourless solutions contain pure nitryl chloride, the yellow colour is due to nitrosyl chloride and chlorine formed by hydrolysis by traces of water present in the more polar solvents:



The only mode of hydrolysis of nitryl chloride previously reported¹¹ was under alkaline conditions when nitrite and hypochlorite are formed:



We confirmed this mode of hydrolysis by a better method.

⁸ Ville, *Mem. Poudres*, 1955, **37**, 343.

⁹ Schumacher and Sprenger, *Z. Electrochem.*, 1929, **34**, 653; *Z. phys. Chem.*, 1931, **12**, B, 115.

¹⁰ Ogg and Wilson, *J. Chem. Phys.*, 1950, **18**, 900.

¹¹ Schmeisser and Gregor-Haschke, *Z. anorg. Chem.*, 1947, **255**, 34.

Ultraviolet absorption spectra of solutions. In Table 2 the absorption maxima of solutions of nitryl chloride are compared with those of solutions of nitrosyl chloride.

TABLE 2. *Ultraviolet maxima of solutions of nitryl chloride and nitrosyl chloride in various solvents.*

Solvent	NO ₂ Cl				NOCl			
	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε
Coloured solutions								
MeNO ₂	373	9.8	460	3.5	373	17.3	460	10.5
EtNO ₂	370	14.4	460	4.2	370	20.7	460	10.7
Me·CO ₂ H	248	1120	460	3.4	248	2820	460	11.6
MeCN	222	3390	460	3.4	221	8760	460	9.8
Ac ₂ O	—	—	460	2—9*	—	—	450	8.5
AcOEt (0.023% H ₂ O) ...	252	—	460	4.1	—	—	—	—
Colourless solutions								
CCl ₄	258	250	—	—	258	420	460	12.8
CH ₂ Cl ₂	No max. above 230				No lower max.			
AcOEt (anhyd.)	252	317	—	—	252	962	460	9.7

* Beer's law not obeyed; ε = 9.3 at 0.015M, ε = 2.0 at 0.22M.

Nitrosyl chloride solutions are characterised by an absorption band at 460 mμ to which they owe their yellow colour. The fact that coloured nitryl chloride solutions also show a maximum at this wavelength and that the extinction coefficient is approximately one third that of pure nitrosyl chloride is consistent with the hydrolysis (1).

The absorption band at *ca.* 370 mμ of solutions in nitromethane and nitroethane is characteristic of the solvent rather than the solute; it appeared with solutes as diverse as chlorine, dinitrogen tetroxide, and ethylamine, but since it was not found with solutions of acids such as nitric, sulphuric, hydrochloric, and acetic it is probably associated with an anionic form of the nitro-alkane, although the nitromethane ion CH₂NO₂⁻ absorbs at 234 mμ in aqueous solution.¹²

The water content of solvents. In acetonitrile, nitromethane, and nitroethane Beer's law was obeyed where the concentration was 0.05M or below. Above this, the extinction coefficient for the maximum at 460 mμ decreased, suggesting that there was then insufficient water present for complete reaction; when water was added to 0.195M-nitryl chloride in acetonitrile, the extinction coefficient rose from 1.5 to 3.1. It is to be expected that these solvents should contain just sufficient water to hydrolyse 0.05M-nitryl chloride, *i.e.*, they should be M/60 in water (0.03% w/v). Table 3 shows that some batches of solvent used contained less than this. Presumably additional water was collected from the atmosphere when the solution was made.

TABLE 3. *Water content of solvents (% H₂O w/v).*

Coloured nitryl chloride solutions		Colourless nitryl chloride solutions	
Acetic acid	0.049, 0.048	Benzene	0.018
(boron acetate dried) ...	0.023, 0.051	Benzene (sodium dried)	0.0022
Acetonitrile	0.025	Carbon tetrachloride	0.0057
Ethyl acetate	0.023, 0.036	Ethyl acetate	0.0088
Nitroethane	0.014, 0.076	Methylene dichloride	0.012
Nitromethane	0.013, 0.091		
	0.021, 0.101		

Rate of coloration of nitryl chloride solutions. Since the solvents forming colourless solutions were not perfectly dry, hydrolysis of nitryl chloride cannot be solely dependent on the water content. Nitryl chloride is apparently not so readily hydrolysed in the less polar solvents. The rate of appearance of colour in an initially colourless solution in nitromethane is autocatalytic (see Fig. 2; note that the absorptions at 373 and 460 mμ

¹² Kortum, *Z. phys. Chem.*, 1939, **43**, B, 271.

increased simultaneously). The induction period varied with the conditions; rise in temperature or addition of polar substances such as quaternary ammonium salts and nitric acid shortened it. Solutions in acetonitrile showed a similar induction period of a few minutes, but in acetic acid the colour appeared immediately. With ethyl acetate the induction period was often very long (1—3 hr.).

FIG. 1. Ultraviolet spectra in nitromethane of A, 0.028M-NOCl; B, 0.026M-Cl₂; and C, 0.030M-NO₂Cl.

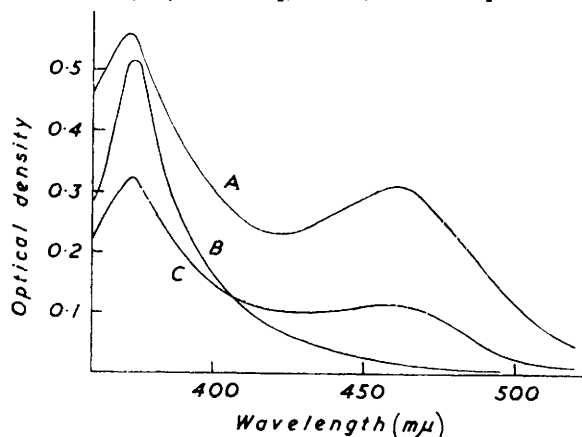
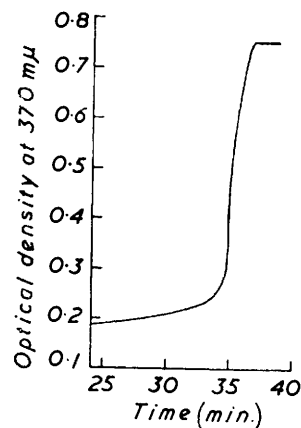


FIG. 2. Rate of development of colour in nitryl chloride solutions in nitromethane.



Infrared absorption spectra. The infrared absorption spectrum of the vapour above a concentrated solution of nitryl chloride in nitromethane (Table 4) shows that the vapour contained, as expected, bands due to nitryl chloride, nitrosyl chloride, and nitromethane.

TABLE 4. Infrared absorption frequencies (cm.⁻¹) of the vapour above various systems; comparison with earlier work (medium resolution).

NO ₂ Cl *	NO ₂ Cl in MeNO ₂ *	NOCl in MeNO ₂ *	Pure MeNO ₂ *	NO ₂ Cl *	NOCl ^b	Comments
—	1795 s	1795 s	—	—	1800 vs	Presence of NOCl
1680 m	1700 m	—	—	1685 vs	—	Presence of NO ₂ Cl
—	1610 vs	1610 vs	1610 vs	—	—	
—	1390 s	1390 s	1390 s	—	—	
1321 s	1300 m	—	—	1318 vs	—	Presence of NO ₂ Cl
1287 s		—	—	1293 vs		
—	930 s	930 s	930 s	—	921 s	
—	910 s	910 s	914 s	—	—	
—	900 s	900 s	905 s	—	—	
800	794 vs	780 m	790 w	794 vs	—	Presence of NO ₂ Cl
790 vs						
780						

* These measurements were made in the Chemical Engineering Department of Imperial College, London, S.W.7.

^a Ryason and Wilson, *J. Chem. Phys.*, 1954, **22**, 2000; ^b Wise and Elmer, *ibid.*, 1950, **18**, 1411.

Vacuum distillation of nitryl chloride solutions. The hydrolysis of nitryl chloride in the yellow solutions was confirmed by the vacuum distillation at room temperature of solutions of nitryl chloride in various solvents. The distillate was initially condensed out in a trap (3) cooled to -80°, and the volatile components were then distilled off and separated into a more volatile early fraction (1) and a second later fraction (2), both of which were condensed -180°. All fractions were finally hydrolysed and analysed for total acid, Cl⁻, OCl⁻, and NO₂⁻. Examples of the results are given in Tables 5 and 6.

Nitryl chloride distils almost unchanged from colourless solutions (Table 5), the hydrolysed distillates containing approximately equivalent amounts of nitric and hydrochloric

acids. The small amounts of nitrous acid found were attributed to slight decomposition of the nitryl chloride. The results thus support the view that colourless solutions contain pure nitryl chloride.

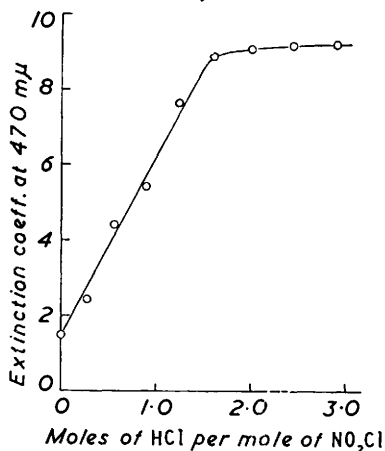
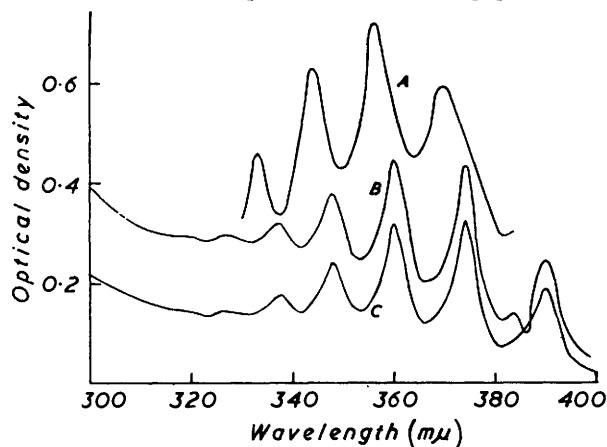
TABLE 5. *Distillation of a colourless solution.*

Solvent, C ₆ H ₆ ; initial concn., NO ₂ Cl = 0.049M (total 2.96 mmoles); 91% of Cl ⁻ distilled.				
Products (mmoles)	OCl ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻
Pump trap, -180°	0	1.41	0.02	1.37
Receiver (1), -180°	0	0.53	0.01	0.54
Receiver (2), -180°	0	0.17	0.09	0.16
Receiver (3), -80°	0	0.30	0	0.39
Residual solution ...	0	0.29	0.06	0.43

TABLE 6. *Distillation of a coloured solution.*

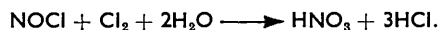
Solvent, Me·CO ₂ H; initial concn., NO ₂ Cl = 0.086M (total 4.30 mmoles); 86% of Cl and 44% of N distilled.			
OCl ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻
0.30	2.85	0	1.27
0	0.30	0.02	0.48
—	—	—	—
0	0.18	0	0.80
0	0.60	0.14	2.29

The results for the distillation of coloured solutions (Table 6) are more confused but show a few clear trends. First, small quantities of hypochlorite are generally found in

FIG. 3. *Effect of addition of hydrogen chloride to a solution of nitryl chloride in methylene dichloride.*FIG. 4. *Ultraviolet spectra in ether of A, 0.009M-Bu^oONO; B, 0.007M-NO₂Cl; and C, 0.0116M-N₂O₄.*

the hydrolyses of initial fractions or in the pump trap. Secondly, the concentration of chloride in the hydrolysed distillate is much greater, often by a factor of 2 or 3, than that of the nitrate.

These results are those expected for the distillation of a solution containing nitrosyl chloride and chlorine if, under vacuum, the nitrosyl chloride and chlorine largely distilled together; the hydrolysis products would then be a mixture of 3 equiv. of chloride to 1 of nitrate:



Effect of Acids on Solutions of Nitryl Chloride in Nitromethane.—Sulphuric acid. The addition of sulphuric acid, like that of chlorosulphuric and perchloric acids, reduced the intensity of the yellow colour. When sulphuric acid was added to a concentrated solution of nitryl chloride in nitromethane, colourless crystals separated which redissolved on further addition of the acid. Analysis showed them to be nitrosonium hydrogen sulphate (NO⁺·HSO₄⁻).

Hydrochloric acid. Hydrochloric acid, unlike sulphuric acid, enhances the absorption of yellow solutions. The extinction coefficient of the absorption maximum at 460 mμ rose from 3.5 to 5.1. We are unable to explain this.

The Reaction of Nitryl Chloride with Hydrogen Chloride.—When hydrogen chloride was bubbled into liquid nitryl chloride at -40° there was exothermic formation of chlorine and nitrosyl chloride. The equation



was shown to be correct by observing the absorption spectrum of a solution of nitryl chloride in methylene dichloride to which increasing quantities of hydrogen chloride were added (Fig. 3).

The Reaction of Nitryl Chloride with Ether.—Although dilute solutions of nitryl chloride in ether were colourless, their ultraviolet absorption spectra differed markedly from those of colourless solutions in other solvents (Fig. 4). The series of maxima observed at 330—400 $\text{m}\mu$ were identical with the spectrum of dinitrogen tetroxide in ether¹³ and characteristic of a nitrite ester.¹⁴ There was no evidence of appreciable reaction between nitryl chloride and the solvent since the spectrum did not vary with time and equivalent quantities of nitric and hydrochloric acids were produced by hydrolysis. However, when concentrated nitryl chloride (2M) in ether was kept between 0° and $+5^{\circ}$ an exothermic reaction took place with reduction of nitryl chloride to nitrosyl chloride and formation of oxidation products of ether.

EXPERIMENTAL

Preparation and Purification of Materials.—Nitric acid was rendered anhydrous by vacuum distillation from sulphuric acid.¹⁵ *Fractional distillation of nitryl chloride.* Crude nitryl chloride was fractionally distilled in a column 75 cm. long packed with Fenske glass helices. A small amount of chlorine (b. p. -34°) generally distilled first, then nitryl chloride which was obtained as a pale yellow liquid, b. p. -14.3° . A small residue, containing mainly nitryl chloride and some dinitrogen tetroxide, was left. The b. p. of nitryl chloride was measured with a thermocouple junction enclosed in a glass capillary in the top of the column. The f. p. was measured with the apparatus shown in Fig. 5. The thermocouple leads were encased in a narrow glass tube filled for several inches with mercury to counter the conduction of heat down the leads. The usual cooling curve was plotted.

Analysis of Nitryl Chloride.—An ampoule containing a known weight of nitryl chloride was smashed under carbon tetrachloride which was covered by a layer of 6N-potassium hydroxide. After being shaken, the aqueous layer was separated and added to the washings of the organic layer. Portions of this solution were analysed for hypochlorite by electrometric titration with arsenite and for nitrogen by Devarda's method. The total chloride was determined gravimetrically as silver chloride after acidification, which allowed the nitrite to reduce the hypochlorite to chloride; independent experiments showed that nitrite and hypochlorite interact rapidly in acid or neutral solution but are stable in solutions $\geq 0.1\text{N}$ in alkali.

Nitromethane.—Prepared from sodium nitrite and sodium chloroacetate,¹⁶ it was dried (CaCl_2) and last traces of water were removed by fractionation since water forms a lower-boiling azeotrope with nitromethane. Since Karl Fischer titration showed the solvent to be still slightly moist, drying with phosphoric oxide was tried but as the water content was only slightly reduced and much nitromethane was lost this treatment was generally omitted.

Some samples of the purified solvent gave solutions of nitryl chloride showing abnormal absorption spectra, apparently owing to an impurity probably produced by thermal decomposition of the nitromethane during fractionation. Careful refractionation under reduced pressure at 60° failed to remove it, but it was eventually removed by shaking with activated alumina for 10 min., decanting, and rapidly distilling. The infrared spectrum of the impure nitromethane was compared with that of the pure material, but no difference could be detected presumably because the concentration of the impurity was too small. We thank Dr. V. S. Griffiths (Battersea Polytechnic) for assistance with these infrared measurements.

Nitroethane.—Purified as for nitromethane, it contained a similarly troublesome impurity which affected the absorption spectra of nitryl chloride solutions; this was removed with alumina.

¹³ Ungnade and Smiley, *J. Org. Chem.*, 1956, **21**, 993.

¹⁴ Haszeldine, *J.*, 1953, 2525.

¹⁵ Hughes, Ingold, and Reed, *J.*, 1950, 2438.

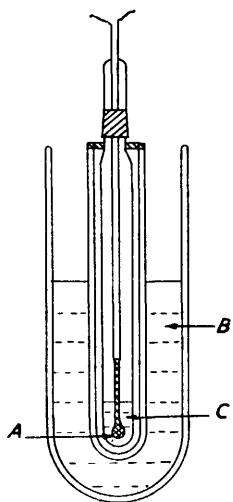
¹⁶ *Org. Synth.*, 2nd edn., Vol. I, p. 401.

Other organic solvents were purified by standard methods.

Rate of Decomposition of Nitril Chloride.—The apparatus is shown in Fig. 6. Nitril chloride was allowed to distil through phosphoric oxide into the glass reaction vessel *F*. When the pressure reached 600 mm., tap T_1 was closed, the nitril chloride in *F* frozen in liquid air, and the flask sealed off at *S*. The flask and spoon gauge were immersed in a thermostat at 25°. The glass spoon gauge was used as a null-point instrument, the tube *P* being connected to a system, similar to that employed by Kabesh and Nyholm,¹⁷ for varying the pressure at *P* until it equalled that in the flask *F*. The absolute pressure was then read from a mercury manometer. The spoon gauge was sensitive to less than 1 mm. difference in pressure.

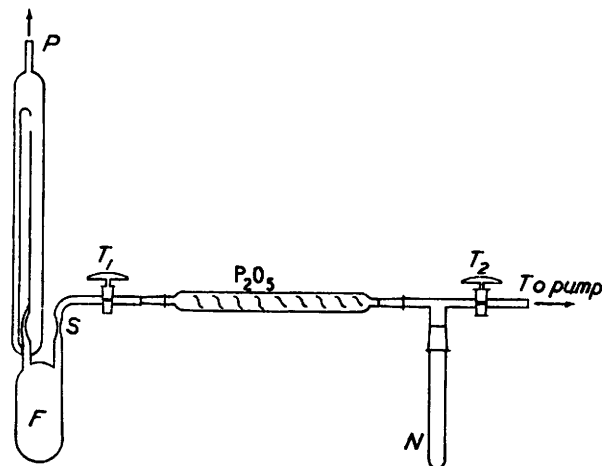
The part of the apparatus in contact with the nitril chloride was entirely of glass except that the ground-glass joints and tap were sealed with chlorofluorocarbon grease.

FIG. 5.



A, Mercury-thermocouple junction; *B*, liquid air; *C*, liquid nitril chloride.

FIG. 6.



When the rate of decomposition of moist nitril chloride was determined the reaction flask *F* was filled initially with water vapour at 5 mm. pressure by means of an ancillary connection which was then sealed off.

Ultraviolet Spectroscopy.—The absorption spectra of solutions were determined by the Unicam S.P.500 Spectrophotometer. Stopped silica cells, of 10 mm. optical path-length, were used.

Solutions of nitril chloride were generally prepared by the rapid transfer of liquid nitril chloride from the storage tubes to the solvent with a pipette, although some were made by distillation of nitril chloride through phosphoric oxide directly into the solvent. The concentration of these solutions was determined by hydrolysing a sample and determining the chloride by Mohr's method, except for solutions in acetic acid and acetonitrile when Volhard's method was used.

Analysis of the Products of the Vacuum Distillation of Solutions of Nitril Chloride.—Nitrite was determined by the standard method by use of either chloramine-T or ceric sulphate, and hypochlorite by titration with thiosulphate, and chloride as above. Nitrate was estimated by difference by titrating the total acid with alkali or, when acetic acid was the solvent, by reduction of the total nitrogen to ammonia. In the acid-alkali titration either methyl-red or bromocresol-green was used as the indicator, although when nitroethane was the solvent the end-point was determined potentiometrically.

Reaction between Sulphuric Acid and Nitril Chloride in Nitromethane.—Sulphuric acid was

¹⁷ Kabesh and Nyholm, *J.*, 1951, 3249.

added dropwise to 100 ml. of 0.5M-nitryl chloride in nitromethane until no more solid was deposited. The solid was filtered off on a sintered glass plate, washed twice with small portions of nitromethane, and dried *in vacuo* [Found: equiv., 43.2; NO⁺ (chloramine-T), 18.7%. Calc. for NO·HSO₄: equiv., 42.3; NO⁺, 23.6%]. Some nitrous acid was probably lost in the hydrolysis.

Reaction of Nitryl Chloride with Hydrogen Chloride.—The volatile products of the reaction were distilled off at room temperature and condensed in a trap at -80° . The residue was a pale yellow liquid which analysis showed to be an aqueous solution of nitric and hydrochloric acids containing a trace of nitrous acid. The volatile product was fractionally distilled and separated into (a) a yellow liquid, b. p. -30° (cf. Cl₂, b. p. -33°); a weighed portion was dissolved in carbon tetrachloride and the solution mixed with aqueous iodide and titrated with thiosulphate (Found: Cl₂, 98.3%), and (b) a cherry-red liquid, b. p. -5° (cf. NOCl, b. p. -6°); a weighed portion was hydrolysed and total acid and chloride determined (Found: equivalent, 35.3; Cl, 50%. Calc. for NOCl: equiv., 32.7; Cl, 54%).

Reaction of Nitryl Chloride with Ether.—The cherry-red mixture was fractionally distilled. Ether containing almost pure nitrosyl chloride (in over 50% yield) distilled first leaving a residue which distilled in the range $70-160^{\circ}$. Chemical tests and the b. p. indicated that ethyl alcohol, ethyl acetate, acetic acid, formic acid, and probably chloroacetic acid were present.

The authors thank the Governors of Chelsea Polytechnic for a research assistantship (to M. J. C.).

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[Received, April 25th, 1957.]
