NITROSYL CHLORIDE

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I. INTRODUCTION

Nitrosyl chloride, although accurately identified only during the first half of the nineteenth century, has been in the hands of alchemists and chemists for many centuries as one of the components of aqua regia. Interest in the compound has been sustained throughout the last hundred and twenty-five years. It reacts with most of the elements and with an extremely wide range of compounds. Despite this versatility, no large market for the substance has yet been developed. Nitrosyl chloride is now available in the United States in cylinders (12); it has also been reported as commercially available in England (1).

Several comparatively brief reviews of the literature on nitrosyl chloride in addition to that of Lynn and Shoemaker (325) have appeared. Those in Gmelin's *Handbuch* (186) and Mellor's *Treatise* (338) are especially good. The present review of the preparation, properties, and uses of nitrosyl chloride covers the literature through 1949 and some articles that appeared in 1950. Many of the references were located in original articles and were not found under headings pertinent to nitrosyl chloride in abstracting journals. Thus it is probable that the early and intermediate literature is covered more thoroughly than the very recent. The indexes of *Chemical Abstracts* have been used as a guide for nomenclature. The terminology of Lewis and Randall has been employed for thermodynamic quantities.

II. PREPARATION OF NITROSYL CHLORIDE

A. FROM HYDROCHLORIC AND NITRIC ACIDS

A concentrated aqueous mixture of hydrochloric and nitric acids evolves nitrosyl chloride and chlorine:

$$HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O$$

Such a system has long been given the name "aqua regia," because of its ability to dissolve gold. Geber, an Arabian chemist, mentioned aqua regia in the eighth century. The earliest observations on nitrosyl chloride, by Davy (125, 126), Baudrimont (34, 35), Koene (284, 285), Gay-Lussac (172, 173, 174), and Weltzien (559), were made with impure nitrosyl chloride that had been evolved from aqua regia. Later work (187, 188 189, 352, 476) by others indicated that Gay-Lussac's material was a mixture of nitrosyl chloride and chlorine. Nitrosyl chloride is more soluble in the aqueous liquid phase of aqua regia than is chlorine; hence the gas given off initially is relatively rich in chlorine (318). If aqua regia is heated, however, the moles of nitrosyl chloride evolved will approach the moles of chlorine evolved.

In sealed glass tubes at 0° and 21°C. aqua regia is a three-phase (two liquids; one gas) system (90). The lower liquid phase is largely nitrosyl chloride and chlorine; the upper is rich in water. At atmospheric temperature and pressure the lower layer is not formed, since the nitrosyl chloride and chlorine are evolved. Vapor pressures over various mixtures of water, hydrochloric acid, and nitric acid have been measured (89).

When concentrated hydrochloric and nitric acids are mixed and sealed in a glass tube, two liquid phases form quickly at 100°C., but at room temperature a period of about 10 hr. is required. In the latter case the electrical conductivity of the upper (aqueous) liquid phase becomes constant in about 20 hr. (91). Approach to equilibrium is thus rather slow at room temperature. If pure liquid nitric acid and gaseous hydrogen chloride are used, the following reaction has been calculated (91) to be exothermic:

$$HNO_3 + 3HCl \rightarrow NOCl(g) + Cl_2(g) + 2H_2O(l)$$

If concentrated aqueous nitric and hydrochloric acids are used, however, the reaction is endothermic.

If manganese dioxide is present (319) in a mixture of hydrochloric and nitric acids, very little nitrosyl chloride is evolved and the reaction is largely:

$$MnO_2 + 2HCl + 2HNO_3 \rightarrow Mn(NO_3)_2 + Cl_2 + 2H_2O$$

The manganous nitrate decomposes to manganese dioxide and nitrogen dioxide upon heating. Both can be recycled to the system after conversion of the nitrogen dioxide to nitric acid by absorption in water and oxidation.

Various processes have been proposed for the commercial preparation of chlorine from hydrochloric and nitric acids (122, 467, 521, 547, 548, 549). Separation of nitrosyl chloride from chlorine is a major problem in such processes. It has been proposed to separate and re-use the nitrosyl chloride, for example, by passing the mixture through sulfuric acid. The chlorine passes through unchanged, accompanied by hydrogen chloride formed from the reaction of nitrosyl chloride with sulfuric acid. The sulfuric acid is gradually converted to nitrosylsulfuric acid and must eventually be decomposed with water. This evolves oxides of nitrogen and re-forms sulfuric acid. Another method of separating nitrosyl chloride and chlorine involves passing the mixed gases into hot nitric acid. This oxidizes the nitrosyl chloride to chlorine and nitrogen dioxide. The gaseous chlorine may be freed of nitrogen dioxide by fractional distillation.

B. FROM METAL CHLORIDES AND NITRIC ACID OR NITROGEN TETROXIDE

When nitric acid is mixed with solid sodium chloride, there are formed sodium nitrate, chlorine, and nitrosyl chloride. Some of the earliest preparations of nitrosyl chloride used this method (125, 126, 133, 317). The reactions that occur may be summarized as follows:

$$3NaCl + 4HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2H_2O$$

The system is similar to aqua regia.

In contrast to the electrolytic process for chlorine, the reaction of sodium chloride with nitric acid produces chlorine without the concomitant production of caustic (231); instead, the production of chlorine accompanies that of sodium nitrate, a widely used fertilizer.[2]

The economic importance of the reaction between metal chlorides and nitric acid is evinced by the large number of patents covering various aspects of the process. One of the problems of the process is separation of the mixture of chlorine and nitrosyl chloride that is formed. It has been proposed to do this by any of several methods involving distillation (48, 60, 102, 514) or reaction of the nitrosyl chloride with sulfuric acid (144), with nitric acid (36, 49, 138, 420, 421, 494) or by air oxidation of the nitrosyl chloride to chlorine and nitrogen dioxide or nitric acid (48, 65, 66, 244, 248, 251, 256, 258, 374, 514).

Some patents (196, 197, 218, 219, 380) disclose methods of minimizing the amount of nitrosyl chloride. By operating at pressures below atmospheric with dilute nitric acid and passing steam or other hot gases through the reaction mixture, hydrogen chloride is evolved as formed and the reaction becomes:

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$$

The formation of nitrosyl chloride has been avoided in the reaction between potassium chloride and nitric acid through the use of low temperatures and low

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[2] At Hopewell, Virginia, the Solvay Process Division of the Allied Chemical and Dye Corporation operates a commercial plant making chlorine and sodium nitrate from sodium chloride and nitric acid (11, 12, 14, 147, 209, 234). Part of the nitrosyl chloride formed in the process is distributed to users outside the company, part is consumed at Hopewell in manufacturing Nytron, a surface-active agent, and part is returned to the chlorine–sodium nitrate process. The Hopewell plant is a potential source of nitrosyl chloride in tank-car quantities, should large-scale need for the product be developed outside the company.

concentrations of nitric acid (341). Related to these methods are procedures (374, 381) for evolving nitrosyl chloride and then reacting it with water and chlorine or water and oxygen and returning the nitric acid so formed to the sodium chloride reactor.

It has been proposed that the reaction between sodium chloride and nitric acid be carried out in several stages (51, 58, 421). Method of heat input (63), reactor construction (265), and various other details of the process (5, 36, 47, 49, 140, 220, 443) have been discussed in other references.

In an early variation (144) chlorine was made by mixing sulfuric acid, sodium chloride, and sodium nitrate.

Chlorides other than sodium chloride have been used in the preparation of nitrosyl chloride and nitrogen tetroxide has often been used in place of nitric acid. Calcium chloride (125, 126), ammonium chloride (74), arsenic trichloride (179, 360), aluminum chloride (360), boron trichloride (377), stannic chloride (377, 470, 471, 472), and titanous chloride (377) have all given nitrosyl chloride when treated with nitric acid or nitrogen tetroxide.

If gaseous nitrogen tetroxide is passed over solid moist potassium chloride at room temperature, potassium nitrate and nitrosyl chloride are formed (578). Free-energy and enthalpy changes for the following reactions have been calculated (579):

$$KCl(s) + N_2O_4(g) \rightarrow KNO_3(s) + NOCl(g) \qquad \begin{aligned} \Delta F_{298.1} &= -4496 \text{ cal.} \\ \Delta H_{291.1} &= -3683 \text{ cal.} \end{aligned}$$

$$KCl(s) + 2NO_2(g) \rightarrow KNO_3(s) + NOCl(g) \qquad \begin{aligned} \Delta F_{298.1} &= -5{,}623 \text{ cal.} \\ \Delta H_{291.1} &= -16{,}691 \text{ cal.} \end{aligned}$$

Dry, or slightly moist, potassium chloride and dry, or slightly moist, sodium nitrate have been converted to potassium nitrate and sodium chloride (260) by treating the potassium chloride at 30–80°C. with nitrogen tetroxide, and passing the nitrosyl chloride thus formed over sodium nitrate at 200–300°C. Calcium nitrate may be used (247, 257) in place of sodium nitrate. Mixtures of nitrogen dioxide, oxygen, and nitrogen from the oxidation of ammonia have been passed through beds of moistened potassium chloride. Complete conversion of an 8 per cent nitrogen dioxide gas has been obtained by stepwise counter-current reaction with potassium chloride with oxidation chambers between beds (403).

A potassium chloride solution saturated at 20°C. has been passed down a tower packed with rings counter to a flow of air containing 6 volume per cent nitrogen tetroxide. A potassium nitrate solution came out at the bottom and nitrosyl chloride and air at the top (464).

Potassium chloride and aluminum nitrate or ferric nitrate have been reacted in hot aqueous solution and then cooled, whereupon potassium nitrate separated (208). Evaporation of the mother liquor evolved a mixture of gases containing nitrosyl chloride.

Proposed industrial processes for making potassium nitrate in which nitrosyl chloride is an intermediate or a coproduct have been described (136, 335).

C. FROM NITRIC OXIDE AND CHLORINE

Nitrosyl chloride can be readily prepared by the direct combination of nitric oxide and chlorine:

$$2NO + Cl_2 \rightarrow 2NOCl$$

This was one of the early methods employed and has been called the method of Gay-Lussac (174, 175). The gas-phase reaction is of the third order (558). A discussion of the kinetics of this reaction is included in the discussion of the equilibrium between nitric oxide, chlorine, and nitrosyl chloride in Section V of this paper.

In one suitable technique for utilizing the reaction of nitric oxide and chlorine for the preparation of nitrosyl chloride (85, 336, 465, 505, 587), liquid chlorine is treated with excess nitric oxide and the excess nitric oxide removed by repeated freezing and evacuating. The reaction is rapid (85, 363, 506), and the product is of good quality. Operation above atmospheric pressure has been proposed (150).

Another technique is to take advantage of the fact that the reaction between gaseous nitric oxide and chlorine can be catalyzed by materials such as activated charcoal or alumina, which provide a large surface area. Such procedures have been described (101, 159, 160, 495) and used by numerous workers (92, 369, 563). In this method purified gaseous nitric oxide and chlorine are passed through the moderately heated catalyst bed (e.g., 40–50°C.) in about a 2:1 volume ratio, and the product is condensed and fractionated to remove any unreacted chlorine. The present authors have used this method extensively, with activated alumina as the catalyst, and have found it to be quite satisfactory.

Measuring the amount of nitric oxide combining with a given weight of elemental chlorine was an early method of determining the atomic weight of chlorine (343, 585).

D. FROM NITRITES

1. Alkyl nitrites

The reaction of alkyl nitrites with hydrogen chloride forms nitrosyl chloride. Extensive use has been made of this reaction for generating nitrosyl chloride *in situ* in preparations of terpene nitrosochlorides (163, 475, 526, 529, 530, 545). Ethyl nitrite and amyl nitrite have been used most frequently. Hydrogen chloride is added as a concentrated aqueous solution (529), or as a solution in ethanol (163), or in a mixture of methanol and water (475), or in a mixture of acetic acid and water (526). The reaction of terpenes with alkyl nitrites and hydrogen chloride has generally been conducted at low temperatures: for example, at −20°C. to −15°C. Olefins other than terpenes have also been converted to nitrosochlorides by mixing with excess amyl nitrite, cooling to −15°C., and slowly adding hydrochloric acid (512). Nitrosyl chloride formed *in situ* from alkyl nitrites and hydrogen chloride has also been used to convert dimethylaniline to nitrosodimethylaniline (28), to convert ketones to nitroso- or isonitrosoketones

(29, 105), and to convert aryl mercury derivatives to nitrosoaryl compounds (445).

Alkyl nitrites react at 20–35°C. with silicon tetrachloride to form nitrosyl chloride and orthosilicate esters (213). Orthosilicate ester yields of 80–90 per cent of theory have been obtained.

Thionyl chloride and alkyl nitrites form nitrosyl chloride and dialkyl sulfites (213).

Arsenic trichloride and ethylene nitrite form nitrosyl chloride by the reaction (213):

$$ONOCH_2CH_2ONO + 2AsCl_3 \rightarrow Cl_2AsOCH_2CH_2OAsCl_2 + 2NOCl$$

Acyl chlorides react with alkyl nitrites, e.g., acetyl chloride with isoamyl nitrite, to form nitrosyl chloride and esters (169, 205, 276, 277, 550).

2. Inorganic nitrites

Heating dry mixtures of aluminum chloride and sodium nitrite forms nitrosyl chloride (359). The following equation would explain the formation of nitrosyl chloride:

$$2AlCl_3 + 3NaNO_2 \rightarrow 3NaCl + Al_2O_3 + 3NOCl$$

Olefin nitrosochlorides have also been made by dissolving an olefin in concentrated alcoholic hydrogen chloride and adding dropwise a concentrated aqueous sodium nitrite solution (468). Nitrosyl chloride probably is an intermediate in the reaction.

A mixture of sulfuric acid, a metal chloride, and a metal nitrite has been used for nitrosating ketones (201) and certain terpenes (314). Here, also, nitrosyl chloride is probably a transient intermediate.

Excess sulfuryl chloride forms nitrosyl chloride from silver nitrite, but with excess silver nitrite no nitrosyl chloride results (33).

Nitrosyl chloride has been formed from phosphoryl chloride and sodium nitrite (444) and from phosphorus pentachloride and sodium nitrite (359) or potassium nitrite (328, 329).

Acetic anhydride and nitrosyl chloride have been detected (16) in the reaction products from potassium nitrite and acetyl chloride. The following reactions may occur:

$$KNO_2 + CH_3COCl \rightarrow NOCl + CH_3COOK$$
$$CH_3COOK + CH_3COCl \rightarrow KCl + (CH_3CO)_2O$$

E. MISCELLANEOUS METHODS

When liquid nitric oxide and hydrogen chloride are mixed, sealed in a tube, and warmed to room temperature, two liquid phases are formed (93, 94, 95, 96). One is rich in water and the other is rich in nitrosyl chloride. It has been proposed that the following reactions occur in sequence:

$$6NO \rightarrow 2N_2O_3 + N_2$$
$$N_2O_3 + 2HCl \rightarrow H_2O + 2NOCl$$

Nitrosyl chloride has been obtained from nitric oxide and hydrogen chloride in the presence of one or more of the following oxidizing agents: oxygen, nitric acid, nitrogen dioxide, nitrogen pentoxide (192).

At a temperature causing sublimation of ferric chloride, nitric oxide reacts with it to form nitrosyl chloride and ferrous chloride (469, 472).

At −150°C. the reaction of nitrogen trichloride and nitric oxide proceeds approximately as follows (361, 362, 363):

$$2NCl_3 + 6NO \rightarrow 4NOCl + 2N_2O + Cl_2$$

At −80°C. the reaction is:

$$NCl_3 + 2NO \rightarrow NOCl + N_2O + Cl_2$$

At −20°C. still less nitrosyl chloride and more chlorine can be isolated. An explanation of the decreasing nitrosyl chloride yield with increasing temperature is that at higher temperatures nitrosyl chloride reacts with nitrogen trichloride, giving nitrous oxide and chlorine.

Nitrosyl chloride has been made from hydrogen chloride and liquid nitrogen trioxide (92).

Preparation of nitrosochlorides by passing a mixture of hydrogen chloride and nitrogen trioxide into a cold solution of limonene or pinene probably involved nitrosyl chloride as an intermediate (423).

Crude nitrosyl chloride has been prepared from nitrous acid and either potassium chlorochromate (202) or phosphorus pentachloride (390).

Olefin nitrosochlorides have been made (512) by mixing olefins with excess thionyl chloride, cooling to −5°C., and adding nitrogen trioxide or nitric acid. Nitrosyl chloride is probably an intermediate, formed by the following reactions:

$$SOCl_2 + N_2O_3 \rightarrow 2NOCl + SO_2$$
$$SOCl_2 + HNO_3 + H_2O \rightarrow NOCl + HCl + H_2SO_4$$

Formation of nitrosyl chloride from nitrosyl bromide and chlorine in the temperature range of 0° to 100°C. is said to be a rapid third-order reaction, not influenced by light or the presence of carbon dioxide (271). It is catalyzed by water.

Tilden (476, 477) made nitrosyl chloride by mixing nitrosylsulfuric acid with dry sodium chloride. A patented process (121) used the reaction as one step in the formation of chlorine and sodium sulfate from sodium chloride, sulfuric acid, and air. Potassium chloride (92) or hydrogen chloride (109, 123, 124, 435) and nitrosylsulfuric acid also form nitrosyl chloride. *Inorganic Syntheses* gives complete directions (109) for the preparation of nitrosyl chloride from hydrogen chloride and nitrosylsulfuric acid. Nitrosyl chloride evolved from the reaction of a chloride with nitrosylsulfuric acid is impure, hydrogen chloride (184, 435) and nitrogen tetroxide (355) being among the contaminants. After purification, however, nitrosyl chloride made by this method has been used for measurement of its molecular weight (584), for determination of the atomic weights of the constituent elements (198, 435), for the determination of various physical constants of nitrosyl chloride (92), and for measurement of its absorption spectrum (275). The nitrosyl chloride used for the measurement of the absorption spectrum may have contained some nitrogen tetroxide (355).

Nitrosyl chloride may also be derived from nitrosylsulfuric acid by treatment with benzoyl chloride (148), acetyl chloride (148), or phosphorus pentachloride (340).

Gaseous hydrogen chloride reacts with *N*-nitrosodiethylamine, forming nitrosyl chloride and diethylamine hydrochloride (178). At low temperatures, the hydrochlorides of *N*-nitrosodimethylamine or *N*-nitrosodiethylamine can be isolated (295). The hydrochlorides decompose to yield nitrosyl chloride and the dialkylamine at about 60°C. In the case of *N*-nitrosodiphenylamine, no hydrochloride can be isolated, even at 0°C., the reaction proceeding directly to diphenylamine and nitrosyl chloride. Nitrosyl chloride has been formed from hydrogen chloride and other nitrosoamines (211, 400).

It has been reported that heating titanium tetrachloride with tetranitromethane often caused explosions. Occasionally the reaction proceeded smoothly (404) according to the equation:

$$8TiCl_4 + 5C(NO_2)_4 \rightarrow 4TiCl_4 \cdot (NOCl)_2 + 6N_2O_3 + 4TiCl_2CO_3 + CO_2$$

Nitrosyl chloride possibly was formed as a transient intermediate in this reaction.

Chloropicrin decomposes to nitrosyl chloride and phosgene in the presence of ultraviolet light (397).

Chlorine and nitrogen dioxide passed through a red-hot tube form some nitrosyl chloride and oxygen (580, 581). This is due to the dissociation of nitrogen dioxide to nitric oxide and oxygen at high temperatures. Upon cooling, the nitric oxide combines with chlorine to form nitrosyl chloride.

Recent absorption spectra measurements (372) have indicated that chlorine and nitrogen tetroxide in the gas phase at room temperature gradually form nitrogen pentoxide, nitrosyl chloride, and nitryl chloride, NO_2Cl.

When nitrogen tetroxide and chlorine are mixed with water the following equilibrium is established (52, 54, 64):

$$3N_2O_4 + Cl_2 + 2H_2O \rightleftharpoons 4HNO_3 + 2NOCl$$

Mixtures of nitrosyl chloride and nitryl chloride have been obtained from nitrogen tetroxide and hydrogen chloride (352, 365).

If nitrogen dioxide and ammonium chloride are heated in sealed tubes to 100°C., the following reactions are said (74) to occur:

$$\begin{aligned}8NO_2 + 6NH_4Cl &\rightarrow 4N_2O + 3N_2 + 3Cl_2 + 12H_2O\\10NO_2 + 8NH_4Cl &\rightarrow 4NOCl + 7N_2 + 2Cl_2 + 16H_2O\\4NO_2 + H_2O &\rightarrow N_2O_3 + 2HNO_3\end{aligned}$$

Diethylammonium chloride in liquid nitrogen tetroxide is converted to nitrosyl chloride and diethylammonium nitrate (2, 3).

Nitrogen trichloride and nitrogen tetroxide at 0° to −35°C. in chloroform give a mixture of products containing a little nitrosyl chloride (364).

Sulfuryl chloride heated in a sealed tube to 180°C. with nitrogen dioxide forms principally nitrosyl chloride and $N_2S_2O_9$, an anhydride of nitrosylsulfuric acid (33). Nitrosyl chloride and presumably this same anhydride result when pyrosulfuryl chloride and nitrogen tetroxide are mixed at room temperature (235).

Nitrosyl chloride has been reported formed from each of the following combinations involving chlorides of phosphorus: nitrogen tetroxide and phosphorus trichloride (181, 360); nitrogen tetroxide and phosphorus pentachloride (180, 195, 425); potassium nitrate and phosphorus pentachloride (354); nitric acid and phosphoryl chloride (581).

Crude nitrosyl chloride was probably obtained in early work on mixtures of phosphoryl chloride and silver nitrate (370), of chlorine and silver nitrate (371), of phosphoryl chloride and lead nitrate (337), and of potassium nitrate and chlorosulfonic acid (337).

Organic acid chlorides react with potassium nitrate to form organic acid anhydrides, nitrosyl chloride, and chlorine (131), e.g.:

$$4CH_3COCl + KNO_3 \rightarrow 2(CH_3CO)_2O + KCl + NOCl + Cl_2$$

A similar reaction occurs when acetyl nitrate is used in place of potassium nitrate:

$$3CH_3COCl + CH_3COONO_2 \rightarrow 2(CH_3CO)_2O + NOCl + Cl_2$$

III. PHYSICAL PROPERTIES

According to the National Bureau of Standards (357b), the triple point for solid, liquid, and gaseous nitrosyl chloride is at 38.6 mm. pressure and −61.5°C. This is in agreement with, and probably is based on, the work of Trautz and Gerwig (505), who claimed a maximum error of ±0.3°C. Various other workers have measured the melting point (85, 160, 206, 579), but for one reason or another the values appear to be less reliable. Such values vary from −60° to −65°C.

The most reliable measurements of the vapor pressure of nitrosyl chloride over a broad temperature range appear to be those of Partington and Whynes (378). Earlier measurements by Trautz and Gerwig (505) are in quite close agreement therewith. Other published work (92, 170) differs considerably and is considered less reliable. Unpublished data from this laboratory lend further support to this view. Partington and Whynes have proposed the equation

$$\log_{10} P(\text{mm. Hg}) = \frac{-1320}{T} + 7.802$$

in the range from 203° to 258°K.

The best value for the normal boiling point appears to be −5.8°C., as reported by Trautz and Gerwig (505), and this value is cited by the National Bureau of Standards (357b). Various other values for the boiling point generally, but not exclusively, fall in the range from −5° to −8°C. (34, 35, 160, 170, 184, 224, 458, 476, 477).

The orthobaric density of liquid nitrosyl chloride in the range from 20.5° to 75°C. has been measured by McGonigle in this laboratory (333) (see table 1). Briner and Pylkoff (92) determined the density in the range from −45° to +40°C. (see table 1). The agreement in the common range is not good. While McGonigle's temperatures are accurate only to the nearest 0.5°C., it is probable that he had a purer sample of nitrosyl chloride than that used by Briner and Pylkoff. Earlier reported values (34, 35, 180) are less certain.

TABLE 1

Density of liquid nitrosyl chloride

DATA OF McGONIGLE (333)		DATA OF BRINER AND PYLKOFF (92)	
Temperature	Density	Temperature	Density
°C.	grams/cc.	°C.	grams/cc.
20.5	1.273	−45	1.550
21.0	1.272	−40	1.446
29.5	1.251	−35	1.434
30.0	1.250	−30	1.422
35.5	1.239	−25	1.400
38.0	1.230	−20	1.398
43.5	1.220	−15	1.384
48.0	1.209	−10	1.373
56.0	1.191	−5	1.360
60.0	1.181	0	1.349
66.5	1.164	5	1.337
73.0	1.147	10	1.325
		15	1.312
		20	1.300
		25	1.280
		30	1.276
		35	1.274
		40	1.221

Nitrosyl chloride vapor deviates significantly from a perfect gas, and this deviation has been measured by Beeson and Yost (72) in terms of the "second virial coefficient, B" in the equation:

$$V = RT/P + B$$

where V is the molar volume and B is in cubic centimeters per mole:

TEMPERATURE	B	TEMPERATURE	B
°C.	cc. per mole	°C.	cc. per mole
0	−389	75	−218
25	−307	100	−196
50	−253		

Wourtzel (77, 584, 586), during studies on atomic weights, estimated the weight of a liter of nitrosyl chloride vapor at 0°C. and 760 mm. of mercury as 2.9919 g.

based on determinations at 720 and 287 mm. of mercury. This corresponds to a B value of about -536 cc./mole, an appreciably greater correction than that indicated by Beeson and Yost. Based on Beeson and Yost's coefficients, the vapor densities at the cited temperatures and 1 atm. pressure are computed to be as follows:

TEMPERATURE	DENSITY	TEMPERATURE	DENSITY
°C.	*grams/liter*	°C.	*grams/liter*
0	2.972	75	2.309
25	2.710	100	2.152
50	2.492		

The above values are considered to be more reliable than direct determinations reported by early workers (34, 35, 160, 459, 461, 477) and are in fair agreement with some of them.

The critical temperature has been measured in this laboratory (333) as 167.5°C. ± 0.5°, in agreement with reported values of 167°C. ± 2° (92) and 163–164°C. (160).

The critical pressure has been estimated by McGonigle in this laboratoy as about 90 atm., based on extrapolation of vapor pressure data (333). Elsewhere it has been estimated as 92.4 atm., using the formula of Dutoit and Friderich (92), and as 83.8 atm. from viscosity data (504). Van Laar (294) lists the critical pressure as 82.2 atm.

The critical density has been estimated in this laboratory as 0.47 g./cc. (111) by application of the law of Cailletet and Mathias, using extrapolated liquid densities (92, 333) and extrapolated vapor densities based on Beeson and Yost's determination of deviations from the gas law (72).

The best available value for the heat of formation of nitrosyl chloride appears to be that based on the measurements of Beeson and Yost (72) for the equilibrium:

$$2NO + Cl_2 \rightleftharpoons 2NOCl$$

and the accurately known heat of formation of nitric oxide (357a). Computed in this way, ΔH^0_{298} for the reaction:

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}Cl_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NOCl(g)$$

is 12,570 cal./mole. This is in agreement with the value cited by the National Bureau of Standards (357d), which may be based thereon. Similar computations have been made from the equilibrium measurements on the reaction of nitric oxide and chlorine by investigators who studied this reaction prior to Beeson and Yost. These computations indicate a ΔH^0 of formation at 18°C. in the range from 12,300 cal./mole to 12,900 cal./mole (76). Jahn (230) has computed the ΔH^0 of formation at 25°C. as 12,970 cal./mole, based on electron diffraction data of Ketelaar and Palmer (269) and spectrographic data of Bailey and Cassie

(30). The authors have computed the ΔH^0 of formation at 18°C. to be 12.5 kcal. per mole from calorimetric data of Trautz and Wachenheim (511) on the reaction:

$$NOCl(g) + 2KOH(aq) \rightarrow KCl(aq) + KNO_2(aq) + H_2O(l)$$

Trautz and Wachenheim computed ΔH_{290} for the reaction,

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

to be −17,735 cal. This leads to a ΔH^0_{290} of formation for nitrosyl chloride of 12.7 kcal. Bichowsky and Rossini indicate that the data of Trautz and Wachenheim yield a value of 13.0 kcal. at 18°C. A corresponding value based on Briner and Pylkoff's (92) calorimetric measurements of the same reaction leads to a very low value of 7700 cal./mole. With the exception of this last citation all the data agree fairly well. For determination of ΔH at other temperatures, it is suggested that such computations be based on the temperature function proposed by Beeson and Yost (72) for the equilibrium of nitric oxide, chlorine, and nitrosyl chloride. The Bureau of Standards (357b) lists ΔH^0_0 as 13.25 kcal./mole.

The best value for the molar entropy, S^0_{298}, of nitrosyl chloride probably is that computed from equilibrium studies of Beeson and Yost (72) and cited by the National Bureau of Standards (357d) as 63.0 cal./degree mole. A third-law value is not available. Calculations from spectroscopic data have been made from Bailey and Cassie's infrared data (30) and Ketelaar and Palmer's (269) electron diffraction data by Jahn (230) and by Beeson and Yost (72). There is some uncertainty as to the interpretation of the spectra in terms of the molecular structure and of the electronic structure of nitrosyl chloride, and various values have been computed by Jahn and by Beeson and Yost depending on the assumptions made. Jahn finally proposed 64.04 cal./degree mole, while Beeson and Yost showed that by certain assumptions as to the fundamental frequencies, a value very close to the 63.0 secured from the equilibrium data could be secured. Wise and Elmer (582a) propose 62.466 cal./degree mole, based on their own spectrographic data. Other calculations from the older data on the equilibrium between nitric oxide, chlorine, and nitrosyl chloride will not be cited here except for recalculation of the value from Dixon's data which yields 62.3 cal./degree mole and to call attention to the error in Dixon's value of ΔS for the equilibrium as noted by Jahn (230).

The value recommended for the standard free energy of formation, ΔF^0_{298}, for gaseous nitrosyl chloride is 15,860 cal./mole, based on the equilibrium measurements of Beeson and Yost (72) for the equilibrium:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

in agreement with the citation of the National Bureau of Standards (357d). Lewis and Randall (313) have computed the free energy ΔF^0_{298} as 16,010 cal./mole, based on Trautz and Wachenheim's data for the same equilibrium. Jahn (230) has recalculated Dixon's (135) data on this equilibrium in view of an error in Dixon's paper. This leads to a ΔF^0_{298} of 15,790 cal./mole. On the basis of his own computations from spectrographic and electron diffraction data, Jahn (230) selected a value of ΔF^0_{298} of 15,960 cal./mole. Latimer (296) states, without citation of source but possibly with reference to Jahn's paper, that thermal and spectrographic data would appear to yield a value of 15,960 cal./mole. The free energy of formation ΔF^0_{298} for aqueous nitrosyl chloride has been determined to be 16,015 cal./mole on the basis of the reaction:

$$\mathrm{NOCl(aq)} + \mathrm{H_2O(l)} \rightarrow \mathrm{HNO_2(aq)} + \mathrm{HCl(aq)}$$

photometric means being used for measuring the concentration of nitrosyl chloride (428).

Beeson and Yost (72) calculated the heat capacity, C_p, of gaseous nitrosyl chloride from spectrographic data using frequencies of 633 cm.$^{-1}$, 923 cm.$^{-1}$, and 1832 cm.$^{-1}$ as the fundamental nondegenerate frequencies, but did not report the result as such, as they combined this with values for nitric oxide and chlorine to obtain ΔC_p for the reaction:

$$\mathrm{2NOCl(g)} \rightarrow \mathrm{2NO(g)} + \mathrm{Cl_2(g)}$$

as

$$\Delta C_p = 8.237 - 0.021416T + 14.525 \times 10^{-6}T^2 \pm 0.01 \text{ cal./degree mole}$$

This equation can be used in conjunction with the known C_p values of nitric oxide and chlorine to secure C_p for nitrosyl chloride. There is some question, however, as to accuracy of this approach, for it may be that the use of the three cited values as fundamental nondegenerate frequencies is incorrect (72). There is some evidence that the three frequencies should be 1832, 633, and 290 cm.$^{-1}$ or perhaps 1832, 462, and 317 cm.$^{-1}$ (72). An alternative method for securing C_p from data based on spectrographic computations is to use the equations or tabulated values of entropy as a function of temperature given by Jahn (230). Kelley (265a) has proposed the following equation for the C_p of nitrosyl chloride based on the 633, 923, and 1832 cm.$^{-1}$ frequencies and Jahn's data:

$$C_p = 10.73 + 1.84 \times 10^{-3}T - 1.66 \times 10^5T^{-2}$$

(A typographical error in this equation as it appears in Kelley's paper has been corrected.) Computations made from Jahn's tabulated entropy values, from Beeson and Yost's equation, and from Kelley's equation all lead to a value of about 9.5 cal./degree mole at 25°C.

The latent heat of vaporization can be computed readily from vapor pressure data. As indicated earlier, the most reliable vapor pressure data seem to be those of Partington and Whynes (378) and of Trautz and Gerwig (505). These lead to values of 6068 and 6091 cal./mole in the ranges from 203° to 258°K. and from 211° to 267°K., respectively. Bichowsky and Rossini (76) state that Trautz and Gerwig's data indicate a value of 6100 cal./mole at about −15°C. Briner and Pylkoff (92) have made computations of the latent heat of vaporization by certain empirical rules as well as from their vapor pressure data, but since their vapor pressure measurements seem to have been in error, these latter are not reliable. In this laboratory (111), the heats of vaporization at higher temperatures have been computed in B.T.U. per pound, using the Clapeyron equation, Trautz and Gerwig's vapor pressure data (505), and Beeson and Yost's gas law corrections (72) by the formula:

$$L = 0.000665T(V_g - V_l)\, dP/dT$$

(L is in B.T.U. per pound, V in cubic centimeters per gram-mole, T in °K., and P in atmospheres.) Values for several temperatures are tabulated:

TEMPERATURE	HEAT OF VAPORIZATION	TEMPERATURE	HEAT OF VAPORIZATION
°C.	*B.T.U./lb.*	*°C.*	*B.T.U./lb.*
0	163	60	150
20	161	80	142
40	156	100	131

Using this method we compute the latent heat of vaporization at the normal boiling point as 5960 cal./mole.

The viscosity of gaseous nitrosyl chloride has been measured by Trautz and Freytag (504), who used the data for various calculations of critical constants and molecular dimensions:

TEMPERATURE	VISCOSITY	TEMPERATURE	VISCOSITY
°K.	*poises*	*°K.*	*poises*
288.1	0.0001139	473.1	0.0001920
323.1	0.0001303	523.1	0.0002210
373.1	0.0001504	576.0	0.0002447
423.1	0.0001711		

These data appear to reflect the decomposition of nitrosyl chloride into nitric oxide and chlorine at the higher temperatures. Trautz and Freytag examined this aspect, supposedly using the equilibrium equations proposed by Dixon (135) and by Trautz and Wachenheim (511); unfortunately, they used incorrect forms of the equilibrium equations so that their calculated values are in error.

The viscosity of liquid nitrosyl chloride has been measured by Briner and Pylkoff (92):

TEMPERATURE	VISCOSITY	TEMPERATURE	VISCOSITY
°C.	*poises*	*°C.*	*poises*
−20.0	0.00547	−29.5	0.00604
−25.2	0.00567	−33.3	0.00642
−27.0	0.00586		

The spectrum of nitrosyl chloride has been measured by several workers in different spectral regions. Results of these measurements are contained in table 2. The early qualitative work of Magnanini (328, 329) has been confirmed by the more modern and accurate work of Goodeve and Katz (191), as well as by

Natanson (355). The fine-line structure reported earlier (275) in the 4000–4500 Å. region has not been observed by later workers (191, 355), who attribute this structure to the presence of nitrogen dioxide as impurity in the nitrosyl chloride used in the earlier work. Nitrosyl chloride in the vapor form has an orange-red color. It forms a dark red liquid and a red solid which in thin layers is

TABLE 2

Spectrum of nitrosyl chloride

WAVE LENGTHS OF ABSORPTION MAXIMA*	REFERENCES	WAVE LENGTHS OF ABSORPTION MAXIMA	REFERENCES
Å.		Å.	
168000	(582a)	5879	(191)
158000	(30)	5870	(355)
		5843–5898	(328, 329)
149000	(582a)		
		5612	(191)
108700	(372)	5610	(355)
108600	(582a)	5600–5634	(328, 329)
108300	(30)		
		5495	(191)
84400	(582a)	5490	(355)
83300	(30)	5481–5532	(328, 329)
55900	(372)	5385	(191)
55600	(582a)	5370	(355)
54600	(30)	5363–5411	(328, 329)
46900	(582a)	4750	(191)
46400	(30)	4690	(275)
			(355)
41800	(582a)		
		4400	(191)
28100	(582a)		
		3350	(191)
6431	(191)	3300	(275)
6375	(328, 329)	†	(355)
6158	(191)	1970	(191)
6180	(355)	1900	(398)
6133–6228	(328, 329)		
		1450 (1350–1600)	(398)
6017	(191)		
5990	(275)		
6030	(355)		
5970–6063	(328, 329)		

* The sets grouped together represent values for the same maximum from different sources.

† Absorption maximum shown graphically in this region.

yellowish. The color of the gas interferes with measurement of its Raman spectrum (9, 117).

The nitrosyl chloride molecule is said to have a nitrogen–oxygen bond distance of 1.14 Å., a nitrogen–chlorine bond distance of 1.95 Å., and a bond angle of 116° (266, 267, 269), according to computations from electron diffraction studies. These bond distances have led Ketelaar and Palmer (267, 269) to the conclusion that the molecule is a resonance hybrid between the normal covalent structure and the ionic form, $\overset{-}{\mathrm{Cl}}\,\overset{+}{\mathrm{N}}\mathrm{O}$, and that it is about half ionic, as the distances are much greater than those computed for a covalent structure. Ketelaar (266) calculated the total bond energy in the nitrosyl chloride molecule to be 159 kcal./mole: 113 kcal. for the nitrogen–oxygen bond and 46 kcal. for the nitrogen–chlorine bond. The energy for a normal covalent nitrogen–chlorine bond was cited as 38 kcal. The difference between these two values for the nitrogen–chlorine bond also is evidence of resonance. Values for the dipole moment of nitrosyl chloride were calculated (268) from measurements of dielectric constants of nitrosyl chloride and its solutions in carbon tetrachloride to be 2.19 and 1.83 D, respectively. These high values likewise support the conclusions as to the resonance structure cited above. The difference between the value for pure liquid nitrosyl chloride and the value in solution has been cited as evidence (268) for some association of the liquid, contrary to earlier published statements (92). The dielectric constant for pure liquid nitrosyl chloride has been found to be 18.2 at 12°C. (268). Force constants for the bonds have been calculated by Bailey and Cassie (30) and by Ketelaar (266), the latter using spectral data of Bailey and Cassie but electron diffraction values for the bond distances and angles.

Adsorption on alumina or kieselguhr leads to increased polarization of the bonds of some compounds. Since the nitrosyl and chloride ions are colorless, polarization of nitrosyl chloride should lead to a disappearance of color. Adsorption of nitrosyl chloride, however, does not cause the color to disappear (557), the homopolar character of the nitrogen–chlorine bond being too great.

Both liquid (19, 582) and gaseous nitrosyl chloride (70) have been found to be diamagnetic.

Sugden (462) computed the parachor for nitrosyl chloride as 110.0 from the components and as 108.1 from the data of Briner and Pylkoff (92) on density and surface tension.

Briner and Pylkoff (92) measured the surface tension by capillary means and found the following values:

TEMPERATURE	SURFACE TENSION
°C.	*dynes/cm.*
−33	34.5
−22	32.7
−5.5	30.3

These values should be considerably more accurate than the earlier measurements of Baudrimont (34).

In view of its low melting point of −61.5°C., only limited data are available on the solubility of solid nitrosyl chloride. Two binary systems, however, have been investigated. Nitrosyl chloride and nitrogen tetroxide (4) form a eutectic at −74.8°C. The two compounds are partially miscible in the solid state with formation of two series of solid solutions. Above −10°C. the system contains only a single liquid phase. Nitrosyl chloride and chlorine (85, 206, 506) form a eutectic at −107.7°C.

Liquid nitrosyl chloride is miscible in all proportions with various liquids even at temperatures below its normal boiling point of −5.8°C. Two such are chlorine and nitrogen tetroxide, as cited above. It is very soluble in the various simple aliphatic chlorides such as chloroform, carbon tetrachloride, and methylene chloride (279). Accurate data on the solubility of liquid and gaseous nitrosyl chloride are quite limited owing, in part, to its tendency to react with most materials. It shows appreciable solubility in many organic compounds with some of which it reacts slowly, e.g., liquid alkanes, benzene (368), acetic acid (368), acetic anhydride (158), ether, and dioxane, while with others, such as alcohols and ketones, it reacts rapidly. Although nitrosyl chloride reacts rapidly with water, some true solubility has been demonstrated (99). It is appreciably soluble in many inorganic compounds, e.g., sulfur monochloride (282) and nitric acid (138), and only sparingly soluble in others, e.g., liquid sulfur dioxide (524) and silicon tetrachloride (551).

Liquid nitrosyl chloride has been employed and studied as a solvent in several instances. The solubility of nitric oxide vapor has been measured (506). Some nitrosyl chloride inorganic adducts dissolve rapidly, e.g., $AlCl_3 \cdot NOCl$, $FeCl_3 \cdot NOCl$, and $SbCl_3 \cdot NOCl$ (99), while others, e.g., $SnCl_4 \cdot 2NOCl$, $TiCl_4 \cdot 2NOCl$, and nitrosylsulfuric acid, do not. Potassium chloride is not soluble in liquid nitrosyl chloride (99).

Data in the literature on nitrosyl chloride have been used to check various theories. These include general theories on geometric classification of reactions (440), equilibrium constants (7), heats of activation (146), surface tension (78), molecular volume (399), and reaction rates (500, 509).

IV. Physiological Action

There have been no extensive investigations of the toxicity of nitrosyl chloride reported in the literature. It is generally considered to combine the toxic properties of chlorine and the nitrogen oxides (333). Mixtures of chlorine and nitrosyl chloride have been found to be more toxic than nitrosyl chloride itself in studios with white rats and guinea pigs (589). Silver and McGrath (442) subjected groups of mice to exposure to nitrosyl chloride at concentrations in the range from 1.31 to 2.45 mg./liter for 10 min. Three of the sixty mice died during a 10-day observation period. The others did not act abnormally during or after exposure. These results with mice indicate nitrosyl chloride to be less toxic than chlorine or nitrogen tetroxide. Cats are reported to have been killed by a 20-min. exposure to a 100 p.p.m. concentration of nitrosyl chloride (154, 379).

V. DISSOCIATION

A. THERMAL DISSOCIATION

Nitrosyl chloride dissociates to nitric oxide and chlorine with formation of an equilibrium mixture:

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

Various workers have determined the equilibrium constant of this reaction at a number of temperatures. Three sets of data appear to warrant particular discussion. Beeson and Yost (72) determined the constants quite accurately in the range from 100° to 200°C., while Trautz and Wachenheim (511) and Dixon (135) studied the reaction in the range from about 175° to 475°C. Of the other work on this subject we may mention that Sudborough and Millar (459, 460, 461) were very considerably in error, while work by Vago (518) and by Trautz and Hinck (207, 508) is in general agreement with the more accurate later work.

Beeson and Yost express their data for the equilibrium constant as follows:

$$\log_{10} K_p(\text{cm. Hg}) = -2.808 - 3591.0/T + 4.1457 \log_{10} T - 0.0023406T + 0.52915 \times 10^{-6} T^2 \pm 0.02$$

Dixon expressed his data in the form:

$$\log_{10} K_p(\text{atm.}) = -3860/T + 3.348 \log_{10} T - 0.002457T - 1.8275$$

Data of Trautz and Wachenheim fit the equation:

$$\log_{10} K_c(\text{moles/liter}) = -3667/T + 1.5 \log_{10} T - 0.079$$

Dixon's work is more recent than that of Trautz and Wachenheim and is perhaps more accurate. The two sets of data agree quite well.

From the equation of Beeson and Yost for the equilibrium, McGonigle (333) has computed the extent of dissociation of nitrosyl chloride under various conditions. Typical values are: at 20°C. under its own vapor pressure, 0.4 per cent; at the critical point, 3.2 per cent; at 25°C. and 1.0 atm., 0.6 per cent; at 125°C. and 1.0 atm., 6.9 per cent.

Extensive study has been devoted to the kinetics of this system, especially in the direction of formation of nitrosyl chloride. This represents one of the rare cases of a homogeneous reaction of the third order. The reverse reaction or decomposition is second order. A critical discussion of much of the work on kinetics is given by Welinsky and Taylor (558). Their own experiments indicate that the reaction of nitric oxide and chlorine is truly third order. They support this conclusion by recalculation of early work of Trautz (496, 497, 498, 499, 501, 502, 503) and of Trautz and Schleuter (510), and show that there is no real evidence to support Trautz's conclusions that there is an $NOCl_2$ intermediate. Results obtained by Trautz and Wachenheim (511) and by Trautz and Henglein (203, 507) likewise show no trends from the third-order kinetics. Attention, however, is called to Bodenstein's hypothesis (80, 81) that there is evidence of nitric oxide dimerization as a basis of the abnormalities in the temperature coefficient.

This suggestion seems to have real merit. Rates on the decomposition were accurately measured by Welinsky and Taylor (558) and by Waddington and Tolman (522). All the data so far cited were recalculated and plotted by Welinsky and Taylor (558), using a function of the rate of formation *vs.* the reciprocal temperature (converting rate of decomposition to formation by use of the equilibrium constant). Very good agreement is shown. Data of Kiss (271) and Krauss and Saracini (288) are included in the plot. Those of the last-cited authors deviate the most.

The following typical values from Welinsky and Taylor's paper (558) indicate the magnitude of the two rates:

TEMPERATURE	DECOMPOSITION, k_2	FORMATION, k_3
°C.	cc./mole sec.	cc.²/mole² sec.
200	78	47 × 10⁷
250	1109	117 × 10⁷
300	10320	259 × 10⁷

where k_2 and k_3 are the rate constants in the equation:

$$\frac{d(NOCl)}{dt} = k_3(NO)^2(Cl_2) - k_2(NOCl)^2$$

This is for the equilibrium:

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

Waddington and Tolman (522) propose the equation:

$$k_2 = 4.3 \times 10^{11}\ T^{0.5}\ e^{-24000/RT}\ \text{cc./mole sec.}$$

for the decomposition reaction with the energy in calories.

Reaction of nitric oxide and chlorine is rapid at room temperature; thus k_3 was found (558) to be 1.597×10^7 cc.²/mole² sec. between 21.5° and 22.0°C. At −25.0°C. the value of k_3 was 0.404×10^7.

The rate of the thermal decomposition of nitrosyl chloride also has been studied (128, 465) in the temperature range from 700° to 900°C. Other early studies on the rate of reaction between nitric oxide and chlorine were made by Coates and Finney (106, 107).

Trautz and Gerwig (506) have studied the kinetics of the liquid-phase reaction and have found that the rates are about what would have been expected by extrapolation of the data on the gas reaction. Thus, rapid reaction has been observed at −80°C. (363) between nitric oxide and liquid chlorine or chlorine dissolved in carbon tetrachloride, e.g., only 7 per cent of the nitric oxide as such being recovered in a 33-min. experiment in which the chlorine and nitric oxide were mixed in a ratio close to that called for by the equation. At −150°C. the rate was still appreciable but at −180°C. less than 33 per cent reaction was obtained in 1.5 hr. Other workers (85) also have found fast reaction at −80° and −150°C.

Energy of activation has been computed by Welinsky and Taylor (558) and by Waddington and Tolman (522). In view of the preference given to the data of these workers for the rate constants, other computations on the energy of activation will not be cited, although they can be found in several of the original papers to which reference has been made. There seems to be a rising energy of activation for the reaction as a function of temperature, as pointed out both by Waddington and Tolman and by Welinsky and Taylor. Values cited by the latter authors for the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

are:

TEMPERATURE RANGE	ΔE	TEMPERATURE RANGE	ΔE
°C.	cal.	°C.	cal.
−25–0	3730	150–200	6400
0–50	4000	200–250	7880
50–100	4460	250–300	9860
100–150	5360		

Waddington and Tolman computed the energy of activation for the formation of nitrosyl chloride in the range of 150° to 250°C. from the equilibrium contant and the decomposition rate. They secured an activation energy of 6860 cal., a value which is in good agreement with the data cited above. The activation energy of the nitrosyl chloride decomposition, $2NOCl \rightarrow 2NO + Cl_2$, was found by Waddington and Tolman (522), as indicated earlier in the rate equation, to be 24,000 cal.

The homogeneous gas reaction can be catalyzed by bromine (271, 274) or by nitrogen dioxide (273, 274). Moreover, in the presence of large quantities of surface such as in tubes packed with glass wool, the heterogeneous wall reaction can be sufficiently accelerated to affect substantially the total velocity (271). This fact has been employed by various workers as an aid in the synthesis of nitrosyl chloride (101, 159, 160). It has been claimed that the homogeneous gas reaction can be retarded by a wall reaction involving a supposed nitric oxide dimer intermediate (455, 455a), a suggestion related to the Bodenstein hypothesis (81).

Water or various inactive gases do not affect the homogeneous reaction (271). It has been shown that a magnetic field is without effect (204). The claim of Pinkus (392, 393, 394) and Pinkus and de Schulthess (395, 396) that ionization accompanies the formation of nitrosyl chloride from nitric oxide and chlorine has been disputed by Trautz and Henglein (203, 507).

The equilibrium can be displaced by removal of either the chlorine or the nitric oxide by physical means or by chemical action. These latter cases are treated under the appropriate chemical reaction, it being uncertain in many cases whether nitrosyl chloride molecules react or whether the reaction is with one of the decomposition products, with reaction continuing by displacement of the equilibrium. Physical means of separation have been suggested, by themselves and in conjunction with chemical means, as processes for obtaining the nitrogen or chlorine components from nitrosyl chloride. It has been proposed to fractionate mixtures which have been cooled from a temperature where the dissociation is appreciable by solvent extraction (279) or by distillation (514).

B. PHOTOCHEMICAL DISSOCIATION

Nitrosyl chloride undergoes primary dissociation under the influence of light, following a first-order reaction rate (272). In contrast to earlier work (88, 272), Kistiakowsky (275, 466) established that the quantum yield was 2; this has been confirmed by Natanson (355) and in unpublished work by Winn as reported by Goodeve and Katz (191). Two mechanisms were considered by Kistiakowsky (275):

$$\text{(1)} \qquad \begin{array}{l} \mathrm{NOCl} + h\nu \rightarrow \mathrm{NO} + \mathrm{Cl} \\ \mathrm{Cl} + \mathrm{NOCl} \rightarrow \mathrm{NO} + \mathrm{Cl_2} \end{array}$$

$$\text{(2)} \qquad \begin{array}{l} \mathrm{NOCl} + h\nu \rightarrow \mathrm{NOCl^*}\ \text{(excited)} \\ \mathrm{NOCl^*} + \mathrm{NOCl} \rightarrow \mathrm{2NO} + \mathrm{Cl_2} \end{array}$$

He selected the second on the basis of two items of evidence discussed below, despite the observed absence of influence of nitrogen on the reaction, a fact which favors the first hypothesis. The first point cited by Kistiakowsky in favor of the second mechanism was the fact that wave lengths up to 6400 Å. were effective, whereas on the basis of his calculations 46,400 cal. was involved in the first reaction corresponding to 6130 Å., i.e., wave lengths of 6400 Å. do not provide sufficient energy to cause primary dissociation. This argument is fallacious, as has been pointed out by Bailey and Cassie (30) and by Natanson (355) in that the cited value of 46,400 cal. is not correct. The same error was made earlier by Bowen and Sharp (88). From data in the tables supplied by the Bureau of Standards (357a, 357c, 357d) for heats of formation of nitrosyl chloride, nitric oxide, and atomic chlorine (ground level $2P_{3/2}$) the value is computed to be 38,040 cal., in excellent agreement with the 38 kcal. cited by Bailey and Cassie (30). This computation error persists in the literature, occurring again in the book by Noyes and Leighton on *Photochemistry of Gases* (366). The second point cited by Kistiakowsky in favor of the second mechanism was the presence of fine structure in the nitrosyl chloride spectrum. This has been shown by Goodeve and Katz (191) and by Natanson (355) to be erroneous and due probably to the presence of nitrogen tetroxide as impurity in Kistiakowsky's nitrosyl chloride. Accordingly, it would appear that the primary reaction is

$$\mathrm{NOCl} + h\nu \rightarrow \mathrm{NO} + \mathrm{Cl}$$

Goodeve and Katz (191) and Natanson (355, 356) discuss predissociation. The quantum efficiency has been measured in solution (20) and values from about 0.32 to 1.0 have been observed, in line with the expected effect of solvent on lowering the efficiency.

VI. REACTIONS WITH INORGANIC COMPOUNDS

A. WATER

Nitrosyl chloride reacts rapidly with water, forming nitrous and hydrochloric acids. The equilibrium constant at 25°C. has been measured (428) for the reaction in dilute aqueous solution:

$$NOCl(aq.) + H_2O(liq.) \rightarrow HNO_2(aq.) + HCl(aq.)$$

$$K = \frac{(HNO_2)(HCl)}{(NOCl)(H_2O)} = 880 \pm 40$$

The ΔF^0_{298} corresponding to this equilibrium constant is -4019 cal.

In concentrated solutions, nitrous acid decomposes to nitric acid and nitric oxide, and the reaction between nitrosyl chloride and water becomes in effect:

$$3NOCl + 2H_2O \rightarrow HNO_3 + 2NO + 3HCl$$

After volatilization of the nitric oxide, the system becomes identical with that which is commonly called aqua regia when the concentrations of hydrochloric and nitric acids are high:

$$HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O$$

This aqua regia system is discussed in Section II, A. Compositions, in terms of hydrochloric, nitrous, and nitric acids, have been determined for solutions made by bubbling different amounts of nitrosyl chloride through water (333). Acidified solutions are obtained that are either reducing or oxidizing depending upon the amount of nitrosyl chloride passed in. Low acidities favor reducing conditions, whereas high acidities, by leading to the decomposition of nitrous acid to nitric acid, favor oxidizing conditions. The maximum acidity which can be developed by absorbing nitrosyl chloride in water ranges from about 6 equivalents per liter at 75°C. to about 8 equivalents per liter at 25°C.

Water can be removed from moist gaseous nitrosyl chloride by passing it over calcium chloride dihydrate or 85 per cent phosphoric acid (48, 52) or bringing it into contact with concentrated aqueous nitric acid (6, 53, 137, 139, 141) or liquid nitrosyl chloride (68).

B. METALS

Either wet or dry nitrosyl chloride is highly corrosive to most metals. Since, in the presence of moisture, some hydrochloric and nitric acid is formed from nitrosyl chloride, the corrosiveness of wet nitrosyl chloride is essentially that of aqua regia. When dry, nitrosyl chloride may be safely used at temperatures below about 50°C. in equipment of pure nickel or lead; Inconel may be used up to somewhat higher temperatures (10, 11, 333). Despite statements in the literature that steel cylinders may be used as containers (110, 344), it has been the experience of this laboratory that steel is corroded far too rapidly by nitrosyl chloride to be used for containers, valves, or piping. Nickel is required for containers used in interstate commerce (225, 226).

With some metals the product is the same as that formed from the metal chloride, as discussed in Section VI, F. In some cases these products seem to be nitrosyl salts, e.g., $(NO)^+(SbCl_6)^-$, rather than the type of coördination compound implied by the formula $SbCl_5 \cdot NOCl$. The latter method of writing the formulas has been employed in this review, however, to emphasize the relation to nitrosyl chloride. Formation of positive nitrosyl ions is indicated by the behavior of some of these nitrosyl salts in solvents such as liquid sulfur dioxide and nitrosyl chloride (436, 438).

1. Metals of Group I of the periodic table

Considerable energy is evolved when nitrosyl chloride reacts with the alloy, NaK_2, to form nitric oxide and metal chloride. At low pressures, electrons are emitted. Energy-distribution curves have been obtained for these electrons (127), and the maximum electron energy has been interpreted as equal to the difference between the chemical energy available in the reaction and the work function of the alloy.

Molten potassium reacts violently with gaseous nitrosyl chloride (35).

Metallic copper and nitrosyl chloride at 100°C. form $CuCl \cdot NOCl$ (35, 125, 126, 198, 376, 458). This product is a deliquescent paramagnetic (19) solid.

Formation of a film of silver chloride retards the reaction between metallic silver and nitrosyl chloride (35, 125, 126, 458). At 400–500°C., however, the reaction between nitrosyl chloride and silver powder to form silver chloride and nitric oxide has been used (198) to determine the atomic weight of chlorine. The nitric oxide formed in this reaction was passed over metallic copper, forming nitrogen and a mixture of copper oxides. Finally the nitrogen was converted to calcium nitride by reaction with metallic calcium. The purity of the nitrosyl chloride and the completeness of the reactions are attested by the fact that these experiments gave an atomic weight of 35.466 for chlorine and 14.006 for nitrogen.

Nitrosyl chloride slowly attacks gold (35, 125, 126, 198, 458, 476, 477). Finely divided gold is attacked at a much lower temperature than is gold strip (377).

2. Metals of Group II of the periodic table

Metallic magnesium has been reported as unattacked by liquid nitrosyl chloride at −8°C. and at 100°C. (3, 458). Magnesium or alloys containing a high percentage of magnesium have been recommended for equipment to hold nitrosyl chloride (21, 282).

Zinc is readily attacked by nitrosyl chloride at room temperature and $ZnCl_2 \cdot NOCl$ is formed (3, 19, 59, 126, 376, 458). The nitrosyl chloride in this compound is very lightly held (19).

Cadmium is attacked vigorously at 100°C., forming cadmium chloride. Unlike zinc, it does not form a nitrosochloride even at room temperature (198, 458).

Mercury reacts readily with nitrosyl chloride at room temperature liberating nitric oxide (35, 74, 96, 125, 126, 173, 174, 198, 377, 454). $HgCl_2 \cdot NOCl$ has been made from mercuric chloride (19, 170, 376) and from mercurous chloride (170, 376) by reaction with nitrosyl chloride at about −20°C. Presumably such a compound could be made from mercury at low temperatures. Since $HgCl_2 \cdot NOCl$ loses nitrosyl chloride at room temperature, it is probable that mercuric chloride has usually been formed in reactions between mercury and excess nitrosyl chloride. With excess mercury at −40°C., mercurous chloride has been formed (377).

3. Metals of Group III of the periodic table

Despite one report (198) in the literature of extraordinarily high resistance by aluminum to attack by nitrosyl chloride, other workers (376, 458) have obtained reaction even at temperatures as low as −20°C. Aluminum chloride (458) and $AlCl_3 \cdot NOCl$ (376) have been formed from the metal and nitrosyl chloride Aluminum has been considered insufficiently resistant to corrosion to be used as a material of construction for equipment to contain nitrosyl chloride (21).

Gallium reacts (376) at −30°C. to form $GaCl_3 \cdot NOCl$.

Indium reacts slowly (376) with nitrosyl chloride, even at 100°C., to form $InCl_3 \cdot NOCl$.

Thallium is unattacked by nitrosyl chloride at room temperature but at 100°C. it slowly reacts (376) to form either Tl_2Cl_3 or $TlCl_3 \cdot NOCl$, the product depending upon reactant ratios and reaction conditions. Another product, $TlCl \cdot TlCl_3 \cdot 2NOCl$, from thallium and nitrosyl chloride has also been reported (458).

4. Metals of Group IV of the periodic table

Titanium is said to be resistant to corrosion by aqua regia at room temperature (151). It might prove suitable for use in handling wet nitrosyl chloride at this temperature.

Silicon has been used as an alloying element to improve the corrosion resistance of iron to moist nitrosyl chloride (441, 519). Silex (15.7 per cent silicon in cast iron) and Mosilex (15.3 per cent silicon; 3.8 per cent molybdenum) are said to be resistant at 100°C. to systems containing water and nitrosyl chloride in either the liquid or the vapor phase. In contrast to other metals, Silex is said to be more resistant to moist than to dry nitrosyl chloride. Durichlor (14.5 per cent silicon, 3 per cent molybdenum, 0.85 per cent carbon, 0.65 per cent manganese, and the rest iron) has fair resistance to wet nitrosyl chloride at 30°C. (333).

Tin reacts readily with nitrosyl chloride (3, 19, 35, 59, 125, 126, 140, 252, 376, 458). Either stannic chloride or the stable compound $SnCl_4 \cdot 2NOCl$ can be formed, depending upon the ratio of nitrosyl chloride to tin available and upon reaction conditions.

Lead is attacked by nitrosyl chloride at 100°C. (125, 126, 198, 458), forming a chloride. No nitrosochloride has been isolated. At atmospheric temperature and pressure, lead is sufficiently resistant to be used as piping for dry gaseous nitrosyl chloride (11).

5. Metals of Group V of the periodic table

Tantalum is not attacked by either dry or moist nitrosyl chloride at atmospheric temperatures (11).

Arsenic, antimony, and bismuth are readily attacked by nitrosyl chloride (3, 35, 59, 125, 126, 458) even near 0°C. Arsenic forms a chloride but no nitrosochloride has been reported. Antimony forms a stable nitrosochloride, $SbCl_5 \cdot NOCl$ (19). Bismuth forms $BiCl_3 \cdot NOCl$.

6. Metals of Group VI of the periodic table

Various alloys containing chromium, molybdenum, or tungsten have been proposed for fabricating equipment to handle nitrosyl chloride (11, 48, 55, 62). For example, alloys containing 15–30 per cent chromium and 0–30 per cent nickel, with the nickel content less than the chromium content and the remainder principally iron, have been proposed for use in the process involving reaction of nitric acid and sodium chloride (55). Some alloys containing chromium or molybdenum have been found unsuited for equipment exposed to nitrosyl chloride (21, 441).

7. Metals of Group VII of the periodic table

At 100°C., manganese is slowly attacked by nitrosyl chloride (198, 458).

8. Metals of Group VIII of the periodic table

Iron is readily attacked by either wet or dry nitrosyl chloride even at temperatures near 0°C. (3, 376, 458). Several patents disclose the use of iron—for example, scrap iron—to recover the nitrogen in nitrosyl chloride as nitric oxide and the chlorine as ferric chloride (245, 246, 262, 515, 516). Iron reacts at ordinary temperatures as follows:

$$Fe + 4NOCl \rightarrow FeCl_3 \cdot NOCl + 3NO$$

If the $FeCl_3 \cdot NOCl$ is heated above about 300°C., it decomposes to ferric chloride and nitrosyl chloride, and the latter can be fed back to the gas passing over the iron. Pyrophoric iron gives some oxychloride as well as ferric chloride when exposed to nitrosyl chloride, the iron capturing some of the oxygen in the nitrosyl chloride (198). In general, alloys whose major constituent is iron are unsuitable for equipment exposed to nitrosyl chloride, although under some conditions, as noted in the preceding paragraphs, a few such alloys with silicon, nickel, or chromium have been employed.

Some alloys of cobalt resist corrosion by nitrosyl chloride. Stellite No. 12, a cobalt–chromium–tungsten alloy, has good resistance under many conditions (333).

Pure nickel or some alloys whose major component is nickel are especially suitable for equipment handling dry nitrosyl chloride (11, 48, 62). Nitrogen tetroxide in mixtures of nitrosyl chloride and chlorine reduces corrosiveness (62). The nitrosyl chloride now commercially available in the United States contains 4–10 weight per cent nitrogen tetroxide and a much smaller amount of chlorine (11). When used at temperatures below 50°C., pure nickel has been satisfactory for valves, pipelines, and cylinders. The material is shipped under Interstate Commerce Commission regulations in nickel cylinders with all-nickel valves (225). Shipment in tank cars has been authorized (226).

At room temperature, palladium charged with hydrogen is attacked by nitrosyl chloride, forming palladous chloride, nitric oxide, and nitrogen (236). A mixture of hydrogen and nitrosyl chloride passed over palladium at 100–230°C. does not appreciably attack the metal, but a considerable amount of ammonium chloride is formed, the palladium catalyzing the reaction between hydrogen and nitrosyl chloride. Palladium strip in liquid nitrosyl chloride at room temperature forms a product that apparently is a mixture of $PdCl_2 \cdot 2NOCl$ and $PdCl_2 \cdot 2NO$ (377).

Dry nitrosyl chloride does not attack platinum at room temperature (11). At higher temperatures, or if wet, nitrosyl chloride slowly corrodes the metal (35, 125, 126, 198, 377, 416, 417, 458, 476, 477). The very stable $PtCl_4 \cdot 2NOCl$ is formed.

C. NONMETALS

At room temperature and in the absence of light or certain other catalysts, mixtures of nitrosyl chloride and hydrogen are very unreactive. Finely divided palladium, platinum, or nickel catalyzes their reaction, ammonium chloride being the major product (236). Nitrogen is also formed. By using platinum and keeping the catalyst cold, hydroxylamine hydrochloride is obtained in an amount equal to about 5 per cent of the ammonium chloride formed simultaneously. At room temperature in the presence of light, or at higher temperatures in the presence of catalysts such as manganese dioxide, alumina, manganous chloride, chromic oxide, silica, or activated carbon, the reaction between nitrosyl chloride and hydrogen can be made to form nitric oxide and hydrogen chloride smoothly and in good yield (249, 250, 252, 259). Passing equal volumes of nitrosyl chloride and hydrogen through an empty reactor at 350°C. gave 90 per cent attack on the nitrosyl chloride. With manganese dioxide in the same reactor the attack was raised to 96 per cent and with alumina to 97 per cent. At 200°C., activated charcoal gave 99 per cent attack.

The reaction between oxygen and nitrosyl chloride has been extensively studied, since two valuable products, chlorine and nitrogen tetroxide, are formed (48, 52, 54, 65, 66, 241, 242, 243, 244, 248, 251, 253, 254, 255, 256, 257, 258, 374, 514). The method of calculating converter size for the reaction has been discussed (560). After the oxidation, the nitrogen tetroxide and chlorine may be separated from each other by fractional distillation or by the use of solvents. Pumice (121), silica gel (217, 261, 401), alumina, chabazite (61, 278), manganese dioxide, iron oxides, and chromium oxides (240) have been used as catalysts for oxidizing gaseous nitrosyl chloride. In the range of 190° to 300°C. it is not essential that a catalyst be present (316). Below 190°C. in the absence of a catalyst little oxidation occurs; above 300°C. the decomposition of nitrogen dioxide to nitric oxide and oxygen becomes excessive. The reaction

$$2NOCl + O_2 \rightarrow Cl_2 + 2NO_2$$

is exothermic. The standard free-energy change of this reaction has been calculated for temperatures between 100° and 1000°K. (143). It ranges from −9980 cal. at 100°K. to −460 cal. at 1000°K. The oxidation rate is retarded by chlorine, and this retarding is not just that which would be expected from a shifting of the equilibrium, since the effect is pronounced far from equilibrium conditions (61).

In the gas phase the reaction between nitrosyl chloride and oxygen occurs rapidly in a temperature range wherein nitrosyl chloride dissociation is extensive. The oxidation proceeds largely by the two steps:

$$2NOCl \rightarrow 2NO + Cl_2$$
$$2NO + O_2 \rightarrow 2NO_2$$

Recently, observations of absorption spectra have indicated that nitryl chloride, NO_2Cl, can also be formed by gas-phase reaction between oxygen and nitrosyl chloride (372).

In the liquid phase (67), nitrosyl chloride reacts reasonably rapidly in the temperature range of 50° to 100°C. at oxygen partial pressures of 150 to 1500 lb. per square inch absolute. The products are nitrogen tetroxide and chlorine.

In the presence of moisture, nitrosyl chloride is readily oxidized by oxygen to nitric acid and hydrochloric acid or chlorine (5, 102, 374, 401, 516). In this case, hydrolysis of the nitrosyl chloride probably precedes oxidation.

Ozone reacts with nitrosyl chloride to form nitryl chloride, NO_2Cl (372, 431, 432). The reaction between ozone and nitrosyl chloride is reported to follow quantitatively the equation:

$$NOCl + O_3 \rightarrow NO_2Cl + O_2$$

Sulfur reacts with nitrosyl chloride to form sulfur monochloride (125, 126, 136, 198, 236, 281, 282). For example (282), nitrosyl chloride may be passed into a solution of sulfur in sulfur monochloride at about 100°C. at 1 atm. pressure to effect the reaction:

$$S_8 + 8NOCl \rightarrow 4S_2Cl_2 + 8NO$$

Equilibrium conversions have been measured for the reaction (333). Ferric chloride, antimony trichloride, aluminum chloride, mercuric chloride, bismuth trichloride, or iodine accelerates the reaction. Nitrosyl chloride is soluble in sulfur monochloride and may be scrubbed from effluent gases with sulfur monochloride and the solution returned to the reactor.

Fused selenium is converted to selenium monochloride by nitrosyl chloride (198).

Liquid nitrosyl chloride at its boiling point has been reported as unreactive with phosphorus (35).

Attempts to combine nitrosyl chloride with chlorine (85, 206) indicate that little, if any, chemical reaction occurs even at low temperatures. A plot of freezing point *versus* composition for mixtures of nitrosyl chloride and chlorine shows a minimum of -107°C. at about 40 mole per cent chlorine. That this minimum is not sharp has been interpreted (85) as evidence for the existence of an addition compound that is considerably dissociated even at this low temperature.

Nitrosyl chloride is a strong inhibitor for the chain reaction between hydrogen and chlorine to form hydrogen chloride (79). The inhibiting action is probably due to removal of atomic chlorine:

$$Cl + NOCl \rightarrow NO + Cl_2$$

The addition of small amounts of nitrosyl chloride to chlorine used for making hexachlorocyclohexane from benzene has been proposed (145). The nitrosyl chloride probably inhibits the unwanted substitution reaction by combining with atomic chlorine. Combination with atomic chlorine has also been postulated (118) as one of the ways by which nitrosyl chloride inhibits the formation of phosgene from carbon monoxide and chlorine. It is paradoxical that nitrosyl chloride sensitizes the reaction between hydrogen and oxygen, apparently by furnishing atomic chlorine to initiate chains (119, 120).

Measurements of equilibria in the system nitric oxide–chlorine–bromine indicate that bromine and nitrosyl chloride should form some nitrosyl bromide and bromine chloride (71).

The reaction of nitrosyl chloride with iodine proceeds as follows:

$$2NOCl + I_2 \rightarrow 2NO + 2ICl$$

It is a rapid, reversible reaction whose equilibrium has been studied at 136.4–178.8°C. (334).

D. BASIC COMPOUNDS

Nitrosyl chloride reacts with aqueous solutions of bases such as sodium, potassium, calcium, and ammonium hydroxides, and sodium, potassium, and ammonium carbonates to form a chloride, a nitrite, and some nitrate and nitric oxide (57, 383). The more strongly alkaline the solution the more nitrite and the less nitrate and nitric oxide are formed. Even quite concentrated solutions, e.g., 50 per cent potassium hydroxide, form appreciable quantities of nitrate and nitric oxide, however. The alternative reactions are:

$$NOCl + 2MOH \rightarrow MCl + MNO_2 + H_2O$$
$$3NOCl + 4MOH \rightarrow 3MCl + MNO_3 + 2NO + 2H_2O$$

This second reaction raises a question as to the validity of determinations of heat of formation of nitrosyl chloride when these have involved the assumption that the first reaction is quantitative. It could not have played a significant role in the work of Trautz and Wachenheim (511), in view of the close approach of their results to those from other methods, but may explain the low value of Briner and Pylkoff (92).

Nitrosyl chloride in melting ammonia forms nitrosamine, H_2NNO, along with some nitrogen trichloride (434).

The reaction of nitrosyl chloride in gaseous nitrogen with solid sodium amide at slightly above −40°C. has been postulated (434) as:

$$3NaNH_2 + 2NOCl \rightarrow 2NaCl + NaNO_2 + 2NH_3 + N_2$$

A small quantity of ammonium chloride has been deposited in reactions of nitrosyl chloride with either sodium amide or potassium amide (492).

Other solid bases react with nitrosyl chloride. Soda lime, composed of sodium hydroxide and calcium oxide, quickly absorbs the gases, containing nitrosyl chloride, evolved from aqua regia (193). It has been proposed to recover oxides of nitrogen from nitrosyl chloride by passing the gas with or without added oxygen over the hot oxides, hydroxides, carbonates, or nitrates of magnesium or an alkaline earth (193, 238, 257, 516). A metal chloride is formed, and the effluent gases consist of oxides of nitrogen. Passing mixtures of nitrosyl chloride and carbon monoxide over hot oxides or carbonates or sulfides of aluminum, zinc, magnesium, and lead has been proposed as a means of preparing metal chlorides and nitric oxide (215). The carbon monoxide is oxidized to carbon dioxide.

Cupric oxide with excess liquid nitrosyl chloride gives cupric chloride (116). Cuprous oxide gives $CuCl \cdot NOCl$ (116, 376), which, when exposed to air, slowly decomposes to cupric chloride and nitric oxide. Thallous oxide has been reported to give $TlCl_2 \cdot 3NOCl$ (116). A later worker (376) found that thallous oxide formed either Tl_2Cl_3 or $TlCl_3 \cdot NOCl$ depending upon reaction conditions and reactant ratios.

E. ACIDIC COMPOUNDS

Nitrosyl chloride is fairly soluble in cool nitric acid. If a gaseous mixture of nitrosyl chloride and chlorine is passed into 53 per cent nitric acid at +20°C. to −30°C., the nitrosyl chloride is dissolved and the chlorine passes on through (138, 420). Upon warming, the nitrosyl chloride distills out. That the first gas evolved from aqua regia is relatively rich in chlorine is due to the fact that nitrosyl chloride is more soluble than chlorine in the liquid-phase mixture of concentrated nitric and hydrochloric acids (318). In contrast to its behavior at low temperatures, at around 100°C. concentrated nitric acid oxidizes nitrosyl chloride to nitrogen dioxide and chlorine (36, 49, 50, 56, 122, 143, 421, 494, 519).

$$2NOCl + 4HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$

The exit gases from this reaction are saturated with water and nitric acid. These components may be removed by cooling and partially condensing the gases. If the concentration of nitric acid in the reactor is only 50 per cent by weight, the amount of moisture in the exit gases is excessive and most of the nitrogen dioxide and chlorine reverts to nitrosyl chloride and nitric acid in this condensation. For this reason, nitric acid of 75–85 per cent concentration in the reactor is preferred (50, 56). At temperatures below 15°C., nitric acid of 50–80 per cent strength has been used for cooling and drying hot moist nitrosyl chloride (6).

Nitrosyl chloride and nitric acid may be passed as a gaseous mixture over silica gel at 40–160°C. to effect the reaction given in the preceding paragraph (402). At first pure chlorine passes through, the nitrogen dioxide and water being retained on the catalyst; finally, nitrogen dioxide starts coming through. The reaction is then stopped, and the silica gel is reactivated by heating to 400°C. or higher to desorb water and nitrogen dioxide.

Recently (372), it has been reported that nitrosyl chloride reacts rapidly with nitrogen pentoxide to form nitrogen tetroxide and nitryl chloride.

Nitrosyl chloride forms an adduct, $SO_3 \cdot NOCl$, with sulfur trioxide (553, 555). The adduct is white, crystalline, and hygroscopic. Upon warming it turns yellow. It decomposes when distilled but is formed again in part in the receiver when the products are cooled.

Sulfuric acid reacts with nitrosyl chloride (476) to form nitrosylsulfuric acid, the white crystalline material often called "lead chamber crystals."

$$NOCl + H_2SO_4 \rightarrow ONOSO_3H + HCl$$

It has been proposed to take advantage of this in separating the mixture of nitrosyl chloride and chlorine formed when nitric acid reacts with a metal chloride. These gases can be passed through concentrated sulfuric acid to form nitrosylsulfuric acid (547, 548). Chlorine and hydrogen chloride pass on through. The latter gases can be separated by selective absorption of the hydrogen chloride in water (144) or by recycling through nitric acid, which oxidizes the hydrogen chloride to chlorine and nitrosyl chloride (467). Alternatively, nitric acid may be present in the sulfuric acid (46, 418, 549), or nitrogen dioxide may be mixed with the gases passed into the sulfuric acid (418). In either of these cases, no hydrogen chloride is evolved, the nitric acid or nitrogen dioxide oxidizing it to chlorine.

Hydrogen sulfide and nitrosyl chloride react readily in ethyl ether or petroleum ether to form ammonium chloride and sulfur (236).

F. INORGANIC SALTS

Reactions of nitrosyl chloride with inorganic salts are of two types. In one, it adds to a metal chloride and only one product is formed. An example of such a reaction is the combination with ferric chloride to form $FeCl_3 \cdot NOCl$. Such products can usually be obtained from either the metal or the metal chloride, nitrosyl chloride converting the metal to the chloride as the first step in the sequence. In the other type of reaction between nitrosyl chloride and metal salts, a metal chloride is formed and the remaining portions of the reacting molecules end up in one or more separate products. An example of this type of reaction is the formation of silver chloride and nitrosylsulfuric acid from nitrosyl chloride and silver bisulfate. In some cases a reaction of the second type is followed by one of the first type.

Dry sodium nitrate heated above 300°C. with nitrosyl chloride forms sodium chloride and nitrogen dioxide (102, 220). The conversion of potassium chloride and sodium nitrate to potassium nitrate and sodium chloride can be accomplished by cycling gaseous nitrogen dioxide, nitrosyl chloride, and chlorine over the solid salts (260).

Aqueous potassium iodide reacts with nitrosyl chloride as follows (319):

$$2NOCl + 2KI \rightarrow 2KCl + I_2 + 2NO$$

The formation of nitrosylsulfuric acid from nitrosyl chloride and silver acid sulfate (73, 283) has been cited as strong evidence that nitrosylsulfuric acid has a N–O–S grouping and not a direct N–S linkage.

Nitrosyl fluoride has been made by passing nitrosyl chloride at atmospheric pressure over silver fluoride at 200–250°C. in a platinum tube (419). Nitrosyl chloride and silver fluoride sealed in a glass tube react at room temperature to form nitrosyl fluoride, but the glass is etched and the gaseous products include silicon tetrafluoride and nitric oxide. Nitrosyl fluoride is a colorless liquid boiling at −56°C.

The action of nitrosyl chloride on a number of other silver salts has been studied (377, 386), most of the reactions being conducted at room temperature in a glass tube. The following reactants and products are reported:

$AgNO_3 + NOCl \rightarrow AgCl + N_2O_4$
$AgClO_4 + NOCl \rightarrow AgCl + ONClO_4$
$AgI + NOCl \rightarrow AgCl + NO + I_2$
$AgBr + NOCl \rightarrow$ only partial reaction even at 200°C.
$AgNO_2 + NOCl \rightarrow AgCl + NO + NO_2$
$Ag_2CO_3 + NOCl \rightarrow AgCl + AgNO_3 + AgNO_2 + NO + CO_2$
$Ag_2SO_3 + NOCl \rightarrow AgCl + NO + SO_2 + S_2N_2O_9$ (nitrosyl pyrosulfate)
$Ag_2N_2O_2$(silver hyponitrite) $+ NOCl \rightarrow AgCl + N_2 + NO$

The reaction between solid silver nitrate and a solution of nitrosyl chloride in liquid nitrogen tetroxide can be carried to completion (2), forming silver chloride and nitrogen tetroxide.

Cuprous chloride with excess liquid nitrosyl chloride at −10°C. gives $CuCl \cdot NOCl$ (19, 170).

Gaseous nitrosyl chloride forms calcium chloride from solid calcium nitrate at 400°C. (247). Hot solid magnesium nitrate is converted to magnesium chloride by gaseous nitrosyl chloride (238).

Zinc chloride forms $ZnCl_2 \cdot NOCl$, a compound that holds its nitrosyl chloride lightly (19).

The comparatively unstable $HgCl_2 \cdot NOCl$ has been made by the action of nitrosyl chloride on either mercuric or mercurous chloride (19, 170).

Boron trichloride and nitrogen tetroxide form $BCl_3 \cdot NOCl$ (179). Nitrosyl chloride is probably an intermediate, since the same product has also been formed by direct combination of boron trichloride and nitrosyl chloride (377).

Aluminum chloride combines with nitrosyl chloride to form $AlCl_3 \cdot NOCl$ (19, 170, 376, 415, 424, 551, 552).

Gallium trichloride and nitrosyl chloride form $GaCl_3 \cdot NOCl$ (376).

InBr, $InBr_3$, InCl, and $InCl_3$ all form $InCl_3 \cdot NOCl$ (376) when treated with nitrosyl chloride.

Several thallium salts have been treated with nitrosyl chloride (376). Most gave either Tl_2Cl_3 or $TlCl_3 \cdot NOCl$, the product apparently depending more upon reaction conditions and reactant ratios than upon what thallium salt was used. Thallous chloride and thallous nitrite formed Tl_2Cl_3. Tl_2Cl_3, $TlCl_3$, and TlBr formed $TlCl_3 \cdot NOCl$. Thallous nitrate was converted to either Tl_2Cl_3 or $TlCl_3 \cdot NOCl$, depending upon reaction conditions. The product from thallous iodide was not identified.

$TiCl_4 \cdot 2NOCl$, a yellow octahedral crystalline material, has been made from titanium tetrachloride and tetranitromethane or chloropicrin (404). It has also been made by direct combination of titanium tetrachloride and nitrosyl chloride (376, 415, 551, 552).

Silicon tetrachloride dissolves a little nitrosyl chloride but forms no compound (551).

Either nitric oxide or nitric acid yields hydroxylamine when treated with stannous chloride in hydrochloric acid (134). It has been suggested that nitrosyl chloride is an intermediate in this reduction. $SnCl_4 \cdot 2NOCl$ has been obtained (376) from nitrosyl chloride and anhydrous stannous chloride.

A product from stannic chloride and nitrogen dioxide has been assigned the composition $3SnCl_4 \cdot 4NOCl$ on the basis of tin and chlorine content (470, 471, 472). In this preparation, nitrosyl chloride may have been formed from nitrogen dioxide and stannic chloride and this then combined with stannic chloride. It is possible that the reported $3SnCl_4 \cdot 4NOCl$ was just a physical mixture of $SnCl_4$ and $SnCl_4 \cdot 2NOCl$. The latter compound has been obtained by other workers by combination of nitrosyl chloride and stannic chloride (19, 22, 206, 376, 415, 551, 552, 554).

Lead tetrachloride combines with nitrosyl chloride to form $PbCl_4 \cdot 2NOCl$ (415).

Nitrogen tetroxide and lead chloride have been obtained by heating lead nitrate and nitrosyl chloride (377).

$SbCl_5 \cdot NOCl$, a solid melting at 180°C., has been obtained from nitrosyl chloride and antimony trichloride and also from nitrosyl chloride and antimony pentachloride (19, 170, 206, 415, 554). Measurements of electrical conductivity have led to the suggestion that nitrosyl chloride and antimony pentachloride form NO^+ and $SbCl_6^-$ in liquid sulfur dioxide (437).

Bismuth trichloride and nitrosyl chloride combine at room temperature to form $BiCl_3 \cdot NOCl$ (415).

Manganous chloride at -10°C. gives $MnCl_2 \cdot NOCl$ (19, 170, 376).

$FeCl_2 \cdot NOCl$ has been obtained from ferrous chloride (170, 376). The reaction between ferrous chloride and nitrosyl chloride is highly exothermic.

Solid ferric chloride reacts with gaseous nitrosyl chloride at ordinary temperature to form $FeCl_3 \cdot NOCl$ (206, 239, 376, 415, 515, 551, 552). Upon heating, the nitrosyl chloride is released and ferric chloride regenerated. A process for isolating nitrosyl chloride involves passing a gaseous mixture through a solution below 25°C. containing 70–75 per cent ferric chloride, 2 per cent hydrochloric acid, 2 per cent nitric acid, and 21–26 per cent water (59). Nitrosyl chloride is absorbed. It may be regenerated by warming the solution and stripping with a gas such as air.

When nitrosyl chloride is passed over ferrous nitrate at about 300°C., ferric chloride and oxides of nitrogen are formed (246, 262).

Platinous or platinic chloride treated with excess nitrosyl chloride forms $PtCl_4 \cdot 2NOCl$ (19, 377). This same product has been made from platinic chloride and nitric acid (556). Nitrosyl chloride probably was an intermediate in this preparation.

Either palladium chloride or palladium nitrate in liquid nitrosyl chloride at 100°C. forms $PdCl_2 \cdot 2NOCl$ (377).

Nitrosyl chloride has been proposed (214) for the treatment of metal phosphates and borates to be used as catalysts for hydrocarbon oxidation. The function of the nitrosyl chloride was not disclosed.

G. INORGANIC COMPOUNDS NOT CLASSIFIED

Several chlorine compounds, which may be present as impurities in electrolytic chlorine, react with nitrosyl chloride and may be removed thereby (112). The following reactions occur:

$$2Cl_2O + 2NOCl \rightarrow 2NO_2 + 3Cl_2$$
$$NCl_3 + NOCl \rightarrow N_2O + 2Cl_2$$

The reaction between nitrosyl chloride and nitrogen trichloride is slow at −80°C. but is appreciably faster at −20°C. (361). This reaction probably accounts for a failure to obtain much nitrogen trichloride from the reaction between phosphorus trichloride and nitrosyl chloride (359).

Nitrosyl chloride may be heated to effect extensive decomposition into nitric oxide and chlorine and the mixture then passed through sulfur monochloride containing a little catalyst such as antimony trichloride. Nitric oxide and unreacted nitrosyl chloride bubble on through and the sulfur monochloride is converted into sulfur dichloride (280). Chlorine may then be evolved by heating the sulfur dichloride. The sulfur monochloride is thereby regenerated and may be reused.

Nitrosyl chloride and bromine trifluoride have been used to form $BF_3 \cdot NOF$, $PF_5 \cdot NOF$, $GeF_4 \cdot 2NOF$, and $SnF_4 \cdot 2NOF$ from boric anhydride, phosphorus pentabromide, germanium dioxide, and stannic tetrafluoride or tetrachloride, respectively (583).

VII. Reactions with Organic Compounds

Much of the early work on the chemistry of nitrosyl chloride concerned its reactions with terpenes. O. Wallach made notable contributions in this field during the latter half of the nineteenth century, much of which was summarized in his book *Terpene und Campher* (543). W. A. Tilden and A. Baeyer also made numerous studies on the organic reactions of nitrosyl chloride in the same period. During the present century less emphasis has been placed on reactions with terpenes and more study has been devoted to the applications of nitrosyl chloride in the treatment of complex natural products and to its use in the synthesis of detergents and other materials.

Many of the early studies were made using amyl nitrite, butyl nitrite, or ethyl nitrite and hydrochloric acid to generate nitrosyl chloride *in situ*, since nitrosyl chloride was not then commercially available as it is now. In the case of most of the reactions cited in the following paragraphs, the specific source of the nitrosyl chloride is not mentioned, as it is believed that the results, in general, were not a function of the method of supplying the nitrosyl chloride. While the alkyl nitrites, together with hydrochloric acid or acetyl chloride, are considered as sources of nitrosyl chloride in this review, sodium nitrite and hydrochloric acid as ordinarily used for diazotization reactions have not been construed to yield nitrosyl chloride as an intermediate.

Since many of the reactions of nitrosyl chloride with organic compounds of various classes are in reality identical reactions with certain specific groups common to all the compounds considered, the literature on the subject is herein classified on this basis. Major groupings include reactions with methyl, methylene, and methylidyne groups; reactions with amino groups, etc. Thus it is possible for the members of some classes of organic compounds to appear in more than one major grouping. For example, in the case of the acids and derivatives, the *N*-substituted amides of acetoacetic acid are discussed under reactions involving methylene groups, while amino acids are included in the section on reactions with amino and similar groups.

A. GENERAL TYPES OF REACTIONS

The type of product obtained in the reaction of nitrosyl chloride with an organic compound is mainly dependent upon the nature of the organic material but is also greatly influenced by reaction conditions. The reactions can be classified into five main groups as follows:

1. Nitrosation

Under mild conditions and in the presence of the available hydrogen atoms of hydroxyl, amino, and similar groups, nitrosyl chloride acts as the acid chloride of nitrous acid. This results in the formation of nitrites, nitrosoamines, and nitrosohydrocarbons. The latter rearrange to oximes in many cases.

2. Chlorination

At elevated temperatures, chlorination rather than nitrosation is most often obtained, leading in some cases to high proportions of polychlorinated compounds.

3. Chloronitrosation

By addition of the chlorine and nitroso groups of nitrosyl chloride to double bonds of olefins and terpenes, chloronitroso compounds result. These reactions are usually carried out at room temperatures or lower. Certain reactions have been encountered in which both the chlorine and the nitroso groups of the nitrosyl chloride enter the organic molecule at the same location. Such reactions can reasonably be considered nitrosations followed by chlorinations.

4. Oxidation

Under relatively vigorous reaction conditions, high temperatures, high concentrations of nitrosyl chloride, and catalysts, the nitrosyl chloride acts as an oxidizing agent, leading to organic acids with concomitant reduction of the nitroso nitrogen to nitric oxide, nitrous oxide, or nitrogen.

5. *Diazotization*

In either aqueous or organic media, primary aromatic amines are diazotized by nitrosyl chloride.

B. REACTIONS WITH METHYL, METHYLENE, AND METHYLIDYNE GROUPS

Many of the reactions of nitrosyl chloride with organic compounds involve the substitution of a nitroso group for a hydrogen atom on a carbon. The methyl, methylene, or methylidyne group involved may be in a hydrocarbon, an acid, a nitrile, or other class of compound. The nitrosation reaction is the same in all cases, but the ease with which the reaction takes place is a function of the activity of the particular group involved. In compounds where an additional hydrogen is available, the initial nitroso compound often isomerizes to the isonitroso structure.

TABLE 3

Saturated aliphatic and aromatic hydrocarbons reacted with nitrosyl chloride

COMPOUND	REFERENCES
Alkyl aromatics in crude benzene	(229)
Anthracene	(336, 384)
Benzene	(22, 155, 192, 336, 350, 424)
Biphenyl	(384)
Butane	(315)
Cyclohexane	(345, 350)
Diphenylmethane	(384)
Ethylbenzene	(384)
Fluorene	(384)
Heptane	(321, 323)
Hexane	(342)
Methane	(155, 192, 350)
Naphthalene	(98, 350, 384)
Pentadecane	(157)
Pentane	(350)
Petroleum ether	(321)
Tetralin	(336)
Toluene	(192, 322, 350, 384)
Trimethylpentane	(156)
Triphenylmethane	(384)
Xylene	(98)

Under vigorous reaction conditions, such as high temperature and high nitrosyl chloride concentration, nitrosyl chloride attacks methyl, methylene, and methylidyne groups to form chlorination and oxidation products.

1. *Hydrocarbons* (*table 3*)

From studies on the reaction of nitrosyl chloride with heptane in the presence of sunlight, it was concluded that di-*n*-propylnitrosomethane (4-nitrosoheptane) is obtained, which then isomerizes to di-*n*-propylketone oxime (butyrone oxime). Under the influence of sunlight or ultraviolet light, formation of nitroso compounds is said to be feasible up to 80°C. (321, 323). Similarly, toluene reacts to form benzaldehyde oxime but without evidence of formation of the blue intermediate nitroso compound (322). Benzene does not react under similar conditions (22, 322). Later studies indicated that hydrocarbons such as hexane exposed to ultraviolet light react with nitrosyl chloride to form 2-chloro-2-nitrosohexane and 3-chloro-3-nitrosohexane. It appears probable that the secondary nitroso compounds first formed pass over to the oximes, which without light are converted to the chloronitroso compounds by excess nitrosyl chloride (342). (See Section VII, B, 5.)

It has been reported that reactions of nitrosyl chloride with toluene, ethylbenzene, anthracene, and diphenylmethane in sunlight at ordinary temperatures yield only 10–20 per cent of oxime or nitrosochloride, while 50–60 per cent of the nitrogen goes to nitrogen and 10–20 per cent to nitric oxide (384).

Hydrocarbons in reaction with nitrosyl chloride at elevated temperatures, i.e., 100°C. or higher, form chlorination products. The extent of polychlorination depends upon the reaction conditions. Typical reactions are: alkyl aromatic compounds to chlorides (benzene purification) (229); anthracene to 9,10-dichloroanthracene (384); benzene to chlorobenzene (22, 155, 192, 336, 350, 424); biphenyl to chlorobiphenyl (384); butane to chlorobutanes and dichlorobutanes (192, 315); cyclohexane to chlorocyclohexane (345, 350); diphenylmethane to chlorodiphenylmethane (384); ethylbenzene to (2-chloroethyl)benzene (phenethyl chloride) (384); fluorene to condensation products (384); methane to carbon tetrachloride, chloroform, etc. (155, 192, 350); naphthalene to α-chloronaphthalene and polychlorinated products (98, 350, 384); pentane to amyl chloride, etc. (350); toluene to benzyl chloride (192, 350, 384); triphenylmethane to chlorotriphenylmethane (384); xylenes to chlorinated products (98).

TABLE 4

Chlorinated hydrocarbons reacted with nitrosyl chloride

COMPOUND	REFERENCE
(2-Chloroethyl)benzene	(384)
α-Chlorotoluene (benzyl chloride)	(384)
α,α-Dichlorotoluene (benzal chloride)	(384)

Reaction of butane and nitrosyl chloride in the liquid phase and in the gas phase under the influence of light and catalysts at 100–250°C. and pressures up to 65 atm. gives, in addition to chlorination products and 2-butanone (through nitrosation and hydrolysis), the oxidation products butyric, propionic, and acetic acids with indications of formic acid (315).

2. Chlorinated hydrocarbons (table 4)

Only a limited amount of work has been carried out on the reactions of nitrosyl chloride with chlorinated hydrocarbons (384). In the cases of α-chlorotoluene (benzyl chloride) and (2-chloroethyl)benzene, evidence of oxime formation was obtained in reaction at ordinary temperatures in sunlight. Presumably reaction takes place with the activated methylene groups.

In sealed tubes at 150°C., nitrosyl chloride reacts with α-chlorotoluene and α,α-dichlorotoluene to form α,α-dichlorotoluene and α,α,α-trichlorotoluene, respectively (384).

3. *Aldehydes* (*table 5*)

Limited studies with benzaldehyde and acetaldehyde indicate that with nitrosyl chloride in sunlight the corresponding acyl chlorides are formed, although in low yields (300).

TABLE 5

Aldehydes reacted with nitrosyl chloride

COMPOUND	REFERENCE	COMPOUND	REFERENCE
Acetaldehyde	(300)	Benzaldehyde	(300)

TABLE 6

Ketones and keto acids reacted with nitrosyl chloride

COMPOUND	REFERENCES
Acetone	(104, 103, 105, 324, 412)
Acetophenone	(103, 105, 336, 412)
2-Butanone (methyl ethyl ketone)	(324, 413, 414)
2-Camphanone (camphor)	(105)
p-Chloroacetophenone	(412)
p-Chloropropiophenone	(201)
Desoxybenzoin (phenyl benzyl ketone)	(389)
Ethyl phenyl ketone	(100)
4-Heptanone (di-*n*-propyl ketone)	(324)
p-Hydroxybutyrophenone	(201)
Levulinic acid	(412)
Levulinic acid ethyl ester	(412)
3-*p*-Menthanone (menthone)	(29)
Mesityl oxide (2-methyl-2-penten-4-one)	(105)
p-Methylacetophenone (methyl *p*-tolyl ketone)	(412)
4-(*p*-Methoxyphenyl)-3-buten-2-one (anisalacetone)	(412)
p-Methoxypropiophenone	(201)
3-Methyl-3-butanone (methyl isopropyl ketone)	(412)
Methyl butyrophenone-*o*-carboxylate	(517)
Methyl tertiary-butyl ketone (pinacolone)	(412, 413, 414)
m-Nitropropiophenone	(201)
3-Pentanone (diethyl ketone)	(104, 105)
2-Pentanone (methyl-*n*-propyl ketone)	(104, 412)
4-Phenyl-3-buten-2-one (benzyl acetone)	(104, 412)
1-Phenyl-2-propanone (phenylacetone)	(412)
Propiophenone	(104, 201)
Valerophenone	(201)

4. *Ketones and keto acids* (*table 6*)

Dialkyl and alkyl aryl ketones have been found to react readily with nitrosyl chloride to form isonitroso compounds:

$$\mathrm{RCOCH_2R' + NOCl \rightarrow RCOC({=}NOH)R' + HCl}$$

The greater ease of reaction of ketones as compared to hydrocarbons indicates activation due to the carbonyl group. Ketones having carbonyl-activated methylene groups form α-isonitrosoketones. This was demonstrated with 2-butanone (methyl ethyl ketone) by Rheinboldt and Schmitz-Dumont (413, 414) in showing that, contrary to the arguments of Lynn and Lee (324), the monoxime of 2,3-butanedione (biacetyl) rather than the 1-isonitroso-2-butanone is formed at −15°C. with nitrosyl chloride gas. 3-Pentanone (diethyl ketone) (104, 105), 4-heptanone (di-*n*-propyl ketone) (324, 413), propiophenone (ethyl phenyl ketone) (104), and 1-phenyl-2-propanone (phenylacetone) (412), each of which has an active methylene group, similarly form the α-isonitroso compounds. The isonitroso compounds result when either nitrosyl chloride or amyl nitrite and hydrochloric acid are used (103, 104; *cf.* 324, 412). Ketones of the terpene series such as menthone (3-*p*-menthanone) react with nitrosyl chloride to form nitrosomenthone (4-nitroso-3-*p*-menthanone) (29). From oxidation studies yielding 2,6-dimethyl-3-oximidoöctanoic acid, the nitroso group was found to be attached to the tertiary carbon. Under certain conditions methyl ketones react with an excess of nitrosyl chloride to produce chloroisonitroso compounds (105, 412, 413, 414).

$$\begin{array}{c}
\mathrm{RCOCH_3 + NOCl \rightarrow RCOCH{=}NOH + HCl} \\
\underline{\mathrm{RCOCH{=}NOH + 2NOCl \rightarrow RCOCCl{=}NOH + 2NO + HCl}} \\
\mathrm{RCOCH_3 + 3NOCl \rightarrow RCOCCl{=}NOH + 2NO + 2HCl}
\end{array}$$

Acetone, 2-pentanone, etc. in carbon tetrachloride solution with a 2:3 mole ratio of added gaseous nitrosyl chloride at low temperatures react to form the chloroisonitroso methyl ketones (324, 412). Exposure of acetone to nitrosyl chloride in the cold also causes condensation to phorone (2,6-dimethyl-2,5-heptadien-4-one) with subsequent formation of mononitrosochloride (324) (see Section VII, F). On the other hand, phenylacetone and *p*-chloracetophenone form only isonitroso derivatives, the former being the α-isonitroso compound, $C_6H_5C({=}NOH)COCH_3$. Chloroisonitroso derivatives have been produced from acetophenone and some other methyl aryl ketones (412).

It has been found that the methylene group of desoxybenzoin (benzyl phenyl ketone) is converted to an isonitroso group with nitrosyl chloride at ordinary temperature in the absence of light (389). The chlorinating action of nitrosyl chloride predominates at 80°C., at which temperature desoxybenzoin is readily chlorinated (389).

It is of note that at elevated temperatures the oxidizing tendencies of nitrosyl chloride come to the fore with certain organic materials. Boiling acetophenone is converted in part to benzoic acid and the nitrosyl chloride to ammonium chloride (412).

In a recent patent describing the preparation of α-isonitrosoketones, nitrosyl chloride is mentioned as a possible intermediate in the reaction of alkyl aryl ketones with an acidified mixture of a chloride of sodium, potassium, calcium, or magnesium, a nitrite of sodium, potassium, calcium, magnesium, or barium, and an alcohol such as ethanol, 2-propanol, 1-butanol, or benzyl alcohol (201).

It is of interest that levulinic acid and its ethyl ester react in a manner similar to the ketones, reportedly giving the oximido derivative of the terminal methyl group (412).

TABLE 7

Aldehyde oximes reacted with nitrosyl chloride

COMPOUND	REFERENCES
Acetaldehyde oxime	(130, 406)
Anisaldehyde oxime (*p*-methoxybenzaldehyde oxime)	(232, 410)
Benzaldehyde	(232, 410)
Butyraldehyde oxime	(130, 406)
Cinnamaldehyde oxime	(232, 410)
o-Chlorobenzaldehyde oxime	(232, 410)
Cumaldehyde oxime (*p*-isopropylbenzaldehyde oxime)	(232, 410)
p-Cyanobenzaldehyde oxime	(232, 410)
Decanal oxime (capraldehyde oxime)	(408)
Dodecanal oxime	(408)
Enanthaldehyde oxime (heptanal oxime)	(130, 406)
Formaldehyde oxime	(130, 406)
Furfuraldehyde oxime	(232, 410)
Isobutyraldehyde oxime	(130, 406)
Isovaleraldehyde oxime	(130, 406)
β-Naphthol methyl ether aldoxime	(232, 410)
m-Nitrobenzaldehyde oxime	(232, 410)
o-Nitrobenzaldehyde oxime	(232, 410)
p-Nitrobenzaldehyde oxime	(232, 410)
2-Nitropiperonal oxime	(232, 410)
Nonanal oxime	(408)
Octadecanal oxime	(408)
Octanal oxime	(406, 408)
Phenylacetaldehyde oxime	(406, 408)
Phthalaldehydic acid oxime	(232, 410)
Piperonal oxime	(232, 410)
Propionaldehyde oxime	(130, 406)
Terephthaldehyde oxime	(232, 410)
Terephthaldehydic acid oxime	(232, 410)
p-Tolualdehyde oxime	(232, 410)
Triformoxime	(130, 406)

5. *Oximes (tables 7 and 8)*

A number of straight-chain aliphatic aldoximes, including those of formaldehyde and octadecanal, form crystalline bimolecular 1-chloro-1-nitroso compounds by reaction with nitrosyl chloride in ether solution. While colorless in the solid form, the chloronitroso compounds form blue solutions and also dissociate on warming to the melting point. By continued heating. usually at the melting point, the nitroso compounds are converted to the monomeric hydroxamic acid chlorides. Certain of the aldoximes investigated, including isovaleraldehyde oxime, are converted only to liquid chloronitroso compounds (130, 406, 408):

$$2RCH{=}NOH + 4NOCl \rightarrow (RCHClNO)_2 + 4NO + 2HCl$$

$$(RCHClNO)_2 \rightarrow 2RCHClNO \rightarrow 2RCCl({=}NOH)$$

TABLE 8

Ketone oximes reacted with nitrosyl chloride

COMPOUND	REFERENCES
Acetone oxime	(130, 407)
1-Acetonaphthone oxime (methyl α-naphthyl ketoxime)	(130, 407)
Acetophenone oxime	(130, 407)
Benzil monoxime	(130, 407)
Benzophenone oxime	(130, 407)
2,3-Butanedione dioxime (biacetyl dioxime, dimethylglyoxime)	(130, 407)
2,3-Butanedione monoxime (biacetyl monoxime)	(130, 407)
2-Butanone oxime (methyl ethyl ketoxime)	(130, 407)
1,4-Cyclohexanedione dioxime	(130, 407)
Cyclohexanone oxime	(130, 407)
Cyclohexyl methyl ketone oxime	(130, 407)
Cyclohexyl phenyl ketone oxime	(130, 407)
Desoxybenzoin oxime (benzyl phenyl ketoxime)	(130, 407)
3,3-Dimethyl-2-butanone oxime (pinacolone oxime)	(130, 407)
2,4-Dimethyl-3-pentanone (dipropyl ketoxime)	(130, 407)
1,3-Diphenyl-2-propanone oxime	(130, 407)
9-Fluorenone oxime	(130, 407)
2-Hendecanone oxime	(130, 407)
2-Hexanone oxime (methyl butyl ketoxime)	(130, 407)
3-Hexanone oxime (ethyl propyl ketoxime)	(130, 407)
16-Hentriacontanone oxime (dipentadecyl ketoxime)	(130, 407)
3-Methyl-2-butanone oxime (methyl isopropyl ketoxime)	(130, 407)
4-Methyl-2-pentanone oxime (methyl isobutyl ketoxime)	(130, 407)
3-Pentanone oxime (diethyl ketoxime)	(130, 407)
2-Pentanone oxime (methyl propyl ketoxime)	(130, 407)
18-Pentatriacontanone oxime (diheptadecyl ketoxime)	(130, 407)
Phenanthrenequinone monoxime	(130, 407)
1-Phenyl-2-propanone oxime (methyl benzyl ketoxime)	(130, 407)
β-Phenylpropiophenone oxime (phenethyl phenyl ketoxime)	(130, 407)
2-Octanone oxime (methyl hexyl ketoxime)	(130, 407)
12-Tricosanone oxime (diundecyl ketoxime)	(130, 407)

The reaction of hexane with nitrosyl chloride to produce chloronitroso derivatives is believed to proceed through the 2-hexanone and 3-hexanone oximes (342) (see Section VII, B, 1).

In contrast to the aliphatic aldoximes, the aromatic aldoximes react with nitrosyl chloride to give the hydroxamic acid chlorides (chloroisonitroso derivatives) directly.

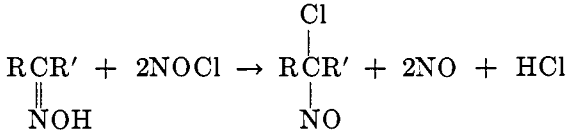
$$RCH{=}NOH + 2NOCl \rightarrow RCCl({=}NOH) + 2NO + HCl$$

Various aromatic aldoximes as well as 2-furaldehyde oxime give intermediate green compounds indicative of the blue-green nitroso stage (232, 410). In the case of piperonal oxime, the intermediate bimolecular chloronitroso compound can actually be isolated. On the other hand, those aromatic aldoximes having cyano, nitro, or carboxyl groups in the ring give no evidence of the colored intermediate, yielding directly the hydroxamic acid chlorides. This more rapid formation of the chloroisonitroso structure is evidence of activation of the hydrogen adjacent to the isonitroso group by the aromatic ring substituent.

The indications of rapid transition from nitroso to isonitroso structures noted here are similar to those observed in the treatment of ketones with nitrosyl chloride in which isonitroso or chloroisonitroso ketones form immediately (see Section VII, B, 4).

Closely related to the behavior of more active aromatic aldoximes are the reactions of isonitrosoacetone, $CH_3COCH{=}NOH$, and isonitrosoacetophenone, $C_6H_5COCH{=}NOH$, with nitrosyl chloride in which the corresponding chloroisonitroso compounds, $RCOC(Cl){=}NOH$, are readily obtained (105, 412).

While the nitroso group of the chloronitroso compounds from aldoximes can rearrange to the isonitroso structure, no hydrogen is available for the rearrangement in the reaction products of ketoximes and nitrosyl chloride.



$$\underset{\underset{\text{NOH}}{\|}}{\text{RCR}'} + 2\text{NOCl} \rightarrow \text{R}\overset{\overset{\text{Cl}}{|}}{\underset{\underset{\text{NO}}{|}}{\text{C}}}\text{R}' + 2\text{NO} + \text{HCl}$$

Rheinboldt and Dewald (130, 407) studied the reactions of nitrosyl chloride with a number of ketoximes in ether solution or suspension and secured blue liquids with the lower members and blue crystalline solids with some of the higher members such as 12-tricosanone oxime (diundecyl ketoxime), 16-hentriacontanone oxime (dipentadecyl ketoxime), 18-pentatriacontanone oxime (diheptadecyl ketoxime) and 1,3-diphenyl-2-propanone oxime (dibenzyl ketoxime). While these typical nitroso-type compounds resulted in most cases, no evidence of nitric oxide or blue color was obtained in the reaction of nitrosyl chloride with the following: benzophenone oxime, biacetyl monoxime, biacetyl dioxime, benzil monoxime, fluorenone oxime, or phenanthrenequinone monoxime.

6. *Acids, amides, and esters* (*table 9*)

Under mild conditions, nitrosyl chloride reacts with the activated methylene groups of acetoacetic acid, malonic acid, and their derivatives to form isonitroso (oximido) compounds. For example, the variously *N*-substituted amides of acetoacetic acid react with nitrosyl chloride in benzene to form the corresponding isonitroso compounds (353).

$$CH_3COCH_2CONHR + NOCl \rightarrow CH_3COC({=}NOH)CONHR + HCl$$

Similarly, the active methylene group of malonamide reacts with liquid or gaseous nitrosyl chloride at 40–45°C. to form the oxime of mesoxamide, $CO(CONH_2)_2$ (576). The *N*-substituted malonamides also form isonitroso derivatives.

$$CH_2(CONHR)_2 + NOCl \rightarrow HON{=}C(CONHR)_2 + HCl$$

The nature of the solvent employed markedly influences the yield of product. Poor yields of the oximido derivative are obtained with malonamide in ether or chloroform, while in acetic acid, ethyl acetate, methanol, or ethanol, high yields are obtained (577). On the other hand, the *N*-substituted malonamides, such as *N*-*p*-tolylmalonamide and *o*-methylmalonanilic acid ethyl ester in chloroform suspension, are converted quantitatively to the corresponding isonitroso derivatives of malonic acid by reaction with nitrosyl chloride gas at 0°C. In the case of *N*-2-naphthylmalonamide, the usual oxime is obtained in toluene, whereas with ethyl acetate as solvent a chlorinated isonitroso compound is produced (577). Succinamide does not react with nitrosyl chloride even in 7 days in a sealed tube (576).

TABLE 9

Acids, amides, and esters reacted with nitrosyl chloride

COMPOUND	REFERENCES
Acetoacetic acid ethyl ester	(336)
Acetoacetanilide	(353)
o-Acetoacetotoluidide	(353)
p-Acetoacetotoluidide	(353)
3,4-Acetoacetoxylidide	(353)
Benzoic acid	(98, 300)
Benzylmalonic acid	(32, 373)
Bromomalon-*p*-toluidide	(439)
n-Butylmalonic acid	(32)
N,*N*'-Dibenzylbromomalonamide	(439)
N,*N*'-Dimethylmalonamide	(577)
N,*N*'-Dimethylmalonanilide	(577)
Ethylmalonic acid	(32)
Isobutylmalonic acid	(373)
Malonanilide	(577)
Malonamide	(485, 576, 577)
o-Malonotoluidide	(577)
p-Malonotoluidide	(577)
p-Methoxybenzylmalonic acid	(32)
o-Methylmalonanilic acid ethyl ester	(577)
Methylmalonic acid	(32)
N-1-Naphthylacetoacetamide	(353)
N-2-Naphthylacetoacetamide	(353)
N-1-Naphthylmalonamide	(577)
N-2-Naphthylmalonamide	(577)
Succinamide	(576)
N-*p*-Tolylmalonamide	(577)

Alkylmalonic acids, such as benzyl- and isobutylmalonic acids, react with nitrosyl chloride with the loss of carbon dioxide to produce the oximes of the corresponding α-keto acids in 75-90 per cent yield (32, 373).

$$RCH(COOH)_2 + NOCl \rightarrow RC(=NOH)COOH + CO_2 + HCl$$

However, the *N*-substituted bromomalonamides, bromomalon-*p*-toluidide and *N*,*N*′-dibenzylbromomalonamide, react with nitrosyl chloride to form the chlorobromo compounds instead of the nitroso compounds (439).

$$CHBr(CONHR)_2 + 2NOCl \rightarrow CClBr(CONHR)_2 + HCl + 2NO$$

In contrast to the reactions of acetoacetic acid derivatives with nitrosyl chloride which yield α-isonitroso compounds, it was found that levulinic acid and its ethyl ester yield chloroisonitroso derivatives. The reaction presumably takes place with the methyl groups of the acid radicals of the two compounds (412) (see Section VII, B, 4).

TABLE 10

Nitriles reacted with nitrosyl chloride

COMPOUND	REFERENCE	COMPOUND	REFERENCE
Acetonitrile	(389)	2-Naphthaleneacetonitrile	(385)
Benzonitrile	(385)	Naphthonitrile	(385)
Benzoylacetonitrile	(385)	*o*-Nitrobenzonitrile	(385)
o-Chloro-α-tolunitrile	(385)	*o*-Nitro-α-tolunitrile	(385)
Dichloroacetonitrile	(389)	*p*-Nitro-α-tolunitrile	(385)
Hydrocinnamonitrile (β-phenylpropionitrile)	(385)	α-Tolunitrile	(385)
o-Methyl-α-tolunitrile	(385)	Trichloroacetonitrile	(389)

Benzoic acid, unlike the acids above with active methylene groups, does not react with nitrosyl chloride even in the presence of sunlight (98, 300).

7. *Nitriles* (*table 10*)

Nitrosyl chloride reacts readily at 60–80°C. with the methylene groups of various alkylaryl nitriles to form the corresponding oximido compounds (385). Ease of reaction in these cases, in comparison with hydrocarbons, also indicates activation of the methylene group. The speed of reaction of variously substituted α-tolunitriles (phenylacetonitriles) with nitrosyl chloride is influenced by the position of the substituent in the ring. A nitro group in the para position accelerates the reaction, while a nitro group in the ortho position retards the reaction.

Not all the reactions of nitrosyl chloride with nitriles involve methylene or methylidyne groups. For example, acetonitrile and dichloroacetonitrile in reactions at 200°C. yield the corresponding acid chlorides (389). Trichloroacetonitrile does not react with nitrosyl chloride below 220°C., at which temperature the nitrile decomposes to hexachloroethane and cyanogen (389).

Benzonitrile and *o*-nitrobenzonitrile react with nitrosyl chloride at about

180°C. to yield benzoyl chloride and *o*-chlorobenzonitrile, respectively. The latter is obtained by replacement of the nitro group. At 180°C. in reaction with nitrosyl chloride, naphthonitrile and α-tolunitrile yield ring-chlorinated compounds (385).

C. REACTIONS WITH AMINO, IMINO, AMIDO, AND IMIDO GROUPS

The reaction of nitrosyl chloride with amino groups gives three types of products: *viz.*, diazonium chlorides or their secondary reaction products, the diazo compounds, in reaction with primary aromatic amines; nitroso derivatives in reaction with secondary and tertiary amines and *N*-substituted amides; and, depending upon reaction conditions, chloro derivatives from certain amines and amino acids. Reactions of amides to yield acyl chlorides are analogous to the latter reactions with amines.

TABLE 11

Amines, hydrazines, and derivatives reacted with nitrosyl chloride

COMPOUND	REFERENCES	COMPOUND	REFERENCES
Allylamine	(447)	Heptylamine	(447)
Aminodinitrophenol	(375)	Hexamethylenediamine	(449)
2-Amino-5-hexene	(447)	Isoamylamine	(447)
Aminophenol	(375)	Isobutylamine	(447)
Aniline	(31, 184, 263, 348, 349, 375, 457, 489)	Isopropylamine	(447)
		Methylaniline	(489)
		l-β-Methylphenethylamine	(310)
Benzylamine	(447)	*d*-β-Methylphenethylamine	(311, 312)
sec-Butylamine	(447)	α-Naphthylhydrazine	(489)
α-Camphylamine	(447)	β-Naphthylhydrazine	(489)
4,4'-Di(dimethylamino)triphenylamine	(327)	*o*-Nitroaniline	(489)
		p-Nitroaniline	(457, 489)
Diisoamylamine	(448)	Nonamethylenediamine	(449)
Diisobutylamine	(448)	Octamethylenediamine	(449)
Dimethylaniline	(28, 185, 489)	Phenylhydrazine	(488, 489)
Dipropylamine	(448)	Piperidine	(448)
Ethylamine	(447)	Propylamine	(447)
Ethylenediamine	(449)	*o*-Toluidine	(184, 348)
d-β-Ethylphenethylamine	(311, 312)	Trimethylamine	(237)
Heptamethylenediamine	(449)		

1. Amines, hydrazines, and derivatives (table 11)

Primary aliphatic amines in organic solvents at −15°C. to −20°C. are converted into alkyl chlorides by nitrosyl chloride (310, 311, 312, 447). Aliphatic diamines are converted to dichloroalkanes (449). Some rearrangement usually occurs in the metathesis. Secondary aliphatic amines are converted to nitrosoamines (448). The tertiary aliphatic amine, trimethylamine, gave dimethylchloromethylamine and tri- and dimethylammonium chlorides in reactions at −80° to 0°C. with nitrosyl chloride (237).

The primary aromatic amines, aniline and *o*-toluidine, in aqueous hydrochloric acid solution are converted by nitrosyl chloride to the corresponding diazonium chlorides in practically quantitative yield (348). Solid diazonium salts (hydrochlorides or sulfates) of good purity have been obtained in high yield from aniline and *p*-nitroaniline in cold organic media (31, 457). Reaction of nitrosyl chloride with an aqueous paste of aniline hydrochloride in the cold results in the complex diazobenzene aniline chloride (263), which can be converted with base to diazoaminobenzene. The latter results directly in good yields from aniline and nitrosyl chloride, using a base or excess aniline (31, 349, 375, 489). A similar product results from *p*-nitroaniline (489). From *o*-nitroaniline and nitrosyl chloride an unstable diazonium chloride results (489). Rearrangement products, aminoazobenzene and aminoazotoluene, have been reported as the direct results of the reaction of gaseous nitrosyl chloride with aniline and *o*-toluidine, respectively (184). Use of nitrosyl chloride in place of nitrite–sulfuric acid mixtures has been reported to decrease the time required for diazotization of amines (433).

The aromatic secondary amine, methylaniline, reacts with nitrosyl chloride to form *N*-nitrosomethylaniline (489). The aromatic tertiary amine, dimethylaniline, forms *p*-nitrosodimethylaniline (28, 185, 489). A complex blue product results from the addition of nitrosyl chloride to 4,4′-di(dimethylamino)triphenylamine (327).

Reaction of nitrosyl chloride with phenylhydrazine (488, 489) and α- and β-naphthylhydrazines (489) yields the corresponding azides.

2. Amides and imides (table 12)

The amino portion of an unsubstituted amide group reacts with nitrosyl chloride in a manner similar to the amino group of aliphatic amines. Nitrogen and water are evolved and acid chlorides are formed.

$$\mathrm{RCONH_2 + NOCl \rightarrow RCOCl + N_2 + H_2O}$$

This type of reaction has been obtained with acetamide, benzamide, urethan, and urea, the last yielding phosgene along with urea hydrochloride (485). Under similar conditions succinamide (576), oxamide (485), and oxanilide (158, 485) do not react, although oxamic acid is converted to oxalic acid (485). Asparagine, containing both amino and amide groups, reacts to form chlorosuccinic acid (485). Hippuric acid (benzoylglycine), like oxanilide, was reported to have failed to react (485), although various *N*-substituted amides or so-called acylamines react with nitrosyl chloride rapidly in an acetic acid–acetic anhydride solution containing potassium acetate to form nitrosoacylamines (158). Malonamide reacts only slowly at room temperature to yield nitrosomalonic acid but more rapidly at 100°C. to yield malonic acid (485). Under suitable conditions malonamides form isonitroso compounds, as discussed in Section VII, B, 6.

The diacyl compounds such as diacetyl-1,4-phenylenediamine form dinitroso derivatives. On the other hand, it has been reported that in the reaction of nitrosyl chloride with acetanilide, the aromatic nucleus rather than the nitrogen is attacked to form *p*-chloroacetanilide (489).

3. *Amino-substituted acids (table 13)*

In reaction with nitrosyl chloride, the amino groups in glycine and asparagine are displaced by chlorine atoms. The asparagine presumably is first converted to aspartic acid and then to chlorosuccinic acid (485, 487). Fumaric acid is also obtained by loss of hydrochloric acid from the chlorosuccinic acid. The same type of reaction was obtained with aspartic and glutamic acids in studies on the

TABLE 12

Amides and imides reacted with nitrosyl chloride

COMPOUND	REFERENCES	COMPOUND	REFERENCES
Acetamide	(485)	Hippuric acid (*N*-benzoylglycine)	(485)
4-Acetamidophthalic acid ethyl ester	(158)	2-Methoxydiacetyl-1,4-phenylenediamine	(158)
3-Acetamidobiphenyl	(158)	*m*-Nitroacetanilide	(158)
Acetanilide	(158, 489)	*o*-Nitroacetanilide	(158)
N-Acetylanthranilic acid ethyl ester	(158)	*p*-Nitroacetanilide	(158)
Asparagine (α-aminosuccinamic acid)	(485)	*p*-Nitrobenzanilide	(158)
Benzamide	(485)	Oxamic acid	(485)
Benzanilide	(158)	Oxamide	(485)
Carbamic acid ethyl ester (urethan)	(485)	Oxanilide	(158, 485)
Diacetyl-1,3-phenylenediamine	(158)	Phthalimide	(485)
Diacetyl-1,4-phenylenediamine	(158)	Succinimide	(485)
2,5-Dimethoxydiacetyl-1,4-phenylenediamine	(158)	Succinamide	(576)
2,4-Dinitroacetanilide	(158)	2,4,6-Trinitroacetanilide	(158)
		Urea	(485)

TABLE 13

Amino-substituted acids reacted with nitrosyl chloride

COMPOUND	REFERENCES
Asparagine (α-aminosuccinamic acid)	(485, 487, 523)
d- and *l*-Aspartic acids (aminosuccinic acid)	(152, 487, 523)
N-Carbethoxymethylanthranilic acid	(210)
N-Carbethoxymethylanthranilic acid ethyl ester	(210)
N-Carbethoxymethylanthranilic acid methyl ester	(210)
N-Carbomethoxymethylanthranilic acid	(210)
N-Carbomethoxymethylanthranilic acid methyl ester	(210)
N-Carboxymethylanthranilic acid	(210)
N,*N*'-Dimethylanthranilic acid methyl ester	(210)
d-Glutamic acid (α-aminoglutaric acid)	(153)
Glycine (aminoacetic acid)	(485)
N-Methylanthranilic acid methyl ester	(212)
N-Methyl-*N*-phenylglycine	(210)
N-Phenylglycine	(210)
Picramic acid (2-amino-4,6-dinitrophenol)	(375)
Sulfanilic acid (*p*-aminobenzenesulfonic acid)	(375)

Walden inversion (152, 153, 523). Treatment of methyl *N*-methylanthranilate with nitrosyl chloride gives the *m*-nitroso derivative (212). *N*-Phenylglycine, *N*-methyl-*N*-phenylglycine, carboxymethylanthranilic acid, and derivatives form nitroso compounds, with the nitroso group entering the ring rather than attaching to the nitrogen (210).

D. REACTIONS WITH HYDROXYL GROUPS (TABLE 14)

In reactions with hydroxy compounds, nitrosyl chloride functions as the acid chloride of nitrous acid, generally leading to the formation of nitrites. This reaction is identical in effect with the nitrosation of amino, methylene, and similar hydrogen-containing groups. In some cases, oxidation of the hydroxyl group takes place, together with chlorination in other parts of the molecule.

TABLE 14

Alcohols, glycols, and phenols reacted with nitrosyl chloride

COMPOUND	REFERENCES
Amyl alcohol	(87)
Benzyl alcohol	(300)
Butyl alcohol (1-butanol)	(300)
Chloretone (1,1,1-trichloro-2-methyl-2-propanol)	(300)
3-Chloro-1-propanol (trimethylene chlorohydrin)	(300)
Cyclohexanol	(336)
Ethyl alcohol (ethanol)	(300, 477)
Ethylene glycol	(300)
3-Ethyl-3-hexanol (diethylpropylcarbinol)	(87, 300)
3-Ethyl-3-pentanol (triethylcarbinol)	(300)
Glycerol	(300)
Isopropyl alcohol (2-propanol)	(300)
Methanol	(301)
Menthol (3-*p*-menthanol)	(300)
3-Methyl-3-pentanol (methyldiethylcarbinol)	(300)
2-Naphthol (and methyl ether)	(336)
d-3-Nonanol (*d*-ethyl-*n*-hexylcarbinol)	(391)
2-Octanol	(87)
d-2-Octanol	(286)
n-Octyl alcohol (1-octanol)	(87)
Phenol	(98, 336, 347, 478)
Tertiary butyl alcohol (2-methyl-2-propanol)	(300)
Thymol (3-hydroxy-*p*-cymene)	(300)

In the gas-phase reaction of methanol and nitrosyl chloride, an equilibrium is instantly established even at 25°C. (301). As has been pointed out (230), an incorrect free-energy value for nitrosyl chloride has been used in thermodynamic calculations relating to this equilibrium.

$$\mathrm{ROH + NOCl \rightleftharpoons RONO + HCl}$$

In view of the equilibrium, it is readily understood why alkyl nitrites plus hydrochloric acid formed a convenient means of preparing nitrosyl chloride *in situ* for organic reactions in much of the early work. Using dry pyridine as an acid acceptor in liquid-phase reaction makes high yields of nitrites possible from alcohols such as amyl, *n*-octyl (87), *d*-3-nonanol (*d*-ethyl-*n*-hexylcarbinol) (391), and tertiary alcohols such as 3-methyl-3-pentanol (methyldiethylcarbinol) and 3-ethyl-3-hexanol (diethylpropylcarbinol) (300). Although use of pyridine was not considered necessary for alcohols of low molecular weight, excepting tertiary ones, removal of the acid formed should prove beneficial in most cases in view of the indicated equilibrium-forming tendencies of the reaction. Under conditions used successfully with the above alcohols, glycerol, ethylene glycol, chloretone, menthol, trimethylene chlorohydrin, and benzyl alcohol do not yield nitrites (300). It is of note that *d*-2-octanol in reaction with nitrosyl chloride gives an 80 per cent yield of the dextrorotatory nitrite (286).

Hydroxyl groups attached to aromatic nuclei do not readily form nitrites. Compounds such as thymol (3-*p*-cymenol) (300) and phenol (347) form nitroso compounds in good yields instead of nitrites.

The formation of principally resinous products was reported in the reaction of nitrosyl chloride with phenol, 2-naphthol (some 1-nitroso compound formed), and cyclohexanol (336). Conversion of the hydroxyl group of the 2-naphthol to the methoxyl analog did not alter the results. On passing nitrosyl chloride gas into a cooled acetic acid solution of phenol, chloranil can be obtained (478). In this case the nitrosyl chloride evidently functions both as an oxidation and as a chlorination agent. It is not clear from the experimental details given why chloranil resulted in this case, while a 60 per cent yield of *p*-nitrosophenol was obtained in another (347) and a trichlorophenol in still another case (98). The use of glacial acetic acid rather than aqueous media and a large excess of nitrosyl chloride in the former case may have been responsible.

E. REACTIONS WITH MERCAPTO GROUPS (TABLE 15)

The reaction of thiols with nitrosyl chloride leads to the formation of thionitrites, which in many instances readily decompose to disulfides with the evolution of nitric oxide (299, 463).

$$\mathrm{RSH + NOCl \rightarrow RSNO + HCl}$$
$$\mathrm{2RSNO \rightarrow RSSR + 2NO}$$

Oxygen can promote thionitrite breakdown when the reaction with nitrosyl chloride is carried out in the presence of air (299).

$$\mathrm{2RSNO + O_2 \rightarrow RSSR + N_2O_4}$$

It has also been found that without a solvent, nitrosyl chloride reacts with thiols such as ethanethiol even at temperatures as low as −80°C. Disulfides and hydroxylamine result, apparently according to the following reaction (236, 299):

$$\mathrm{4RSH + NOCl \rightarrow 2RSSR + NH_2OH \cdot HCl}$$

Yields of ethyl thionitrite as high as 80 per cent were reported (299)

TABLE 15

Thiols, selenols, and derivatives reacted with nitrosyl chloride

COMPOUND	REFERENCES
1-Anthraquinonethiol mercury salt	(132, 405)
p-Benzenedithiol	(132, 405)
Benzenethiol (thiophenol)	(298, 463)
Benzenethiol lead salt	(463)
Benzenethiol mercury salt	(132, 298, 405)
p-Bromobenzenethiol	(132, 405)
p-Bromobenzenethiol lead salt	(405)
m-Bromobenzenethiol	(132, 405)
o-Bromobenzenethiol	(132, 405)
Butanethiol	(453)
Cetanethiol mercury salt	(132, 405)
p-Dimethylaminobenzenethiol	(132, 405)
p-Dimethylaminobenzenethiol lead salt	(405)
4,4-Dimercaptobiphenyl	(132, 405, 409)
4,4'-Dimercapto-2'-dimethylbiphenyl	(132, 405, 409)
Diphenylmethanethiol (thiobenzhydrol)	(132, 405)
Ethanethiol	(236, 298, 299, 463)
Ethanethiol lead salt	(463)
Ethanethiol mercury salt	(132, 298, 405)
Methanethiol lead salt	(463)
Methanethiol mercury salt	(132, 463)
o-Methoxybenzenethiol	(132, 405)
o-Methoxybenzenethiol lead salt	(405)
2-Methyl-1-propanethiol mercury salt	(132, 405)
2-Methyl-2-butanethiol mercury salt	(405, 409)
2-Methyl-2-butanethiol (*tert*-amylmercaptan)	(132, 405, 409)
2-Methyl-2-propanethiol (*tert*-butylmercaptan)	(132, 405, 409)
2-Methyl-2-propanethiol mercury salt	(405, 409, 411)
1-Naphthalenethiol mercury salt	(132, 405)
p-Phenylbenzenethiol	(132, 405)
p-Phenylbenzenethiol lead salt	(405)
1,3-Propanediselenolmercuri chloride	(132)
1,3-Propanediselenol mercury salt	(405)
1,3-Propanedithiol lead salt	(132, 405)
2-Propanethiol mercury salt	(132, 405)
2-Propene-1-thiol (allymercaptan)	(132, 405)
Sulfur compounds, removed by nitrosyl chloride	(229)
"Thiobiazoldihydrosulfide"	(132, 405)
"Thiobiazoldihydrosulfide monobenzyl ether"	(132, 405)
p-Toluenethiol	(132, 405)
o- and *m*-Toluenethiols (mixed)	(132)
Toluenethiol sodium salt	(132, 405)
Triphenylmethanethiol	(409)
Triphenylmethanethiol sodium salt	(132, 405, 409)

when 1,1,2,2-tetrachloroethane or decalin was used as a solvent at −40° to −60°C. In general, primary and secondary thionitrites are unstable and lead to disulfides (405). Tertiary thiols, such as 2-methyl-2-propanethiol, 2-methyl-

2-butanethiol, and triphenylmethanethiol, form stable thionitrites with nitrosyl chloride (409, 411). It has been said that nitrosyl chloride catalyzes the decomposition of thionitrites and is particularly unsuitable for the preparation of such simple thionitrites as ethyl and phenyl thionitrites from the corresponding thiols or mercury salts (298). However, the use of a solvent, as indicated above, appears to avoid the difficulty. Certain mercaptobiphenyls such as 4,4′-dimercaptobiphenyl and 4,4′-dimercapto-2,2′-dimethylbiphenyl form the corresponding thionitrites, which can be isolated although they are unstable (409). The stability and color, a characteristic dichroic green-red for tertiary aliphatic and aromatic thionitrites, are said to be influenced by ring substitution in aromatic thiols (132).

Thionitrites obtained from thiols and nitrosyl chloride at −10° and −5°C. have been suggested as Diesel fuel additives (453). Nitrosyl chloride has also been recommended for removal of sulfur compounds from aromatic hydrocarbons (229). This may or may not involve reactions with thiols.

F. REACTIONS WITH CARBON-TO-CARBON MULTIPLE BONDS

The reactions of this classification involve principally the addition of nitrosyl chloride to double bonds, i.e., chloronitrosation. The ease of addition of the nitroso group and chlorine atom to adjacent carbons is largely dependent upon structure. In some cases the adducts dimerize to white crystalline solids, often in equilibrium with the blue monomeric form. Isomerization to oximido structures yielding chloroöximes is feasible where the labile hydrogen on the carbon of nitroso group attachment is available. Some chlorinated olefins have been reported as forming chloronitro rather than chloronitroso compounds. Under sufficiently vigorous conditions, olefinic compounds are chlorinated or oxidized just as the saturated hydrocarbons are.

1. Alkenes, alkadienes, alkynes, and derivatives (tables 16 and 17)

The addition of nitrosyl chloride to compounds containing carbon-to-carbon double bonds has been studied extensively and on a large variety of compounds in addition to terpenes (see Section VII, F, 4). From early experiments with alkenes, it was concluded that solid adducts were not obtained with compounds of the type —CH═CH— and —CH═CH$_2$ but only with the more highly substituted ethylenes, such as 3-ethyl-2-pentene (227, 228). However, as techniques were improved, solid crystalline nitrosyl chloride adducts were obtained from ethylene (42), propylene (42), and 1-pentadecene (451) and many other olefinic compounds. It is true, however, that crystalline adducts are more readily formed with compounds of the type R$_2$C═CHR and R$_2$C═CR$_2$ than with those of the RCH═CHR structure (512). The nitrosyl chloride adduct of tetramethylethylene (2,3-dimethyl-2-butene) was first isolated many years ago as a blue solid, 2-chloro-2,3-dimethyl-3-nitrosobutane (468). Since this compound does not contain a labile hydrogen on the carbon bonding the nitroso group, isomerization to the oxime form cannot take place. The molecular weight and blue color indicate a true monomeric chloronitroso compound. It might be concluded that, owing to steric hindrance, formation of the bimolecular compound is prevented.

TABLE 16

Acyclic alkenes, alkynes, and alkadienes reacted with nitrosyl chloride

	COMPOUND	REFERENCES
C_2	Acetylene	(350)
	Ethylene	(42, 171, 192, 350, 484, 491)
	Chloroethylene (vinyl chloride)	(588)
	1,1-Dichloroethylene (vinylidene chloride)	(588)
	1,1,2-Trichloroethylene	(588)
C_3	1,3-Butadiene	(345, 346)
	Propene	(42, 171, 473, 484, 491)
	3-Chloropropene (allyl chloride)	(588)
C_4	2-Butene	(192, 228)
	2-Methylpropene (isobutylene)	(84, 113, 142, 228, 330, 331, 332, 345, 346, 484, 491, 588)
C_5	Amylene	(98, 493)
	Isoprene (2-methyl-1,3-butadiene)	(149)
	3-Methyl-1-butene	(227)
	2-Methyl-2-butene (trimethylethylene)	(429, 484, 491)
C_6	2,3-Dimethyl-2-butene (tetramethylethylene)	(97, 468)
	2-Hexene	(227, 484)
	2-Methyl-2-pentene	(227, 512)
	3-Methyl-2-pentene	(227, 512)
C_7	3-Ethyl-2-pentene	(227, 512)
	3-Heptene	(512)
	2-Methyl-2-hexene	(512)
C_8	Diisobutylene	(228)
	2,4-Dimethyl-4-hexene	(512)
	2,5-Dimethyl-2-hexene	(545)
	4-Ethyl-3-hexene	(228)
	2-Methyl-2-heptene	(512)
	4-Methyl-3-heptene	(228)
	2-Octene	(484)
	3-Octene	(512)
C_9	2,5-Dimethyl-4-heptene	(512)
	"Isononylene"	(345, 346)
	1-Nonene	(451, 473)
	2-Nonene	(512)
	3-Propyl-2-hexene	(228)
	2,3,5-Trimethyl-2-hexene	(512)
C_{10}	Diamylene	(227)
C_{11}	2,4,7-Trimethyl-4-octene	(512)

TABLE 16—*Concluded*

COMPOUND		REFERENCES
C_{12}	1-Dodecene	(43)
C_{13}	11-Methyl-1-dodecene	(43)
	1-Tridecene	(473)
C_{14}	1-Tetradecene	(43)
C_{15}	1-Pentadecene	(43, 451, 473)
C_{16}	1-Hexadecene	(43)
C_{18}	1-Octadecene	(43)
Olefins in general		(40, 41, 43, 44, 45, 69, 113, 264, 351, 450)

TABLE 17

Unsaturated ethers and ketones reacted with nitrosyl chloride

COMPOUND	REFERENCE
2,6-Dimethyl-2,5-heptadien-4-one (phorone)	(324)
Ethyl 3-ethyl-2-pentenyl ether (ethyl diethylallyl ether)	(227)
Ethyl 3-methyl-2-butenyl ether (ethyl dimethylallyl ether)	(227)
Ethyl 3-methyl-2-pentenyl ether (ethyl methylethylallyl ether)	(227)

Later investigators attributed chloro oxime structures to the white crystalline adducts obtained with nitrosyl chloride. It is probable that many of the reaction products described are in reality dimeric chloronitroso compounds (*cf.* 113, 142, 530). Although the branched-chain higher olefins are reported to give crystalline adducts more readily than normal olefins (512), stable dimeric crystalline compounds of 1-nonene, 1-tridecene, and 1-pentadecene can be prepared (473). Through oxidation studies on the propylene addition product leading to lactic acid, it has been concluded that the chlorine of the nitrosyl chloride adds principally to the β-carbon and the nitroso group to the α-carbon (113; *cf.* 473).

The yield of adduct is influenced greatly by the reaction conditions, particularly the temperature and the nature of the solvent (346, 451). For example, with 1-nonene, best results are obtained without a solvent at -20°C. Use of pentane as solvent decreases the yield, and almost no dimeric addition product is obtained using ether (451). The solvent used appears to influence also the distribution between solid (dimeric) and liquid (colored monomer) adduct (346). When the olefinic compounds are sufficiently reactive, crystalline products are probably most conveniently produced by passing gaseous nitrosyl chloride into an excess of the liquid reactant at a temperature below 0°C. or under superatmospheric pressure at 25°C. (113). With compounds such as ethylene and propylene, this procedure does not lead to good results. An effective procedure for these materials is to use solvents such as methylene chloride, chloroform, or carbon tetrachloride with metallic nickel, nickelous chloride, ferric chloride, or cuprous chloride as a catalyst (42, 171). Nitromethane and nitroethane (83) and liquid sulfur dioxide (8) have been used as reaction solvents to obtain high yields of crystalline nitrosochlorides from limonene and other olefins. Activated clay, bauxite, or carbon has been used to accelerate formation of the adduct of nitrosyl chloride and isobutylene (330, 331, 332). Unsaturated aliphatic ethers such as ethyl 3-ethyl-2-pentenyl ether, ethyl 3-methyl-2-butenyl ether, and ethyl 3-methyl-2-pentenyl ether also readily form white solid adducts (227) (table 17).

In contrast to the nitrosyl chloride addition reactions which take place with olefinic groups at low temperatures, chlorination or oxidation effects are obtained at elevated temperatures and in some cases even at room temperature.

The reported formation of nitro derivatives from nitrosyl chloride and some chlorinated olefins (588) apparently involves oxidation of the initially formed nitroso compound.

At temperatures of 300°C. and above, the reaction of nitrosyl chloride and ethylene or acetylene leads mainly to addition of chlorine, forming 1,2-dichloroethane and 1,2-dichloroethylene, respectively (192, 350) (see Section VII, B, 1).

Reaction of nitrosyl chloride with 2-methylpropene (isobutylene) has been used as the first step in the synthesis of methacrylonitrile (84, 452), methacrylaldoxime (113), or alkoxyisobutyraldoximes (100).

Addition of nitrosyl chloride to higher-molecular-weight olefins or derivatives and improvements in the procedures have formed the basis of a number of patents for the manufacture of surface-active agents (37, 38, 39, 40, 41, 43, 44, 45, 69, 351, 450). Generally the nitrosyl chloride addition products of the higher-molecular-weight olefins are found to be liquids. Diolefins such as phorone (2,6-dimethyl-2,5-heptadien-4-one) add nitrosyl chloride to one or both double bonds (324). 1,3-Butadiene forms an unstable adduct (345, 346). On the other hand, nitrosyl chloride is said to catalyze the polymerization of isoprene (2-methyl-1,3-butadiene) (149).

2. Unsaturated cyclic hydrocarbons and derivatives (table 18)

Compounds such as cyclopentadiene (422), dicyclopentadiene (287), and styrene (388) form crystalline adducts with nitrosyl chloride. Similarly a number of more complex materials, such as β-bromostyrene, stilbene, 1,1-diphenylethylene, 1,4-dihydronaphthalene, p-ethoxy-β-methylstyrene, and 2,2,4,β-tetramethylstyrene, form solid adducts (276, 277, 388). While the adducts result from reaction with nitrosyl chloride in the cold and with solvents, chlorination and oxidation effects are obtained at elevated temperatures and at times at room temperature. (1,2-Dichloroethyl)benzene ($C_6H_5CHClCH_2Cl$) and β-nitrostyrene ($C_6H_5CH{=}CHNO_2$) are produced from styrene at room temperature (387). Similar products are obtained with variously substituted styrenes, 1,1-diphenyl-

TABLE 18

Unsaturated cyclic hydrocarbons and derivatives reacted with nitrosyl chloride

COMPOUND	REFERENCES
Acenaphthalene	(484)
Anethole (*p*-propenylanisole)	(388, 484, 493, 530)
Benzylideneacetophenone	(388)
β-Bromostyrene	(387, 388)
α, β, and γ-Caryophyllenes	(129, 426)
α-Chlorostyrene	(387)
β-Chlorostyrene	(387)
β-Cyanostyrene	(387)
1,3-Cyclohexadiene	(23)
Cyclohexene	(8, 23, 345, 346, 387, 388, 533)
10-Cyclohexyl-1-decene	(43)
Cyclopentadiene	(422)
7-Cyclopentyl-5-ethyl-1-heptene	(43)
Dicyclopentadiene	(287)
1,2-Dihydronaphthalene	(456)
1,4-Dihydronaphthalene	(388)
p,β-Dimethylstyrene	(276)
2,4-Dimethyl-β-tetradecylstyrene	(276)
1,2-Diphenylacetylene	(388)
1,1-Diphenylethylene	(387, 388)
1,1-Diphenyl-2-methyl-1-propene	(387)
1,1-Diphenyl-1-propene	(387)
p-Ethoxy-β-methylstyrene	(277)
1-Ethylcyclohexene	(537)
1-Ethylcyclopentene	(538)
β-Ethyl-2,4-dimethylstyrene	(276)
Ethylidenecyclohexane	(537, 542)
1-Ethylidene-3-methylcyclohexane	(537, 542)
1-Ethylidene-4-methylcyclohexane	(382, 537, 538)
Ethylidenecyclopentane	(538)
p-Ethylstyrene	(276)
β-Ethyl-2,4,6-trimethylstyrene	(276)
Eugenol (4-allyl-2-methoxyphenol)	(484)
Eugenol ethyl ether (4-allyl-1-ethoxy-2-methoxybenzene)	(484)
Indene	(345, 346, 388, 456)
1-Isopropylcyclohexene	(537)
1-Isopropylcyclopentene	(536)
Isopropylidenecyclohexane	(537)
Isopropylidenecyclopentane	(536)
Isosafrole (1,2-methylenedioxy-4-propenylbenzene)	(484, 530)
1-Methylcycloheptene	(534)
Methylenecycloheptane	(534)
Methylenecyclohexene	(535)
Methylenecyclopentane	(535)
1-Methylene-4-methylcyclohexane	(538)
3-Methylindene	(531)
1-Methyl-2-methylenecyclohexane	(535)

TABLE 18—*Concluded*

COMPOUND	REFERENCES
1-Methyl-3-methylenecyclohexane	(535)
1-Methyl-4-methylenecyclohexane	(535)
3-Methyl-2-phenyl-1-butene	(387)
1-Methyl-4-propylidenecyclohexane	(537)
p-Methylstyrene	(276, 387)
1-(β-1'-Naphthylethyl)cyclopentene	(108)
β-Nitrostyrene	(387, 484)
Phenanthrene	(484)
2-Phenyl-2-butene	(388)
1-(β-Phenylethyl)cyclohexene	(108)
1-Phenyl-2-methyl-1-propene	(388)
1-Phenylpropene	(388)
2-Phenylpropene	(387, 388)
4-Propenylveratrole (isoeugenol methyl ether)	(530)
1-Propylcyclohexene	(537)
Propylidenecyclohexane	(537)
1-Propylidene-3-methylcyclohexane	(537)
Safrole (4-allyl-1,2-methylenedioxybenzene)	(484)
Stilbene	(388, 484)
Styrene (phenethylene)	(387, 388, 484, 491)
2,2,4,β-Tetramethylstyrene	(276)
Tetraphenylethylene	(387)
p-Tolylethylene	(388)

ethylene, etc. On the other hand, tetraphenylethylene is unattacked by nitrosyl chloride at ordinary temperatures. At 150°C. dichlorodiphenylmethane and chlorinated ring compounds result (387). Diphenylacetylene (tolane) in reaction with nitrosyl chloride yields principally benzoyl chloride (389).

Extensive tests were carried out by Wallach *et al.* on the addition of nitrosyl chloride to the double bonds of various unsaturated cyclohexane and cyclopentane derivatives related to the cyclic terpenes. The characteristics of many of the adducts were studied and their behavior with various agents described (530, 537, 542, 544). Most of the compounds, such as 1-ethylidene-4-methylcyclohexane (382, 537, 538), ethylidenecyclohexane (537, 542), propylidenecyclohexane (537), and 1-propylidene-3-methylcyclohexane (537), give high yields of adduct with nitrosyl chloride and in general behave like the closely related terpenes.

3. Unsaturated acids and derivatives (*table 19*)

Unsaturated fatty acids and their derivatives, such as esters, amides, and nitriles, add nitrosyl chloride at the double bond (38), just as olefins do. Esters such as dimethylallylmalonic acid diethyl ester also form adducts (227), but cinnamic, fumaric, and maleic acids do not form such addition products (484).

Nitrosyl chloride is useful as an analytical agent in determining the unsaturation of fats and fatty acids. A review of information on the determination of nitrosyl numbers and on the addition of nitrosyl chloride to unsaturated hydrocarbons was made by Kaufmann and Rover (264).

4. Cyclic terpenes (table 20)

Much of the early work on the reactions of nitrosyl chloride with organic compounds concerned its addition to the double bonds of cyclic terpenes. Sufficient work has been done on pinene, menthenes, and the menthadienes to warrant detailed discussion under separate headings.

TABLE 19

Unsaturated acids and derivatives reacted with nitrosyl chloride

COMPOUND	REFERENCES
Abietic acid	(18)
Cinnamic acid	(484)
Cinnamic acid ethyl ester	(484)
Citronellonitrile	(541)
Crotonic acid	(484)
3,3-Diethylallylmalonic acid diethyl ester	(227)
3,3-Dimethylallylmalonic acid diethyl ester	(227)
Elaidic acid	(484)
Erucic acid	(339, 484)
Fumaric acid	(484)
Isocrotonic acid	(484)
Linoleic acid	(339)
Linolenic acid	(339)
Maleic acid	(484)
Oleic acid	(339, 484)
Tiglic acid	(339)
Unsaturated fatty acids, general	(264, 339)
Unsaturated fatty acid esters, amides, nitriles, salts, acids, chlorides	(38)

Menthenes and derivatives: Solid nitrosyl chloride adducts have been obtained from a number of menthenes, including 1-*p*-menthene (8, 520), 3-*p*-menthene, 1-*m*-menthene, 2(8)-*o*-menthene, and 4(8)-*p*-menthene (537). The 3(8)-*m*-menthene did not yield a solid but formed a blue oil. 8(9)-*p*-Menthen-1-ol (β-terpineol) also forms a solid adduct in good yield (534). Dihydrocarvone (8(9)-*p*-menthen-2-one) forms a blue adduct indicative of the presence of the 8(9) tertiary carbon double bond (26). However, 4(8)-*p*-menthen-3-one (pulegone) gives a bisnitroso compound even in the cold. With more vigorous treatment the isopropyl group is cleaved and a 2,4-dioximidoketone results (27). (For the reactions of 3-*p*-menthanone (menthone), 2-camphanone (camphor), and saturated terpenes, see Section VII, B, 4 (29).)

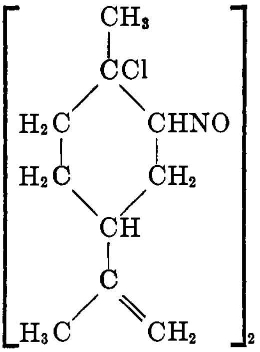
Menthadienes: The *d*- and *l*-limonenes (1,8(9)-*p*-menthadienes), as well as

TABLE 20

Cyclic terpenes and derivatives reacted with nitrosyl chloride

COMPOUND	REFERENCES
"Apofenene"	(86)
Camphene (3,3-dimethyl-2-methylenenorcamphane)	(525)
Carone	(25)
α-Fencholenonitrile	(540)
β-Fencholenonitrile	(540, 541)
Hydrocarbon, C_9H_{15}, from sodium fencholate	(539)
3,8(9)-*p*-Menthadiene	(382)
1,8(9)-*p*-Menthadiene (limonene)	(8, 82, 83, 114, 129, 190, 200, 289, 297, 314, 326, 423, 484, 486, 525, 526, 527, 528, 529)
1,5-*p*-Menthadiene (α-phellandrene)	(162, 163, 164, 165, 166, 167, 575)
1(7)-2-*p*-Menthadiene (β-phellandrene)	(165, 168, 532, 575)
1,8(9)-*p*-Menthadien-6-ol(carveol)	(25)
1-*m*-Menthene	(537)
1-*p*-Menthene	(8, 520)
3(8)-*m*-Menthene	(537)
2(8)-*o*-Menthene	(537)
3-*p*-Menthene	(537)
4(8)-*p*-Menthene	(537)
3-*p*-Menthen-8-ol	(382)
8(9)-*p*-Menthen-1-ol(β-terpineol)	(534)
4(8)-*p*-Menthen-1-ol acetate	(24)
8(9)-*p*-Menthen-2-one (dihydrocarvone)	(26)
4(8)-*p*-Menthen-3-one (pulegone)	(27)
Pinol	(546)
Pulegenonitrile	(541)
2,6,6-Trimethylbicyclo-[3.1.1]-2-heptene (α-pinene)	(115, 129, 176, 182, 290, 291, 292, 293, 314, 320, 423, 426, 430, 474, 475, 481, 482, 483, 484, 525, 527, 545)

the inactive modification (*dl*-limonene or dipentene), readily form the bimolecular chloronitroso adducts.



Of particular interest is the formation of α- and β-forms of each of the optical modifications. These appear to be stereoisomers (289, 297, 326, 484, 486, 525, 526, 529). The locations of the chlorine and nitroso groups in the adducts are indicated by the formation of carvone oxime, 6,8(9)-*p*-menthadien-2-one oxime (190). The α- and β-forms of adduct yield the same oxime but of opposite optical activity from the original adduct (326). Indications that the mode of preparation, in this case the amount of hydrochloric acid used with amyl nitrite, influences the proportions of α- and β-isomers obtained have been reported in studies on *d*-limonene (114, 529). Less acid appeared to produce more of the α-isomers and *vice versa* (114). Since the solubilities of the two isomers are quite different, yields might be influenced by this alone if conditions of preparation are changed. Various modifications of procedures have been used to obtain chloronitrosolimonenes and to separate these menthadienes from natural products (129, 423, 527). It is reported that if aqueous systems are avoided, better yields are obtained (314, 423). Indications that oxidation products of limonene can result during the preparation of the nitrosyl chloride derivative under some conditions have been reported (200). *d*-Limonene constitutes about 95 per cent of orange and grapefruit oils and is potentially available in large quantities as a by-product of the citrus industry. Recently (82), attention has been given to its conversion *via* reaction with nitrosyl chloride, dehydrochlorination, and hydrolysis to *l*-carvone, the major constituent of oil of spearmint.

The terpene β-phellandrene (1(7),2-*p*-menthadiene) also forms a crystalline chloronitroso compound (165, 168, 575). The 1,5-*p*-menthadiene, α-phellandrene, on the other hand, does not. The difference in behavior has been suggested as a means of detecting the former in a mixture of the two menthadienes (575). A solid product is also obtained in the reaction of nitrosyl chloride with 3,8(9)-*p*-menthadiene (382).

α-Pinene (2,6,6-trimethylbicyclo-[3.1.1]-2-heptene), in its dextro, levo, or inactive form, gives a white crystalline bimolecular adduct with nitrosyl chloride. Nitrosyl chloride *per se* in organic solvents such as chloroform and petroleum ether and alkyl nitrites with acids has been used to obtain the adduct (115, 293, 320, 475, 481, 484, 545). Yields have been low with the highly optically active forms but generally about 50 per cent with optically inactive mixtures (129, 182, 290, 291, 292, 293, 426, 430, 474, 481, 482, 525). However, yields of the order of 90 per cent have been reported (314, 423). There is evidence that the presence of a small amount of water is necessary to catalyze adduct formation in organic solvents (475). While Tilden (426, 481) believed the heat of inversion of some of the compound caused loss of adduct with optically active pinenes, Lynn (320) and Kremers and Smith (292) considered the lower yields of adducts to be due to the solubility of active chloronitrosopinenes in the solvents used for the reaction. An optically active chloronitrosopinene (dextrorotatory as original pinene) in 15 per cent yield was isolated by an improved procedure and offered as proof that poor yields of adducts with pinene of high rotation had previously been due to failure to isolate the product because of high solubility in most organic solvents (320). No additional product was obtained on rapidly mixing filtrates from nitrosyl chloride adduct preparations of *d*- and *l*-pinenes (182), although enhanced yields of adduct are obtained if dextro and levo forms are mixed and then reacted with nitrosyl chloride (292, 481). It has been found that oxidation products of α-pinene are produced in the preparation of chloronitrosopinene and may account in part for the relatively low yields of adduct (30 per cent) under certain conditions (545).

The nitrosyl chloride adducts of *dl*-, *d*-, and *l*-pinenes (adducts have corresponding rotatory powers) react with aniline (475) as well as methylaniline (481, 482) to regenerate the original *dl*- (527), *d*- (320), or *l*-pinene (475). The regenerated pinene can be recombined with nitrosyl chloride (481, 483, 527).

The reaction of nitrosyl chloride with α-pinene to form the adduct has been of value in the identification of this terpene in various oils (176, 527).

Pinol ($C_{10}H_{16}O$), the oxidation product of pinene, still retains a double bond which reacts with nitrosyl chloride to form a solid dimeric product (545, 546).

G. REACTIONS WITH GROUPS NOT CLASSIFIED (TABLE 21)

1. Azines

Nitrosyl chloride formed from acetyl chloride and an organic nitrite reacts with azines such as benzaldehyde azine, $C_6H_5CH{=}NN{=}CHC_6H_5$, and *p*-isopropylbenzaldehyde azine, $C_3H_7C_6H_4CH{=}NN{=}CHC_6H_4C_3H_7$, to form the corresponding benzylidene chloride, the corresponding benzaldehyde, nitrogen, and nitrous oxide. Salicylaldehyde azine or *o*-methoxybenzaldehyde azine reacts little or not at all under the same conditions (169).

$$RCH{=}NN{=}CHR + 2NOCl \rightarrow RCH_2Cl_2 + RCHO + N_2 + N_2O$$

2. Carbon and carbon monoxide

Nitrosyl chloride does not react with dry elemental carbon at ordinary temperatures. In fact, activated carbons have served as catalysts for other reactions even at somewhat elevated temperatures (252). Moist carbon in the form of brown coal, coke, wood, or charcoal reacts with nitrosyl chloride in accordance with the following equation (216).

$$4NOCl + 2H_2O + C \rightarrow 4NO + 4HCl + CO_2$$

Similarly, carbon monoxide is converted to carbon dioxide with concomitant formation of phosgene, using nitrosyl chloride with moist charcoal as a catalyst (252). Phosgene also results on reaction of carbon monoxide and nitrosyl chloride at 350°C. (389). By substituting metal oxides, carbonates, or sulfides for water in reaction with carbon monoxide and nitrosyl chloride, the metal chlorides and carbon dioxide are obtained (215). For example:

$$6NOCl + 3CO + Al_2O_3 \xrightarrow{500°C.} 2AlCl_3 + 6NO + 3CO_2$$

3. Cyanogen and hydrogen cyanide

At 200°C., cyanogen reacts with nitrosyl chloride to yield cyanogen chloride and carbon dioxide, while hydrogen cyanide under the same conditions yields cyanogen chloride, nitric oxide, and hydrogen chloride (389).

TABLE 21

Miscellaneous compounds reacted with nitrosyl chloride

COMPOUND	REFERENCSE
Azines:	
Benzaldehyde azine	(169)
p-Isopropylbenzaldehyde azine	(169)
o-Methoxybenzaldehyde azine	(169)
Salicylaldehyde azine	(169)
Carbon	(216)
Carbon monoxide	(215, 252, 389)
Cyanogen and hydrogen cyanide	(389)
Diazo compounds:	
Ethyl diazoacetate	(444)
Free radicals:	
Triphenylmethyl	(427)
Heterocycles:	
Antipyrine (1,5-dimethyl-2-phenyl-3-pyrazolone)	(300, 336)
Hydroxylamine derivatives:	
Nitrosophenylhydroxylamine	(358)
Metalloörganic compounds:	
Acetoxymercuridurene	(445)
Acetoxymercuriisodurene	(445)
Acetoxymercurimesitylene	(445)
Acetoxymercuriprehnitene	(445)
Acetoxymercuripseudocumene	(445)
2-Chloromercurifuran	(183)
Diphenylchloroarsine	(400)
Diphenylmercury	(22)
10-Methyl-9,10-dihydrophenarsazine	(400)
Phenylmagnesium bromide	(369)
Triphenylarsine	(400)
Zinc ethyl	(75)
Schiff bases:	
N-Benzylideneaniline	(513)
N-Benzylidene-*p*-bromoaniline	(513)
N-Benzylidene-α-naphthylamine	(513)
N-Enanthylideneaniline	(513)
Silver salts of organic acids:	
Silver acetate	(161)
Silver benzoate	(161)
Silver cyanate	(386)
Silver formate	(161)

TABLE 21—*Concluded*

COMPOUND	REFERENCES
Silver salts of organic acids—*Concluded:*	
Silver oxalate	(386)
Silver propionate	(161)
Silver thiocyanate	(386)

4. Diazo compounds

Nitrosyl chloride reacts with ethyl diazoacetate to form ethyl chloroacetate and a polymeric nitrile oxide, oxalic ethyl ester nitrile oxide ($C_2H_5O_2CC{\equiv}NO$) (444).

$$N_2CHCOOC_2H_5 + NOCl \rightarrow HCl + N_2 + ON{\equiv}CCOOC_2H_5$$
$$N_2CHCOOC_2H_5 + HCl \rightarrow CH_2ClCOOC_2H_5 + N_2$$

5. Free radicals

Reaction of gaseous nitrosyl chloride with a solution of triphenylmethyl forms both nitrosotriphenylmethane and chlorotriphenylmethane. Chlorotriphenylmethane and nitrosyl chloride combine to form a deep yellow-brown addition product (427).

6. Heterocyclic compounds

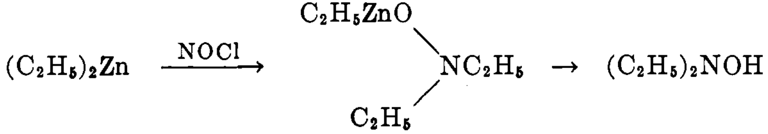
Antipyrine, 1,5-dimethyl-2-phenyl-3-pyrazolone, reacts with nitrosyl chloride to produce a high yield of 4-nitrosoantipyrine (300, 336).

7. Hydroxylamine derivatives

The salt of nitrosophenylhydroxylamine in reaction with nitrosyl chloride produces phenyldiazonium nitrate (358).

8. Metalloörganic compounds

Nitroso compounds are formed in yields as high as 90 per cent by the reaction of nitrosyl chloride, from ethyl nitrite and hydrochloric acid, on acetoxymercuri polymethylbenzenes. The nitroso derivatives of durene (1,2,4,5-tetramethylbenzene), isodurene (1,2,3,5-tetramethylbenzene), prehnitene (1,2,3,4-tetramethylbenzene), mesitylene (1,3,5-trimethylbenzene), and pseudocumene (1,2,4-trimethylbenzene) were obtained in this way (445). On the other hand, no definite product could be isolated from the reaction of 2-chloromercurifuran with nitrosyl chloride in chloroform at −30°C. (183). Nitrosyl chloride reacts with zinc ethyl to form a metallic derivative readily converted to the *N*-dialkylhydroxylamine (75).

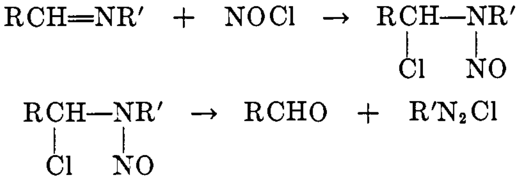


$$(C_2H_5)_2Zn \xrightarrow{NOCl} \overset{C_2H_5ZnO\diagdown}{\underset{C_2H_5\diagup}{NC_2H_5}} \rightarrow (C_2H_5)_2NOH$$

Nitrosyl chloride reacts with trivalent arsenic compounds such as 10-methyl-5,10-dihydrophenarsazine, triphenylarsine, and diphenylchloroarsine in organic media to form 10-methyl-10-chloro-10-hydroxy-5,10-dihydrophenarsazine, triphenylchlorohydroxyarsine, and tetraphenyltetrachloroarsine oxide, respectively (400). Diphenylmercury reacts with nitrosyl chloride, as the $SnCl_4 \cdot 2NOCl$ complex, to form nitrosobenzene (22). Bromobenzene was converted to nitrosobenzene in 56 mole per cent yield by forming the Grignard reagent and then reacting with nitrosyl chloride (369).

9. Schiff bases

Nitrosyl chloride adds to various Schiff bases, such as *N*-benzylideneaniline, *N*-enanthylideneaniline, *N*-benzylidene-*p*-bromoaniline, and *N*-benzylidene-α-naphthylamine, in anhydrous media to form unstable addition products which decompose into the original aldehyde and the diazonium chloride of the original amine (513).



$$\mathrm{RCH{=}NR'} + \mathrm{NOCl} \rightarrow \underset{\mathrm{Cl}}{\underset{|}{\mathrm{RCH}}}\text{—}\underset{\mathrm{NO}}{\underset{|}{\mathrm{NR'}}}$$

$$\underset{\mathrm{Cl}}{\underset{|}{\mathrm{RCH}}}\text{—}\underset{\mathrm{NO}}{\underset{|}{\mathrm{NR'}}} \rightarrow \mathrm{RCHO} + \mathrm{R'N_2Cl}$$

10. Silver salts of organic acids

The silver salts of acetic, propionic, and benzoic acids react with nitrosyl chloride to yield acetyl, propionyl, and benzoyl nitrites, respectively. Reaction of nitrosyl chloride with silver formate results in an explosion (161). Nitrosyl chloride at room temperature decomposes silver cyanate to silver chloride, carbon dioxide, and nitrogen; silver thiocyanate to silver chloride, nitric oxide, and polymeric thiocyanogen; and silver oxalate to silver chloride, carbon dioxide, and nitric oxide (386).

H. USE IN THE STUDY OR TREATMENT OF NATURAL PRODUCTS (TABLE 22)

1. Bleaching of flour

Nitrosyl chloride was first suggested some years ago as an agent for bleaching flour. It is currently used to a limited extent in conjunction with chlorine. A number of patents have been obtained on improved mixtures containing chlorine and a small proportion of nitrosyl chloride (569, 570, 572, 573). Methods and equipment for the use of these mixtures have also been the subject of a number of patents (194, 221, 561, 564, 568, 571). Modifications involving the use of the chlorine and nitrosyl chloride with ammonia (222, 223) and the use of nitrosyl chloride together with nitrogen tetroxide have also been patented (567). Benefits have been claimed for the use of inert gases, air, oxygen, or nitrogen as diluents and carriers for nitrosyl chloride and chlorine–nitrosyl chloride mixtures (562. 563, 565, 566). As a means of adding a solid or liquid nitrosyl chloride-containing material to flour for bleaching purposes, complexes of nitrosyl chloride with stannic chloride or ferric chloride and solutions of the chloride in benzene or glacial acetic acid have been suggested (367, 368).

Wesener and Teller (574) reported that the use of nitrosyl chloride for bleaching does not affect the bread-making qualities of the flour nor does the bread from the bleached flour have impaired nutritional value or cause digestive disturbances of any kind. One advantage of the use of nitrosyl chloride is that it is readily liquefied and yet has a convenient autogenous pressure for handling (15–20 lb. per square inch). Nitrosyl chloride is said to have an action similar to that of oxidizing agents such as chlorine, benzoyl peroxide, and nitrogen peroxide (233).

TABLE 22

Natural products treated with nitrosyl chloride

PRODUCT	REFERENCES
Essential oils	(129, 162, 163, 164, 165, 166, 167, 176, 177, 426, 479, 480, 490)
Flour	(194, 221, 222, 223, 233, 367, 368, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574)
Petroleum products	(302, 303, 304, 305, 306, 307, 308, 309)
Rubber	(550)
Wool	(199, 270)

Flour bleached with nitrosyl chloride has not caused running fits in dogs, as has flour bleached with nitrogen trichloride (13, 15, 17).

2. Essential oils

Nitrosyl chloride often has been used to separate crystalline adducts from various natural products including turpentines and essential oils such as oil of sage, oil of bergamot, oil of lavender, and oil of lemon (176, 177, 479, 480, 490). A series of studies on the essence of *Bupleurum fruticosum*, an herb of the carrot family, led to the identification of α-phellandrene through the formation of the chloronitroso compound and conversion to the related dihydrocumaldehyde (162, 163, 164, 165, 166, 167). Nitrosyl chloride adducts of α-, β-, and γ-caryophyllenes were obtained from clove stalk oil (129, 426).

3. Petroleum products

In a series of patents held by Lelgemann, it is claimed that the use of nitrosyl chloride in conjunction with other catalysts in hydrocarbon cracking enhances the yield of gasoline and greatly reduces carbon and tar deposition. The catalysts studied included: calcium oxide plus nitrosyl chloride (304, 306, 309); aluminum chloride plus nitrosyl chloride (302, 303, 305, 308); aluminum plus nitrosyl chloride (304, 309); ferric chloride plus aluminum chloride plus nitrosyl chloride (303, 307); ferric chloride plus nitrosyl chloride (303, 308); aluminum alloys plus nitrosyl chloride (309); bauxite plus nitrosyl chloride (304).

4. Rubber

The reaction of nitrosyl chloride with natural rubber in benzene led to a glue-like product which evolved a gas and gave mainly unchanged rubber on precipitation with absolute alcohol (550).

5. Shrinkproofing wool

Nitrosyl chloride has been found to render wool less subject to shrinking and felting (199, 270). The process is evidently a controlled chlorination of the wool.

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