portions of tribromhydrin into a flask containing powdered potassium hydroxide. The flask is heated in an oil bath kept at 145° to 150° C., and at this temperature the reaction is complete. The oil is then steam-distilled by cooling the reaction flask to 130° C., adding water, and distilling. Upon redistilling the oil, the fraction boiling between 139° and 141° C. is collected. The yield as given by Gustavson is one-fifth of the original tribromhydrin used. In our work a 28% yield was obtained.

Propadiene is readily made by dropping 1,2-dibrompropylene into a flask containing zinc dust and 80% alcohol. The flask is heated on a water-bath under a reflux condenser. The apparatus used was essentially that described by us in connection with the preparation of methyl acetylene.[1] A 76% yield of pure propadiene was obtained. Twenty Gms. of the dibrompropylene gives about two liters of propadiene.

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THE CHEMISTRY OF NITROSYL CHLORIDE.*

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The remarkable stability of nitrosyl chloride, coupled with the contradictory fact that it easily reacts with numerous substances, makes the subject of its chemical behavior decidedly interesting. There is probably no known compound which provides a greater variety of reactions compared to the simplicity of its structure and to the resistance shown toward decomposition by physical agencies. Furthermore, few organic or inorganic compounds fail to react with nitrosyl chloride in some way or other. We are presenting this short review of the known facts as introductory to an extensive investigation of its general behavior.

Nitrosyl chloride has been prepared in a variety of ways,† all depending upon the reaction of chlorine or of a chloride with an oxide or acid of nitrogen or with some simple nitrogen derivative. Undoubtedly most of these are meritorious and efficient for certain purposes, but the best practical method for general use is the reaction of nitrosyl sulphate upon sodium chloride.[9] The former can easily be produced by saturating sulphuric acid with the vapors from aqua regia or by heating a mixture of nitric and sulphuric acids with sulphur, the latter being a modification of a method by Girard and Pabst.[23]

So manufactured, nitrosyl chloride is a reddish brown gas with a characteristic odor, condensing to a dark red liquid boiling[74] at —5.8° C., and solidifying to blood red crystals[46] melting at[49] —60° to —61° C. The liquid has a specific gravity[29] of 41.165 at —12° C., and a critical temperature[49] of 163-4° C. The absorption spectrum has been investigated by Manganini.[33] Other physical constants are given in the references cited. The vapor pressure agrees with the formula NOCl at all temperatures up to 700° but above this it rapidly becomes dissociated[34,35]

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[1] Tapley and Giesy, JOUR. A. PH. A., February 1926, p. 115.
* Scientific Section, A. PH. A., Des Moines meeting, 1926.
† See references, 2, 3, 4, 5, 7, 9, 12, 15, 23, 26, 27, 28, 29, 33, 41, 47, 50, 53, 55, 59, 60, 61, 63, 64, 69, 73, 75.

until at 985° it is nearly 50 per cent decomposed into nitric oxide and chlorine. It is thus seen that nitrosyl chloride is one of the most stable of nitrogen compounds.

Water decomposes it without the formation of gas in the same way as acetyl chloride,

$$NOCl + H_2O \rightarrow HONO + HCl$$
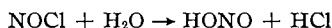
The mechanism of this hydrolysis has been examined by Noyes.[76]   Bases form chlorides and nitrites.   Sulphuric acid reacts to give nitrosyl sulphate and hydrogen chloride.   Some, but not all, of the metals and their oxides are converted into chlorides, setting free nitric oxide, the salts thus formed in many cases combining with more nitrosyl chloride to stable molecular addition products, which are decomposed by water with the formation of nitric oxide and hydrogen chloride.[1,9,14,36,46,71]   Thus tin or stannic chloride react

$$Sn + 6NOCl \rightarrow SnCl_4.2NOCl + 4NO$$
$$SnCl_4 + 2NOCl \rightarrow SnCl_4.2NOCl$$
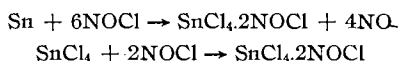
The most interesting reactions, however, are those with organic compounds. In general these may be divided into three groups: addition; condensation with
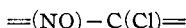
$$=(NO) - C(Cl)=$$

the elimination of water; condensation with the formation of hydrogen chloride.

(1) $=C=C= + NOCl \rightarrow =C(NO) - C(Cl)=$
(2) $RH_2 + ONCl \rightarrow RNCl + H_2O$
(3) $RH + ClNO \rightarrow RNO + HCl$

Secondary reactions may modify these types considerably.

The addition to unsaturated compounds has been known for many years[15] and is of great assistance to investigation of the volatile oils and their components, having been developed chiefly through the work of Wallach and of Baeyer.   The true nitroso compounds which are blue are but seldom obtained as the product because they rearrange to isonitroso compounds or oximes.   Upon hydrolysis the latter give hydroxylamine and a ketone or aldehyde.

$$R.CH(NO).CH(Cl)R \rightarrow R.C(=NOH).CH(Cl)R \rightarrow NH_2OH + R.C(=O).CH(Cl)R$$

The primary amines react by true condensation[42,43,44] forming water and a diazo compound, which in the case of the alkyl amines, decomposes giving nitrogen

$$R.NH_2 + NOCl \rightarrow H_2O + R.N=N.Cl \rightarrow RCl + N_2$$
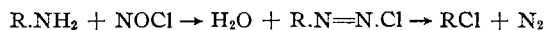
Thus urea forms phosgene and propyl amine forms propyl chloride.   As far as can be learned, no other compounds have been found to condense with nitrosyl chloride through the oxygen group.

The splitting out of hydrogen chloride is much more common.   Phenol,[10] acetanilide,[10] dimethyl aniline[12,13], and ethyl aniline [11] react in para position to give a nitroso compound
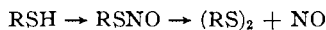
$$C_6H_5.N(CH_3)_2 + NOCl \rightarrow NO.C_6H_4.N(CH_3)_2$$
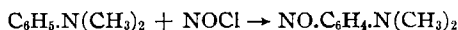
Secondary amines[44] form nitrosamines

$$R_2NH + NOCl \rightarrow R.N.NO + HCl$$

while acetone[28] and acetophenone[28] form nitroso and, by rearrangement, isonitroso derivatives

$$CH_3.CO.CH_3 \rightarrow CH_3.CO.CH_2NO \rightarrow CH_3.CO.CH{=}NOH$$
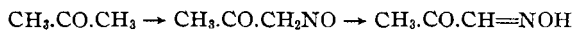
Mercaptan[54,57] reacts in a similar way to give an unstable nitroso compound,

$$RSH \rightarrow RSNO \rightarrow (RS)_2 + NO$$

Recently one of us has shown[66,67] that the paraffin hydrocarbons condense with nitrosyl chloride in the sunlight to form nitroso compounds and then oximes by rearrangement, hydrolysis of the latter giving the corresponding ketones. Thus *n*-heptane forms dipropyl ketone,

$$(CH_3.CH_2.CH_2)_2CH_2 \rightarrow (CH_3.CH_2.CH_2)_2CHNO \rightarrow (CH_3.CH_2.CH_2)_2C:NOH \rightarrow$$
$$(CH_3.CH_2.CH_2)_2C:O$$
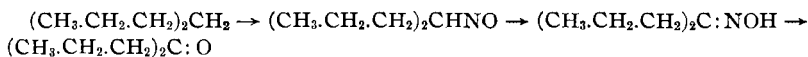
Later[72] he found that toluene gave in a similar way benzaldehyde,

$$C_6H_5.CH_3 \rightarrow C_6H_5.CH_2NO \rightarrow C_6H_5.CH:NOH \rightarrow C_6H_5.CH:O$$
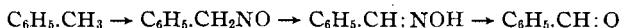
To our knowledge these are the only reported reactions of nitrosyl chloride upon hydrocarbons.

In many of the chemical experiments which are here reviewed nitrosyl chloride was not used as such but a mixture of some nitrite and hydrochloric acid. Theoretically this might amount to the same thing but practically it may be quite different. For instance, we have found anhydrous acetone to give with gaseous nitrosyl chloride a compound which contains chlorine and no nitrogen, while Claisen[28] received isonitrosoacetone using amyl nitrite, hydrochloric acid, and acetone. One of the principal factors responsible for such a difference may be the length of time with which the reagents may be kept in contact, since this may be indefinite in the case of pure nitrosyl chloride. The possibility of using catalytic agents and light rays also may play a part.

We have observed a reaction with almost every organic substance available, including such diverse compounds as carbon tetrachloride, chloroform, alcohol, ether, acetaldehyde, ethyl acetate, etc. As fast as possible we propose to investigate these and hope to present the results in the near future. Incidently it might be mentioned that Tilden,[10] in 1874, considered the principal role of nitrosyl chloride to be that of an oxidizing agent, mainly because phenol was eventually converted into quinone. More recently Bewad[52] has also suggested an action as oxidizer but there is as yet no conclusive evidence of this. The formation of ammonium chloride in many reactions of nitrosyl chloride might easily indicate reduction of the latter but we now know that hydroxylamine is readily produced and, as is well known, this substance gives ammonium chloride as a decomposition product. The mechanism and products of the action upon *n*-heptane was puzzling at first because of the appearance in quantity of this ammonium chloride, but the above explanation quickly cleared the way to follow the true course of the reaction.

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THE DETERMINATION OF ACIDITY.

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The subject of electrometric titrations has recently been discussed in the publications of the AMERICAN PHARMACEUTICAL ASSOCIATION by Kolthoff,[1] Popoff and McHenry [2] Wagener and McGill,[3] Giesy,[4] Krantz[5], and others.   In these articles many practical applications of the hydrogen electrode have been indicated but no comprehensive presentation of the subject as applying to acidity determinations has been made.   It occurred to the writer, therefore, that it might be of value to have presented a complete discussion of "The Determination of Acidity," showing recent applications of physical chemical measurements and bringing together in one paper various phases of the subject which are presented in more detail in various scattered sources.   All data presented in this article are original and all graphs or curves were developed by the writer as a result of his own experimental work.

It was not many years ago that our knowledge of acidity determinations was considered to be quite complete, due primarily to the fact that it was so very limited.   An acidity determination consisted merely of adding to a measured quantity of the acid material a mysterious substance called an indicator, which was supposed to possess one color in an acid solution and quite a different color in an alkaline solution, and then running in standard alkali until the desired color change occurred.   Thus the acidity was determined.   It was, of course, observed that in some acid solutions the indicator functioned well and in others poorly, but these facts caused no great concern.   In order to determine which indicator might be most suitable for a particular titration the scientific method used was to try in turn a great number of indicators and observe which one gave the best color change and hence seemed most desirable.   The crudity of this procedure has been recognized and it is no longer used, but it is at least still of historical interest.

It was soon observed that it is possible to have a solution which is acid to one indicator and alkaline toward another.   For example, a dilute solution of acetic acid which has its ionization repressed by the addition of sodium acetate may be acid toward phenolphthalein, alkaline toward methyl orange and neutral toward litmus.   This information constituted a tremendous advance and showed at once that various indicators change at different degrees of acidity or concentration of hydrogen ion, represented by (H^+).   The (H^+) means simply the number of hydrogen ions per liter.   The degree of acidity is also sometimes represented in terms of the logarithm of the reciprocal of this value, as recommended by Sorensen,[6] and is known as the p_H value.

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