Conclusions.

(1) The molecular conductivities and colors of approximately 0.001 *N* solutions of phenol-, tetrabromophenol-, and tetranitrophenolsulfonphthalein show that these indicators are at least 60% in the quinoidal form. The *yellow* color is dependent upon the quinone group and not appreciably on the *primary ionization*, that of the sulfonic acid group.

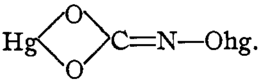
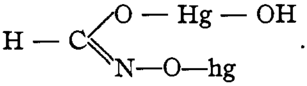
(2) A comparison of the colors, conductivities, and P_H values of the phenol- and tetrabromophenolsulfonphthalein with those of the tetranitrophenolsulfonphthalein show that the *intense red or blue* colors of these indicators develop simultaneously with the *secondary ionization*, that of the phenol groups, and thus with the formation of quinone phenolate ions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

THE PREPARATION OF ALKYLHYDROXYUREA CHLORIDES AND THEIR RELATION TO ESTERS OF CARBON DIOXIDE OXIME, R — O — N = C = O.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.[1]

Received January 5, 1917.

In the course of investigations with nitroparaffins and fulminates, Nef believed that he had prepared the first derivative of the oxime of carbon dioxide.[2] By the action of mercuric chloride on sodium isonitromethane, a yellow salt was obtained to which Nef assigned the formula  $Hg\langle O_2 \rangle C{=}N{-}Ohg$.[3] He supposed it to be a basic mercury salt of carbon dioxide oxime, $H—O—N=C=O$, but attempts to prepare the alkyl esters of this acid by the action of alkyl iodides on the yellow mercury salt proved unsuccessful. Later Jones[4] showed that Nef's salt was probably a basic mercury salt of formhydroximic acid,  $H—C\begin{matrix} /O—Hg—OH \\ \backslash\backslash N—O—hg \end{matrix}$. Attempts were then made by Jones[5] to prepare the derivatives of carbon dioxide oxime by removing alcohol from the salts and esters of hydroxyurethane. The work was based on the assumption that Lossen's formula for the hydroxamic acids,[6]

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[1] The material presented here is used by Leonora Neuffer in her dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Cincinnati.

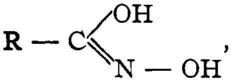
[2] *Ann.*, **280**, 279 (1894).

[3] Hg represents a half atom of bivalent mercury.

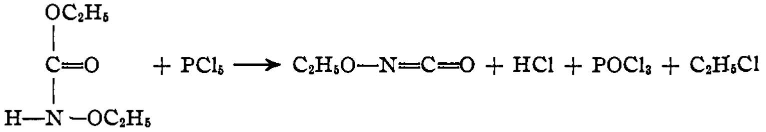
[4] *Am. Chem. J.*, **20**, 1 (1898).

[5] *Loc. cit.*

[6] *Ann.*, **287**, 295 (1898).

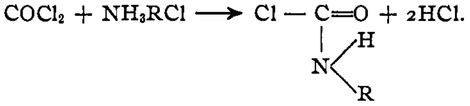


, was correct; but the desired esters were not obtained. However, experiments with the ethyl ester of hydroxyurethane and phosphorus pentachloride undoubtedly resulted in the formation of the ethyl ester of carbon dioxide oxime, $C_2H_5{-}O{-}N{=}C{=}O$, although the ester itself was not isolated.

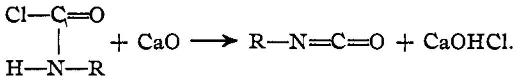


$$\begin{array}{l} \mathrm{OC_2H_5} \\ | \\ \mathrm{C{=}O} \quad + \mathrm{PCl_5} \longrightarrow \mathrm{C_2H_5O{-}N{=}C{=}O} + \mathrm{HCl} + \mathrm{POCl_3} + \mathrm{C_2H_5Cl} \\ | \\ \mathrm{H{-}N{-}OC_2H_5} \end{array}$$

Gattermann and Schmidt,[1] in the preparation of urea chlorides, have described the action of phosgene on ammonium chloride and on alkyl ammonium chlorides. By passing phosgene gas over these heated chlorides, urea chloride itself, as well as the mono- and di-methyl and ethyl urea chlorides were obtained.

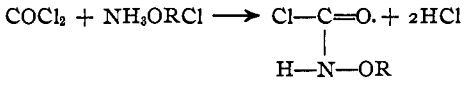


From these urea chlorides, Gattermann and Schmidt prepared esters of isocyanic acid by treatment with lime.



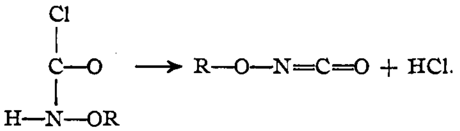
$$\begin{array}{l} \mathrm{Cl{-}C{=}O} \\ \quad | \qquad + \mathrm{CaO} \longrightarrow \mathrm{R{-}N{=}C{=}O} + \mathrm{CaOHCl}. \\ \mathrm{H{-}N{-}R} \end{array}$$

It was also found that, during the distillation of the urea chlorides, dissociation into hydrogen chloride and esters of isocyanic acid occurred. A recombination took place upon cooling.[2] It was to be expected, therefore, that hydroxylamine, or hydroxylammonium chloride, and the substituted derivatives of these compounds might react with phosgene in a similar manner:



$$\begin{array}{l} \mathrm{COCl_2} + \mathrm{NH_3ORCl} \longrightarrow \mathrm{Cl{-}C{=}O.} + 2\mathrm{HCl} \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad \mathrm{H{-}N{-}OR} \end{array}$$

and that by treatment of the resulting substituted hydroxyurea chlorides with suitable reagents, hydrochloric acid would be removed and the esters of the oxime of carbon dioxide would result.



$$\begin{array}{l} \quad \mathrm{Cl} \\ \quad | \\ \quad \mathrm{C{-}O} \quad \longrightarrow \mathrm{R{-}O{-}N{=}C{=}O} + \mathrm{HCl}. \\ \quad | \\ \mathrm{H{-}N{-}OR} \end{array}$$

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[1] *Ber.*, **20**, 118, 858 (1887).

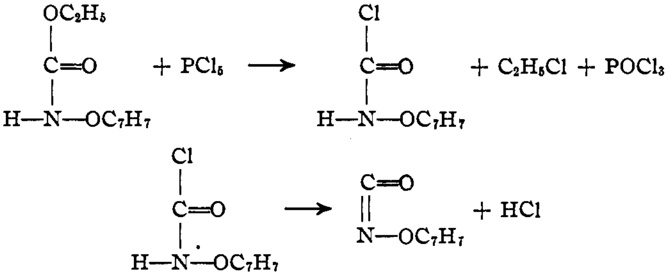
[2] *Ibid.*, **20**, 119 (1887).

The purpose of this paper is to describe experiments carried out with phosphorus pentachloride and alkyl hydroxyurethanes, and experiments with phosgene and substituted hydroxylamines and their chlorides, in an attempt directly or indirectly to isolate the esters of the oxime of carbon dioxide, R—O—N=C=O.

EXPERIMENTAL PART.

I. The Action of Phosphorus Pentachloride on the Esters of Hydroxyurethane.

(*a*) **Phosphorus Pentachloride and α-Benzyl Hydroxyurethane.**—Five grams of α-benzyl hydroxyurethane were treated with 5.26 g. of phosphorus pentachloride, added slowly while the mixture was cooled. A reaction began almost immediately, and was hastened by gently heating the mixture on a water bath. Both *hydrogen chloride* and *ethyl chloride* were evolved. All the phosphorus pentachloride was used up when the temperature of the bath reached 50°. A little above 50°, the reaction mixture suffered a sudden change, turned brown with a sudden puff, and considerable heat was evolved. A dark brown liquid remained which was distilled under diminished pressure. The phosphorus oxychloride present was first removed, and, then, a light yellow oil distilled, which investigation showed to contain no nitrogen and which resembled benzal chloride in properties. The results were very similar to those obtained by Jones with α-ethyl hydroxyurethane. Indications are that the course of the reaction was as follows:

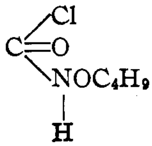


$$\begin{array}{c} OC_2H_5 \\ | \\ C{=}O \\ | \\ H{-}N{-}OC_7H_7 \end{array} + PCl_5 \longrightarrow \begin{array}{c} Cl \\ | \\ C{=}O \\ | \\ H{-}N{-}OC_7H_7 \end{array} + C_2H_5Cl + POCl_3$$

$$\begin{array}{c} Cl \\ | \\ C{=}O \\ | \\ H{-}N{-}OC_7H_7 \end{array} \longrightarrow \begin{array}{c} C{=}O \\ \| \\ N{-}OC_7H_7 \end{array} + HCl$$

and that the product $C_7H_7ON{=}C{=}O$ probably polymerized in part, or decomposed above 50° by intramolecular oxidation to give, among other products, benzal chloride.

(*b*) **The Preparation of α-*sec.*-Butylhydroxyurea Chloride,**



$$C\begin{array}{l} \diagup Cl \\ {=}O \\ \diagdown NOC_4H_9 \\ \quad\;\; | \\ \quad\;\; H \end{array}$$

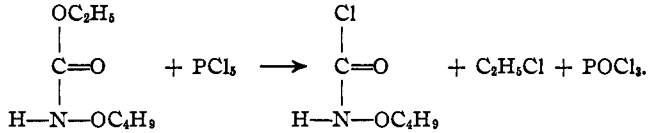
—Five and nine-tenths grams of α-secondary butyl hydroxyurethane were treated with 7.8 g. of phosphorus pentachloride. Reaction began at once, and both *hydrogen chloride* and *ethyl chloride* were evolved. The reaction-mixture, a clear liquid, was poured into the water. Some carbon dioxide was given off and a yellow oil separated which was extracted with ether. The extraction was dried with anhydrous sodium sulfate and the ether removed in a desiccator. Two and one-tenth g. of the oil were obtained. It contained chlorine, and was analyzed for nitrogen with the following result:

0.1262·g. gave 10.6 cc. of N_2 at 21° and 740 mm.
Calc. for $C_5H_{10}NO_2Cl$: N, 9.25. Found: N, 9.34.

The water solution from which the oil had been separated was made alkaline by adding sodium hydroxide and the product was distilled into dilute hydrochloric acid. When the hydrochloric solution was evaporated to dryness, a white solid remained, which, upon extraction with absolute alcohol, was found to be a mixture of a small amount of ammonium chloride and a larger amount of α-secondary butyl hydroxylammonium chloride. The latter was converted to the chloroplatinate and gave the following analysis.

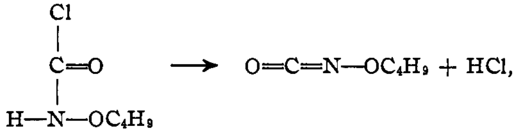
0.0964 g. gave 0.0315 g. Pt.
Calc. for $C_8H_{24}N_2O_2PtCl_6$: Pt, 33.14. Found: Pt, 32.67.

These results show that the action of phosphorus pentachloride on α-secondary butyl hydroxyurethane gave, first, the secondary butyl derivative of hydroxyurea chloride.



$$\begin{array}{c}OC_2H_5\\ |\\ C{=}O\\ |\\ H{-}N{-}OC_4H_9\end{array} + PCl_5 \longrightarrow \begin{array}{c}Cl\\ |\\ C{=}O\\ |\\ H{-}N{-}OC_4H_9\end{array} + C_2H_5Cl + POCl_3.$$

When poured into water, this substance separated partially as an oil. The formation of hydrogen chloride, evolved with ethyl chloride in the beginning of the experiment may be accounted for by assuming a partial dissociation of the principal product of the reaction



$$\begin{array}{c}Cl\\ |\\ C{=}O\\ |\\ H{-}N{-}OC_4H_9\end{array} \longrightarrow O{=}C{=}N{-}OC_4H_9 + HCl,$$

a decomposition which is perfectly analogous to the dissociation of alkyl ureachlorides into hydrogen chlorides and an ester of isocyanic acid, as observed by Gattermann and Schmidt.[1] The secondary butyl ester of carbon dioxide oxime may be assumed to have existed in contact with the water solution and to have been hydrolyzed to give the hydroxylamine derivative and carbon dioxide, just as isocyanates give amines and carbon dioxide.

(*c*) **The Preparation of α-Ethyl, β-*sec*.-Butylhydroxyurea Chloride,**

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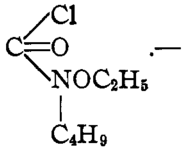
[1] *Ber.*, 20, 119 (1887).

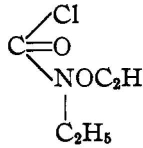

$Cl-C(=O)-N(OC_2H_5)-C_4H_9$

.—Five grams of α-ethyl β-secondary butyl hydroxyurethane were treated with 5.51 g. of phosphorus pentachloride. Ethyl chloride was evolved. The product was poured into water and an oil separated. *No evolution of carbon dioxide was noted.* The oil was extracted with ether, the extraction dried, and the oil recovered by evaporation of the solvent. The product responded readily to a test for chlorine. When it was distilled under diminished pressure, 1.2 g. of a clear, colorless liquid, boiling at 80° under 25 mm. pressure, were obtained. Above 80°, rapid decomposition took place in the distilling flask. The distillate, which still contained chlorine, was analyzed for nitrogen.

0.1270 g. gave 9.7 cc. N_2 at 28° and 739 mm.
Calc. for $C_7H_{14}NO_2Cl$: N, 7.80. Found: N, 8.19.

The water solution, which remained after the ether extraction mentioned above, was made alkaline with sodium hydroxide and distilled into dilute hydrochloric acid. Upon evaporation of the acid solution, a small amount of a white solid was obtained which was found to be ammonium chloride. In this case none of the substituted hydroxylammonium chloride was recovered.

(*d*) The Preparation of α,β-Diethylhydroxyurea Chloride,


$Cl-C(=O)-N(OC_2H_5)-C_2H_5$

—Eighteen grams α,β-diethyl hydroxyurethane were treated with 23.27 g. of phosphorus pentachloride. All of the phosphorus pentachloride was used up, and again ethyl chloride was evolved. When the reaction mixture was poured into water, some carbon dioxide was evolved and an oil separated in large quantity. When this was removed from the water solution, dried, and distilled under diminished pressure, 5.1 g. were obtained which boiled at 74–76° at 25 mm. It contained chlorine and possessed a sharp, penetrating odor. It was analyzed for nitrogen.

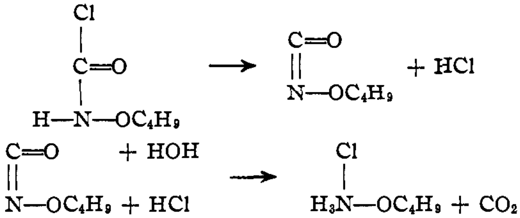
0.2732 g. gave 21.5 cc. N_2 at 24.5° and 749 mm.
Calc. for $C_5H_{10}NO_2Cl$: N, 9.24. Found: N, 8.72.

The water solution was made alkaline with sodium hydroxide and distilled into dilute hydrochloric acid. From the acid solution, a white solid was obtained, which, when separated from a small amount of ammonium chloride by means of absolute alcohol, weighed 5.8 g. This was converted to a yellow crystalline solid by means of chloroplatinic acid.

0.1129 g. gave 0.0735 g. Pt.
Calc. for $C_8H_{24}N_2O_2PtCl_6$: Pt, 33.14. Found: Pt, 33.21.

This result proves that the compound was α,β-diethylhydroxylammonium chloroplatinate.

We conclude that the reactions between phosphorus pentachloride and the ester of hydroxyurethane result in the formation of substituted hydroxyurea chlorides, which, in some cases, are more readily decomposed in the presence of water into hydroxylamine derivatives and carbon dioxide than in others. When both ethyl chloride and hydrogen chlorine are evolved, the intermediate formation of esters of the oxime of carbon dioxide may be assumed in the case of mono-alkyl derivatives.



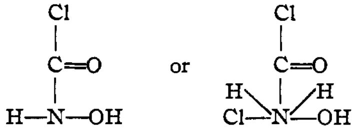
$$\begin{array}{c} Cl \\ | \\ C{=}O \\ | \\ H{-}N{-}OC_4H_9 \end{array} \longrightarrow \begin{array}{c} C{=}O \\ \| \\ N{-}OC_4H_9 \end{array} + HCl$$

$$\begin{array}{l} C{=}O \quad + HOH \\ \| \\ N{-}OC_4H_9 + HCl \end{array} \longrightarrow \begin{array}{c} Cl \\ | \\ H_3N{-}OC_4H_9 + CO_2 \end{array}$$

II. The Action of Phosgene on Substituted Hydroxylamines, and on their Hydrochlorides.

(*a*) **Phosgene and Hydroxylammonium Chloride.**—Dry phosgene gas was passed over hydroxylammonium chloride until all air was expelled from the system, and the solid was then heated gradually to 100°. At this temperature reaction was apparent. A clear liquid was formed which began to distil when a violent explosion burst the containing flask, due, probably, to the fact that the temperature of reaction was about the same as the decomposition temperature of hydroxylammonium chloride in an atmosphere of phosgene. Attempts were made to combine hydroxylammonium chloride, suspended in toluene and in carbon tetrachloride, with phosgene, but no apparent reactions occurred.

(*b*) **Phosgene and Hydroxylamine.**—Dry phosgene was passed for two and one-half hours over 4 g. of free hydroxylamine warmed on a water bath to 45°. A slightly oily white solid was formed, part of which was found to be hydroxylammonium chloride. The remainder was a white crystalline solid, insoluble in alcohol and ether, and soluble in water. It melted at 79.5–81°, with decomposition, but did not sublime, above 80°. It contained chlorine, gave a purple coloration with ferric chloride solution and formed a green copper salt with copper acetate. Attempts to establish the identity of this substance have been unsuccessful so far, but indications were that it corresponded to the formula,



$$\begin{array}{c} Cl \\ | \\ C{=}O \\ | \\ H{-}N{-}OH \end{array} \quad \text{or} \quad \begin{array}{c} Cl \\ | \\ C{=}O \\ H\diagdown \ | \ \diagup H \\ Cl{-}N{-}OH \end{array}$$

or some compound closely related to these.

(*c*) **Phosgene and α-Ethyl Hydroxylammonium Chloride.**—Dry phosgene gas was led over 3 g. of dry α-ethyl hydroxylammonium chloride heated gradually to 200°. Slight charring occurred and a clear, colorless oil distilled when the temperature was between 190–200°. When no more liquid distilled, the apparatus was disconnected and a small amount of unchanged α-ethyl hydroxylammonium chloride was recovered from the charred contents of the flask in which the reaction occurred. The colorless oil was found to contain chlorine and gave the following analysis for nitrogen:

0.1821 g. gave 14.7 cc. N_2 at 20.5° and 741.2 mm.

Calc. for $C_3H_7NO_2Cl_2$: N, 8.75. Found: N, 9.02.

Investigations are now being made for the purpose of establishing the constitution of this compound and of others of a similar nature. It is observed, however, that the compound having the empirical formula, $C_3H_7NO_2Cl_2$, consists of molecular proportions of phosgene and α-ethyl hydroxylamine.

(*d*) **Phosgene and α-Ethyl Hydroxylamine.**—Fifteen grams of α-ethyl hydroxylamine, dried with potassium hydroxide, were dissolved in ether and poured gradually into an excess of liquid phosgene, cooled in a freezing mixture. Vigorous reaction occurred. Six and eighty-four hundredths g. of a white solid formed, which was found to be α-ethyl hydroxylammonium chloride. This was separated from the ether solution which gave a thick, colorless oil upon evaporation of the ether in a desiccator. The oil was allowed to stand for some time to remove all traces of the solvent. It was again extracted with absolute ether. A small amount of α-ethyl hydroxylammonium chloride remained undissolved. Upon evaporation of the ether, a clear, colorless oil was obtained, which gave a strong test for chlorine.

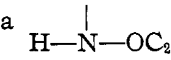
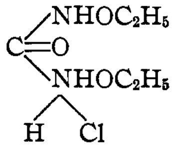
0.2131 g. gave 30.3 cc. N_2 at 27° and 740.5 mm.

Calc. for $C_5H_{13}N_2O_3Cl$: N, 15.18. Found: N, 15.38.

The following equation accounts for the results obtained:

$$COCl_2 + 3NH_2OC_2H_5 \longrightarrow C_5H_{13}N_2O_3Cl + C_2H_5ONH_3Cl$$

The amount of α-ethyl hydroxylammonium chloride which should be formed according to this equation is 7.9 g. Seven grams were obtained.

Investigations, so far, have established only the facts mentioned. The compound formed according to the equation, consists, however, of equimolecular quantities of α-ethyl hydroxylamine and a compound of the formula  $\begin{array}{l} Cl{-}C{=}O \\ \quad\;| \\ H{-}N{-}OC_2H_5 \end{array}$, which is analogous to the substances prepared by the action of phosphorus pentachloride on esters of hydroxyurethane. The formula  is also possible.

(*e*) **Phosgene and α-Benzyl Hydroxylammonium Chloride.**—Phosgene gas was passed over 1.77 g. of α-benzyl hydroxylammonium chloride which was gradually heated to 180° in the air bath for four hours. Most of the original solid was converted into a liquid. Little charring occurred. The excess phosgene used and the hydrogen chloride liberated during the reaction were passed into a barium hydroxide solution. A precipitate of barium carbonate was formed which was collected and weighed. The chlorine in the solution was precipitated as silver chloride and weighed. The reaction mixture was extracted with ether. A slightly brown solid weighing 0.1008 g. remained undissolved. Upon evaporation of the ether, a yellow oil was obtained which weighed 2.16 g. When an attempt was made to distil this oil under diminished pressure, a small amount of a clear liquid, boiling at 97.5–100° at 49 mm. passed over into the receiver. Much decomposition occurred above 100°. The distillate contained chlorine and was analyzed for nitrogen.

0.2221 g. gave 13.6 cc. N_2 at 28.5° and 740 mm.
Calc. for $C_8H_9NO_2Cl_2$: N, 6.31. Found: N, 6.57.

The equation which best represents the results obtained is

$$C_7H_7 - ONH_3Cl + COCl_2 \longrightarrow C_8H_9NO_2Cl_2 + HCl.$$

CINCINNATI, OHIO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI.]

HYDROXAMIC ACIDS RELATED TO α-HYDROXY ACIDS AND TO ACRYLIC ACID, AND A STUDY OF THEIR REARRANGEMENTS.

BY LAUDER WILLIAM JONES AND LEONORA NEUFFER.[1]

Received January 5, 1917.

Since Lossen,[2] in 1869, prepared oxalohydroxamic acid by the action of hydroxylamine on oxalic ethyl ester and distinguished a class of compounds having the "structure of amides and the character of acids," many representatives of the hydroxamic acids have been prepared. The principle work on hydroxamic acids containing aromatic groups was done by Lossen[3] and his collaborators, who described the preparation and properties of many of the acids themselves, as well as of their acyl esters and alkyl derivatives.

The chemistry of the hydroxamic acids of the aliphatic series has been developed to some extent by Hoffmann,[4] who prepared acethydroxamic

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[1] The material presented here is used by Leonora Neuffer in her dissertation in part fulfillment of the requirements for the Ph.D. degree of the University of Cincinnati.

[2] *Ann.*, **150**, 314 (1869).

[3] *Ibid.*, **175**, 284 (1875); **178**, 213 (1874); **205**, 273 (1880).

[4] *Ber.*, **22**, 2854 (1889).