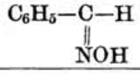
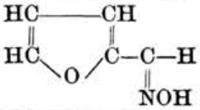
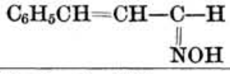
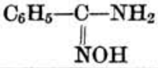
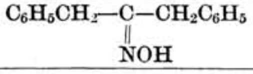
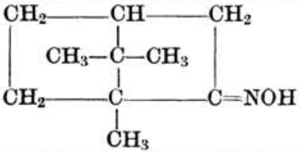
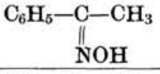
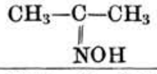
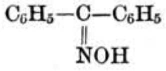
CATALYTIC ACTION OF REDUCED COPPER ON OXIMES. (ON BECKMANN'S REARRANGEMENT. XVI.)

By Shozo YAMAGUCHI.

Received December 18, 1925. Published March 28, 1926.

Since the first report of these researches was published by the writer and Professor Komatsu(1), the present writer has described some experimental results on the same subject, which are now summarised with the present experiment in the following table :

Oxime used	Reaction product in mol %				
	RCONH$_2$	RCN	RCOOH	Base	$^{R}_{R'}{>}C{=}O$
1.  $C_6H_5{-}\underset{\underset{NOH}{\Vert}}{C}{-}H$	51.9	27.5	20.6	–	–
2. 	44.6	–	trace	trace	55.4
3.  $C_6H_5CH{=}CH{-}\underset{\underset{NOH}{\Vert}}{C}{-}H$	–	+	–	trace	+
4.  $C_6H_5{-}\underset{\underset{NOH}{\Vert}}{C}{-}NH_2$	58.3	29.3	12.4	–	–
5.  $C_6H_5CH_2{-}\underset{\underset{NOH}{\Vert}}{C}{-}CH_2C_6H_5$	11.2	12.9	11.2	–	64.7
6. 	+	+	+	trace	+
7.  $C_6H_5{-}\underset{\underset{NOH}{\Vert}}{C}{-}CH_3$	–	+	+	+	+
8.  $CH_3{-}\underset{\underset{NOH}{\Vert}}{C}{-}CH_3$	–	–	–	+	+
9.  $C_6H_5{-}\underset{\underset{NOH}{\Vert}}{C}{-}C_6H_5$	–	–	–	trace	+
	Diphenyl-ketimine 3.3	Tetraphenyl-ethane 17.8		Diphenyl-methane 46.1	Ketone 32.8

---

(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, 6, (1923) 245; A, 7, (1925) 281; A, 9, (1925) 35.

When the oximes of different ketones or aldehydes are passed on reduced copper heated at about 200° in an atmosphere of hydrogen, as will be seen in the above table, yield acid amide ($RCONH_2$), nitrile (RCN), acid ($RCOOH$), bases ($R_2C=NH$, R_2CHNH_2, $(R_2CH_2)_2NH$, NH_3) ketone or aldehyde and hydrocarbons (R_2CH_2) and $(R_2CH)_2$. The yields of these compounds seem to depend more or less on the structure of the oximes; by hydrolysis all oximes excepting benzaldoximes and benzhydroxamic acid yield principally the ketones or aldehydes from which the oximes were derived, the oximes of cinnamyl aldehyde, of acetone, of acetophenone and of benzophenone yield an acidamide of the type $RCONH_2$ as the main reaction product.

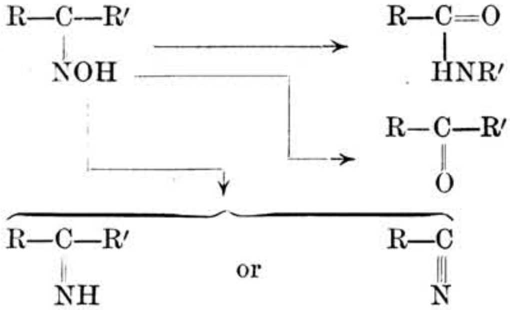
The oximes, thus, will be classified into three groups according to the chemical nature of the principal reaction products by the contact action of reduced copper at 200°.

1st. Group. The oxime of this group yields aldehyde or ketone and some basic compounds as the main reaction products, and the benzophenone and acetone oximes belong to this group. The carbonyl compound resulting by the hydrolysis of the oxime, will be transformed into hydrocarbons by the further catalytic action of reduced copper in an atmosphere of hydrogen, as actually observed in the case of benzophenone oxime.

2nd. Group. Benzaldoxime and benzhydroxamic acid each yields an acid amide which by the contact action of reduced copper, is transformed into nitrile and acid.

3rd. Group. The oxime of this group stands between the two groups of oximes above-mentioned in its behavior toward reduced copper heated at 200°, and yields the acid amide and carbonyl compounds with some basic ones. Their relative amount in the reaction product depending more or less upon the chemical or electronical nature of the hydrocarbon radicals linked to the carbon atom of the methane nucleus of the oxime. Furfuraldoxime, cinnamylaldoxime, dibenzylketoxime, camphoroxime and acetophenone oxime belong to this group.

As a matter of fact, aldoximes and ketoximes or their salts, probably suffer the chemical reactions from heat, being transformed directly; (1) into its isomeric acid amides—Beckmann's rearrangement; (2) into carbonyl compounds—aldehyde or ketone by hydrolysis; (3) into imine or nitrile by dehydration and the latter substance will also result from an acid amide:



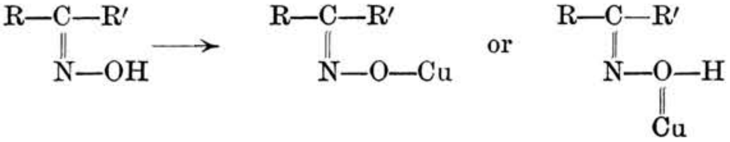
(1)

(2)

(3)

Such direct transformations of the oximes or their salts by heat would take place independently or simultaneously according to the chemical nature of the oximes. In presence of reduced copper, the velocity of these reactions will also evidently be modified, some reactions being accelerated and others retarded, and as a consequence, the oxime, from the view point of the nature of chemical reactions, were classified into the three groups mentioned above.

With regard to the catalytic action of reduced copper on the behavior of the oxime toward heat, the writer has attempted to explain its mechanism with the following interpretations. When an oxime is passed in a vapour state over finely divided copper, it would be condensed in a thin layer on the surface of the catalyst, and temporarily form a compound—a salt or an oxonium compound,—though its combination is in a labile state.



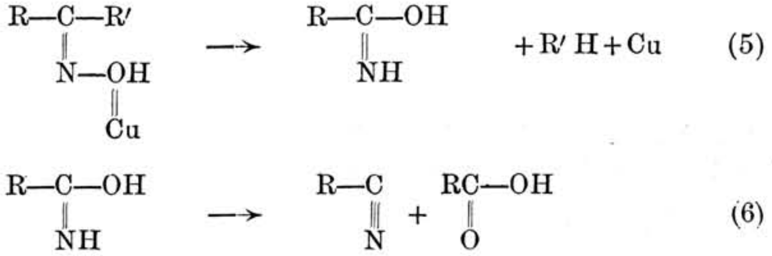
$$R-C(=N-OH)-R' \longrightarrow R-C(=N-O-Cu)-R' \quad \text{or} \quad R-C(=N-O(=Cu)-H)-R' \qquad (4)$$

Moreover, in the present case, an hypothetical substance of the composition CuH_2 should occur in the reaction system, since hydrogen is spread uniformly in the reaction system. The dissociation of these compounds will take place, in the course of evaporation, on the surface of the metal, and where the chemical transformations mentioned above take place. During the evaporation of the oxonium compound on the surface of the catalyst, the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms. Moreover, when the metal combined with the oxime behaves to lose the strength of the former affinity by acting as a donor of electrons, as sodium does in the molecular rearrangement of the oxime observed by S. Komatsu and T. Hiraidzumi⁽¹⁾. The molecular rearrangement of the oxime into its isomeric acid amide will take place with a prominent yield, but in the meantime, the hydrocarbon radical detached by the influence of

---

(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, **8**, (1925) 273.

the catalyst, is left in a free state without entering into combination with the nitrogen atom, and as a consequence the simple acid amide of the formula $RCONH_2$ results, and this by the further action of the catalyst is soon transformed partly into nitrile and acid, which may be represented by the following scheme:



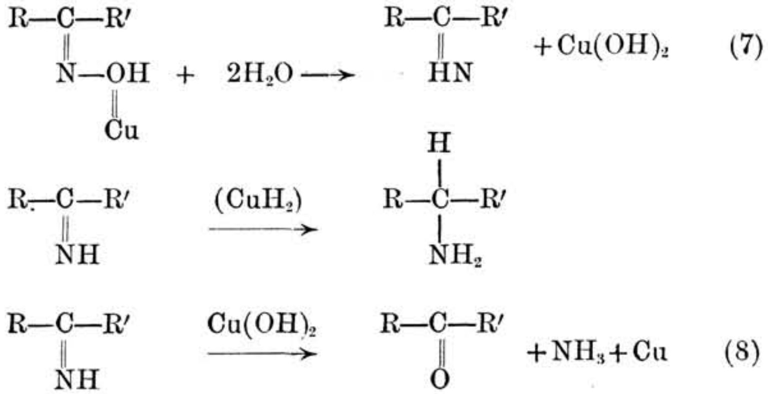
$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{N{-}OH}\\ \|\\ \mathrm{Cu}\end{array} \longrightarrow \begin{array}{c}\mathrm{R{-}C{-}OH}\\ \|\\ \mathrm{NH}\end{array} + \mathrm{R'\,H} + \mathrm{Cu} \qquad (5)$$

$$\begin{array}{c}\mathrm{R{-}C{-}OH}\\ \|\\ \mathrm{NH}\end{array} \longrightarrow \begin{array}{c}\mathrm{R{-}C}\\ \equiv\\ \mathrm{N}\end{array} + \begin{array}{c}\mathrm{RC{-}OH}\\ \|\\ \mathrm{O}\end{array} \qquad (6)$$

The transformation of the second group of oximes into acid amide, nitrile and acid by the contact action of the catalyst, will be represented by the schemes (1) and (6).

When however, the linkings between the hydrocarbon radicals or the hydrogen and the carbon atom of the methane nucleus of the oxime are quite strong, and the metal exerts no appreciable influence on these affinities, the hydrolysis will results in the formation of an aldehyde or a ketone, one part of which will be reduced into hydrocarbon, by the catalytic action of reduced copper in an atmosphere of hydrogen as noticed in the case of the benzophenone oxime. The hypothesis would be applied to the explanation of the reactions of the first group of oximes.

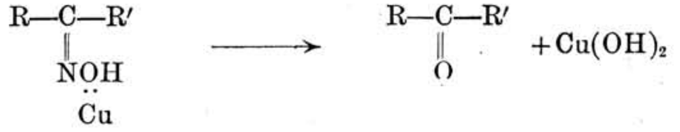
If the dissociation of the linking between the hydroxyl group and the nitrogen atom, by heat or by the catalytic influence of reduced copper, takes place very easily, then the formation of imine or nitrile will occur and the conversion of the imine into base or ketone by catalytic reduction or hydrolysis in presence of the catalyst will take place in turn:



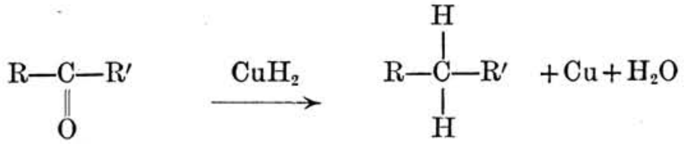
$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{N{-}OH}\\ \|\\ \mathrm{Cu}\end{array} + 2H_2O \longrightarrow \begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{HN}\end{array} + Cu(OH)_2 \qquad (7)$$

$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{NH}\end{array} \xrightarrow{(CuH_2)} \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{R{-}C{-}R'}\\ |\\ \mathrm{NH_2}\end{array}$$

$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{NH}\end{array} \xrightarrow{Cu(OH)_2} \begin{array}{c}\mathrm{R{-}C{-}R'}\\ \|\\ \mathrm{O}\end{array} + NH_3 + Cu \qquad (8)$$



$$\underset{\substack{\| \\ \mathrm{NOH} \\ \cdot\cdot \\ \mathrm{Cu}}}{\mathrm{R{-}C{-}R'}} \longrightarrow \underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C{-}R'}} + \mathrm{Cu(OH)_2} \qquad (9)$$



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R{-}C{-}R'}} \xrightarrow{\mathrm{CuH_2}} \mathrm{R{-}}\underset{\substack{| \\ \mathrm{H}}}{\overset{\substack{\mathrm{H} \\ |}}{\mathrm{C}}}\mathrm{{-}R'} + \mathrm{Cu} + \mathrm{H_2O} \qquad (10)$$

The behavior of the oximes of the first group, by the contact action of reduced copper will be represented in schemes (7) (8) and (10).

As was mentioned in the previous article,(1) the chemical reactions of the oximes will depend more or less upon the chemical and electronical nature of the hydrocarbon radicals, or in other words, the mobility of the radicals from the carbon atom of the methane nucleus depending mostly upon their electronical character, and also upon the catalytic influence of the catalyst presented in the reaction system, and all of the reactions shown in the schemes (1) (7) (8) and (10) would take place of some oximes belonging to the 3rd. group, possessing the chemical characters of both groups, in some degree. The conception of these ideas with respect to the conversion of the oxime into the acid amide, the carbonyl compound, and bases was thus fully illustrated by the experimental results mentioned in the above table.

January 1925.

Laboratory of Organic and Bio-Chemistry,
College of Science, Kyoto Imperial University.

---

(1) S. Komatsu and T. Hiraidzumi, *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, **8**, (1925) 273.