Studies on Catalytic Action, VI.
Catalytic Action of Reduced Copper on Acid Amide.

By

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One of the authors (S. K.) has claimed that reduced copper acts on alcohols as a catalyst of dehydration at high temperature[1]. The authors have observed that the molecular conversion of menthone oxime by the catalytic action of reduced copper into menthonisoxime was accompanied by the simultaneous formation of menthonitrile and decylenic acid[2]. To confirm the latter fact, two compounds were derived from menthonisoxime by catalytic dehydration and hydration or hydrolysis of reduced capper, menthonisoxime prepared from menthone oxime by the action of conc. sulphuric acid, was passed on reduced copper heated at 200°, and the formation of menthonitrile and decylenic acid as the authors had expected, were observed, the former was confirmed by its smell and other chemical properties, and the latter by transforming into its silver salt.

This fact leads the authors to the notion that these opposed reactions —the hydration and dehydration— of the acid amides, actually take place simultaneously the catalytic action of reduced copper at high temperature. The formation of campholenic acid and campholenitrile from camphor oxime[3], and of benzonitrile from acetophenone oxime[4],

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1 These Memoirs, 7, (1923).
2 Ibid., 7, (1923).
3 Ibid., 6, 245 (1923).
4 S. Yamaguchi: unpublished work.

were cited here as examples to support our assumption. Such assumption seems to us highly probable since the catalyst, in general, is capable, under different conditions, of exercising a catalytic influence in promoting the opposite reaction.

To make sure whether or nor this anticipation was accurate, 7.6 grm. benzamide M. p. 127—128°, were passed on reduced copper heated at 250°, during an interval of three hours. The products escaped from the reaction tube, condensed in the first receiver cooled with ice water, and the escaped ammonia gas was absorbed in the second one which was filled with dilute hydrochloric acid. On opening the apparatus, the characteristic smell of benzonitril was noticeable.

The reaction product in the first receiver, amounting to 7.4 grm., was treated with dry ether, the insoluble acid amide filtered (amounting to 6.2 grm.), and passed in dry ammonia gas to precipitate benzoic acid as the ammonium salt and filtered. The yield of ammonium benzoate was 0.7 grm. 0.5 grm. of benzoic acid were obtained in pure state from the salt.

It melts at 121°, and gave on analysis the following results;

C=68.48; H=5.13, theory requires C=68.85;

H=4.92 for $C_7H_6O_2$.

On distilling off the solvent of the etherial solution separated from the ammonium salt, there remains an oily substance possesing the odour of benzonitrile, which was reduced metallic sodium in alcoholic solution to an amine. The amine isolated from the reaction products was converted into the hydrochloride which amounted to 0.2 grm., then converted into the double salt with platiunm chloride, and analysed with the following results:

Pt=31.64, theory requires Pt=31.28 for $C_{12}H_{16}N_2PtCl_6$.

The quantity of ammonia in the second receiver, which was generated from the acid amide by reaction, was found to be 0.074 grm., by titration, which showed agreement with the required value 0.086 grm., caluculated from the quantity of ammonium bezoate.

The chemical reactions which occurred by the interaction between the acid amide and the reduced copper at 250°, will be involved in the following equations:

$$2C_6H_5CONH_2 = \begin{cases} C_6H_5CN + H_2O \ \ldots\ldots\ldots\ldots (a) \\ C_6H_5COOH + NH_3 \ \ldots\ldots\ldots\ldots (b) \end{cases}$$

1 mol.	1 mol.	theory
1 mol.	0.9 mol.	observed.

When benzamide comes into contact with reduced copper at 250°, as stated above, dehydration (*a*) will take place, decomposing it into benzanitrile and water, and the water generated by the reaction acts on the amide immediately, in presence of the catalyst, to hydrolyse it into benzoic acid and ammonia (*b*); namely, benzamide by the contact action of the reduced copper suffers simultaneously dedydration and hydration.

Acetamide, analogously, behaves toward the catalyst; a pure sample when passed on the reduced copper heated at 200°, was decomposed into acetic acid, ammonia and acetnitrile. Acetic acid and ammonia were identified by the usual chemical methods, and the nitrile was recognized by its characteristic smell and also by reducing it to methyl amine.

The authors, therefore, venture to affirm that reduced copper under certain conditions, promotes simultaneously both reactions, dehydration and hydration, or hydrolysis of the monobasic acid amides.

It will be noticed that our reaction compared with the Cannizzaro reaction shows the parallelism existing between the two reactions.

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