Reduction of Cupric Ion to Zero Valent Metal by Benzophenone Ketyl Radical

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While photoreduction of benzophenone in hydrogen-donating solvent has been extensively studied,[1-3] not many works[1,3] have been carried out on the reactivity of benzophenone ketyl radical ($C_6H_5\dot{C}OH-C_6H_5$), the intermediate of photoreduction of benzophenone. The present communication deals with the reduction of metallic ions such as Cu^{2+} to zero valent metal by benzophenone ketyl radical.

Irradiation of 0.5 M benzophenone and 0.5 M cupric acetate in isopropyl alcohol by near ultraviolet rays from a high or low pressure mercury vapor lamp for a few minutes, led to form a metallic mirror of copper on the inner wall of the reaction vessel. The copper mirror was retained unchanged in the absence of oxygen, but it was oxidized into cupric oxide followed by the conversion to cupric acetate by the introduction of air.

Other metallic salts such as $Co(OCOCH_3)_2$, $Ni(OCOCH_3)_2$, $Pb(OCOCH_3)_2$, $Cd(OCOCH_3)_2$, $Hg(OCOCH_3)_2$, $PdCl_2$, Bi_2O_3 were also reduced to the metallic state in the same reaction system.

We have concluded that cupric ion was reduced to zero valent metal by the reaction with benzophenone ketyl radical *via* the following sequence of reactions.

$$(C_6H_5)_2C{=}O + (CH_3)_2CHOH \xrightarrow{h\nu} (C_6H_5)_2\dot{C}{-}OH + (CH_3)_2\dot{C}{-}OH$$

$$(CH_3)_2\dot{C}{-}OH + (C_6H_5)_2C{=}O \rightarrow (CH_3)_2C{=}O + (C_6H_5)_2\dot{C}{-}OH$$

$$2(C_6H_5)_2\dot{C}{-}OH \longrightarrow (C_6H_5)_2C(OH)C(C_6H_5)_2OH$$

$$2(C_6H_5)_2\dot{C}{-}OH + Cu^{2+}(OCOCH_3)_2 \rightarrow 2(C_6H_5)_2C{=}O + Cu^0 + 2CH_3COOH$$

Benzophenone ketyl radical was reconverted to benzophenone by cupric acetate, while cupric acetate was converted to copper metal and acetic acid. Acetic acid was detected by gas chromatography. Acetylacetone was also detected by the same method when bisacetylacetonatocopper(II) was used in place of cupric acetate.

Support for the mechanism is based on the following experimental observations: (1) Both benzophenone and isopropyl alcohol were necessary for reduction of cupric ion to the metallic state by ultraviolet rays irradiation. Cupric ion was also reduced in the reaction system consisting of carbonyl compounds such as benzophenone, 4-methylbenzophenone, 4-methoxybenzophenone, acetophenone, propiophenone, *etc.* and of hydrogen-donating solvents such as methyl, ethyl, propyl, and butyl alcohols, ethanolamine and dicyclohexylamine, *etc.* On the other hand, carbonyl compounds such as 4-hydroxybenzophenone, 4-nitrobenzophenone, 4-phenylbenzophenone and benzoin, *etc.* which are not reduced to pinacol and solvents with no labile hydrogen such as benzene and carbon tetrachloride were ineffective reagents. For example, cupric ion in a reaction mixture consisting of 2-hydroxybenzophenone, cupric acetate and isopropyl alcohol was not reduced to the metallic state. In another reaction mixture consisting of benzophenone, 2-hydroxybenzophenonecopper chelate and isopropyl alcohol, cupric ion was reduced to zero valence. Other chelate compounds such as bisglycinatobisethylenediaminecopper(II) and bissalcilaldehydatocopper (II) were also reduced to metallic copper.

(2) Reduction to zero valence occurred in the reaction system involving only one intermediate radical, $(C_6H_5)_2\dot{C}{-}OH$, *i. e.*, benzophenone-benzhydrol system. Reduction of cupric ion by the radical $(CH_3)_2\dot{C}{-}OH$ is still under investigation.

(3) Reduction of benzophenone to benzopinacol was retarded or inhibited by cupric ion. Irradiation of 0.5 M benzophenone in isopropyl alcohol for 12 hr led to 84.8% isolation of benzopinacol, however, 10^{-2} M of cupric acetate retarded the reduction of benzophenone and trace amount of benzopinacol were obtained.

(4) Studies by polarography supported the possibily of the reduction of cupric ion by benzophenone ketyl radical. The halfwave potentials of benzophenone and cupric acetate in isopropyl alcohol were -1.54 and -0.32 V (*vs.* Hg pool) respectively using 0.1 M LiCl as the supporting electrolyte.

Further investigations are desirable to elucidate the mechanism of the reaction between bezophenone ketyl radical and metallic ions.

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[3] S. G. Cohen, S. Orman and D. A. Laufer, *ibid.*, **84**, 3905 (1962).