Electron Spin Resonance Study on Photolysis of Acetone and Benzophenone

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Recently several trapped radicals formed in photolysis have been identified with organic compounds of low molecular weight by the ESR method[1]. By the use of a X-band spectrometer of high sensitivity it became possible to study the radical intermediates formed in photolysis of some ketones. Preliminary investigation on acetone and benzophenone will be reported here.

According to the kinetic studies on the photolysis of gaseous acetone, formation of several types of free radicals was proposed[2]:

$$CH_3COCH_3 + h\nu \rightarrow CH_3\dot{C}O + \dot{C}H_3$$

$$(CH_3\dot{C}O \rightarrow \dot{C}H_3 + CO)$$

$$\dot{C}H_3 + CH_3COCH_3 \rightarrow CH_4 + \dot{C}H_2COCH_3$$

$$\dot{C}H_2COCH_3 \rightarrow \dot{C}H_3 + CH_2CO$$

$$\dot{C}H_3 + \dot{C}H_2COCH_3 \rightarrow CH_3COCH_2CH_3$$

In the liquid phase photolysis of the both ketones, formation of the active intermediates was proposed[5], but their natures were not well known. Observation of ESR for these free radical intermediates will give a confirmative evidence for such mechanisms.

The spectrometer used was a type of high frequency field modulation, being similar to that of Fujimoto and Ingram, but the frequency of the field modulation was 455 kilocycles/sec. Design of a low temperature resonant cavity is shown in Fig. 1.

After an irradiation of ultraviolet light for several hours, any signal could not be observed in pure acetone, while a broad singlet was observed in pure benzophenone and in 0.1~1% solutions of the both ketones. However, the intensity of the signal decreased rapidly in the case of acetone, a half life being 50 min. at about 77°K. The characteristics of the signals observed are shown in Table I.

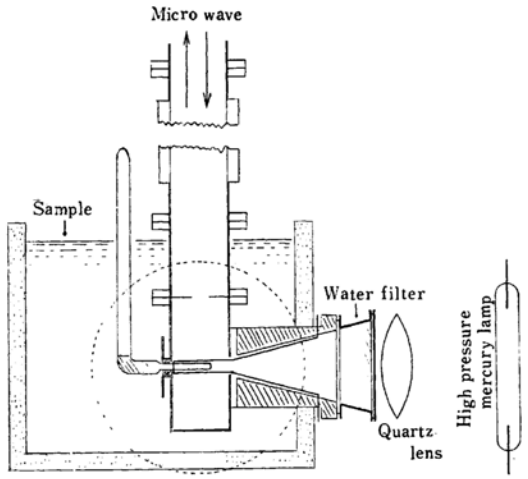

Fig. 1

TABLE I. ESR OF TRAPPED RADICALS AT ABOUT 77°K

	Line width (H_{msl})	Line shape	*g*-Factor
Acetone in ethanol and EPA (Ether, iso-Pentane and Alcohol)	30 gauss	(gaussian)	2.003
Benzophenone	23 gauss	〃	2.003
Benzophenone in ethanol and EPA	24 gauss	〃	2.003

An unstable free radical in the solution of acetone would be the methyl radical, but confirmative evidence for this assignment was not yet given since no hyperfine structure was observed. In the case of benzophenone a hyperfine structure neither of a quartet for the phenyl radical nor of a quartet with the small separations for the benzoyl radical was observed. The result indicates that two types of free radicals were present together or broadning of the line width occurred by some reasons, so that the hyperfine structure was smeared out. Detailed research will be published elsewhere.

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1) Cf. A. M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals", Academic Press, New York (1960), p. 239.
2) Cf. J. A. Leermakers, *J. Am. Chem. Soc.*, **16**, 1899 (1934).
3) H. H. Glazebrock and T. G. Pearson, *J. Chem. Soc.*, **1937**, 557.
4) S. W. Benson and G. S. Fordes, *J. Am. Chem. Soc.*, **65**, 1399 (1943).
5) E. J. Bowen and E. de la Prandiere, *J. Chem. Soc.*, **1934**, 1503.