BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(10), 2593—2594 (1974)

Blue-colored Matter Appearing in an Alkaline Solution of Benzoin and Benzil in Aqueous Dimethyl Sulfoxide

Takehiro ABE and Masamoto IWAIZUMI*

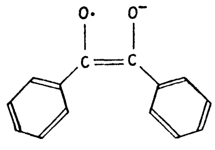
College of General Education, Tohoku University, Kawauchi, Sendai 980

* *Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-2-chome, Sendai 980*

(Received January 16, 1974)

Synopsis. Blue-colored matter appearing in the alkaline solution of benzoin and benzil in aqueous dimethyl sulfoxide (DMSO) was confirmed to be a benzil anion-radical by visible and ESR spectroscopy.

The intensely purple-colored matter appearing during the course of the oxidation of benzoin to benzil in an alkaline alcoholic solution was confirmed by Ihrig and Caldwell[1] to be stable free radical with a Gouy-type magnetic balance. Although they assigned the colored matter to an aliphatic semiquinone such as benzil anion-radical (I), no evidence for the structure was given. The visible spectrum has not been given, since the matter is usually very labile.[2]



I

The colored matter can be more distinctly observed on addition of sodium hydroxide to a solution of benzoin and benzil in DMSO (blue) than in alcohol (purple). Benzil is an oxidizing agent appropriate for the formation of the colored matter.[1,3] We have investigated the colored species in DMSO by visible and ESR spectroscopy.

The blue species has bands at *ca.* 620 (shoulder), 650 and 720 nm (shoulder) in the visible region (Fig. 1). The disagreement in absorbance at 700 nm between the two measurements is due to the gradual disappearance of the blue matter. The solution resulting

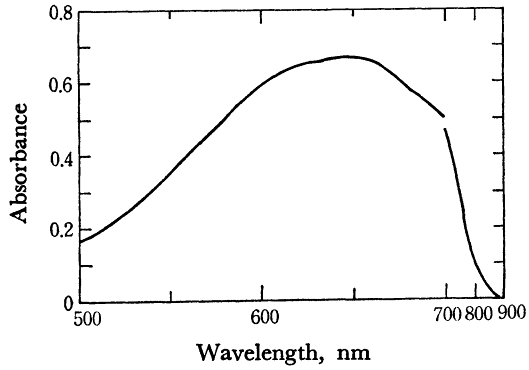


Fig. 1. The spectrum observed with the DMSO solution containing benzoin (5.5×10^{-4} M), benzil (6.3×10^{-4} M), sodium hydroxide (3.9×10^{-3} M) and 2%(v/v) water, at *ca.* 1 min after mixing.

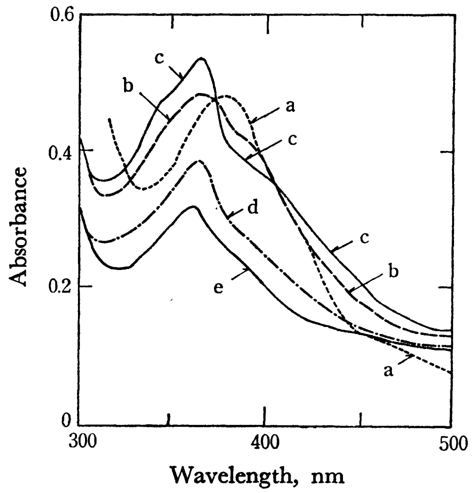


Fig. 2. The spectra observed with the DMSO solution containing benzoin (5×10^{-4} M), benzil (5×10^{-4} M), sodium hydroxide (3.9×10^{-3} M) and 2%(v/v) water. Time after mixing: a, 5 s; b, 30 s; c, 1 min; d, 8.3 min; e, 13.3 min.

from mixing shows an absorption peak at 380 nm at the initial stage and a peak at 359 nm later on (Fig. 2). The initial 380-nm band appeared before the appearance of the visible bands and disappeared with the increasing absorption intensities in the visible region, and it is therefore not due to the blue matter. On the other hand, the band at 359 nm seems to be ascribed to the blue matter, since the band decreased in intensity with the decreasing absorption intensities in the visible region.

The benzil anion-radical generated by electrolytic reduction in dimethylformamide solution[4] and by reduction with alkali metals in several solvents[5] is blue and purple, respectively. The benzil anion-radical produced in a γ-irradiated rigid solution in methyltetrahydrofuran at 77 K shows absorption bands at 650, 700 and 750 nm.[6] Thus the blue matter could be assigned to the benzil anion-radical.

The purple solution prepared by adding sodium hydroxide to a solution of benzoin and benzil in aqueous ethanol showed a very broad band with an absorption maximum at *ca.* 550 nm. The whole broad band shifted to the blue as compared with that of the blue DMSO solution. The difference in color between the blue DMSO solution and the purple ethanolic one seems to be due to a solvent effect.

The calculation made by Kawai[2] by the free-electron method predicts the peak position of 667 nm for radical I. The predicted position agrees closely with that observed in the present work.

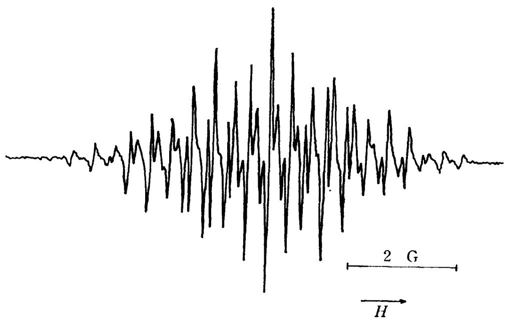


Fig. 3. The ESR Spectrum of the blue-colored species (the benzil anion-radical) produced by adding a drop of 4.9 M NaOH solution into the DMSO solution of benzoin (1×10^{-2} M) and benzil (1×10^{-2} M) in a thin sample tube open to the air at room temperature.

TABLE 1. HYPERFINE SPLITTING CONSTANTS OF THE BENZIL ANION-RADICAL

Position	Splitting constants (*G*)		
	Present work	Ref. 4	Ref. 7
ortho	1.010	0.99	0.99
meta	0.368	0.36	0.37
para	1.123	1.12	0.99

The assignment of the benzil anion-radical for the blue matter can be confirmed by its ESR spectrum (Fig. 3), which is similar to that of the blue benzil anion-radical.[4] We see from Table 1 that the hyperfine splitting constants obtained from Fig. 3 agree closely with those reported for the benzil anion-radical.[4,7] Thus the blue matter can be confirmed to be the benzil anion-radical.

The DMSO solution of benzil in the presence of sodium hydroxide showed a band at 385 nm at the initial stage but no absorption bands in the visible region. In the DMSO solution of benzoin (1.5×10^{-3} M) and sodium hydroxide (3.9×10^{-3} M) in the absence of benzil, the blue-colored matter showing a visible spectrum similar to that shown in Fig. 1 appeared and disappeared later on. In this case the oxidation of benzoin proceeds owing to the presence of the oxygen dissolved in the solution.[3] It is thus evident that the blue matter is produced from benzoin. In the presence of benzil, however, it may also be produced by the reduction of benzil with benzoin.

Experimental

Commercial benzoin (G. R. Tokyo Kasei) was purified by recrystallization. Benzil (ultra-pure grade, Tokyo Kasei) was used. DMSO was dried with calcium hydride and fractionated under reduced pressure.

The electronic absorption spectra of the solutions were measured at room temperature with a Hitachi recording spectrophotometer EPS-3 having a path length of 1.00 cm, and with a Hitachi rapid scan spectrophotometer RSP-2 having a path length of 1.0 cm. Water was used as a reference. The ESR spectrum was measured with a Hitachi ESR spectrometer, Model 771, at 22 °C.

The authors are indebted to Professor Taro Isobe, Tohoku University, for his kind advice

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