BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1161—1162(1971)

Spontaneous Electron Transfer from Amines to Simple Quinones in an Aqueous Medium

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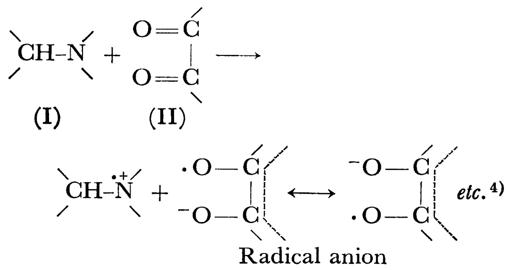
(Received November 6, 1970)

The formation of radical anions arising from thermal electron transfer between tetrahalogenated *p*-benzoquinone and *N*-tetramethyl-*p*-phenylenediamine has already been established.[1] Photochemically-activated electron transfer from amines to carbonyl compounds to result in the corresponding radical anions has also been recently reported by Davidson and Wilson.[2] The use of tetrahalogenated *p*- or *o*-benzoquinones as mild dehydrogenating reagents provides us with a useful method for preparing less stable quinones from the corresponding hydroquinones; the subject has been well documented by several authors.[3]

Recently we found that spontaneous electron transfer from amines to simple quinones without any electron-attracting substituents can occur in a deaerated aqueous medium. Stable radical anions of quinones, such as phenanthraquinone, acenaphthenequinone, and potassium phenanthraquinone-2-sulfonate, can be detected by ESR spectroscopy. The radical anions thus obtained are identified by comparison with that produced by the reduction of the corresponding quinone with alkali metal in tetrahydrofuran. Although phenanthraquinone and acenaphthenequinone are only slightly soluble in water, one can observe a strong ESR signal if the aqueous quinone solution saturated with a suitable amine is deaerated thoroughly. The ESR spectra of typical radical anions observed are shown in Fig. 1, together with that of the radical anion produced by the reduction of phenanthraquinone with calcium metal. The amines examined in these expreiments are ethylamine, diethylamine, and triethylamine. The mode of electron transfer may be formulated as follows:



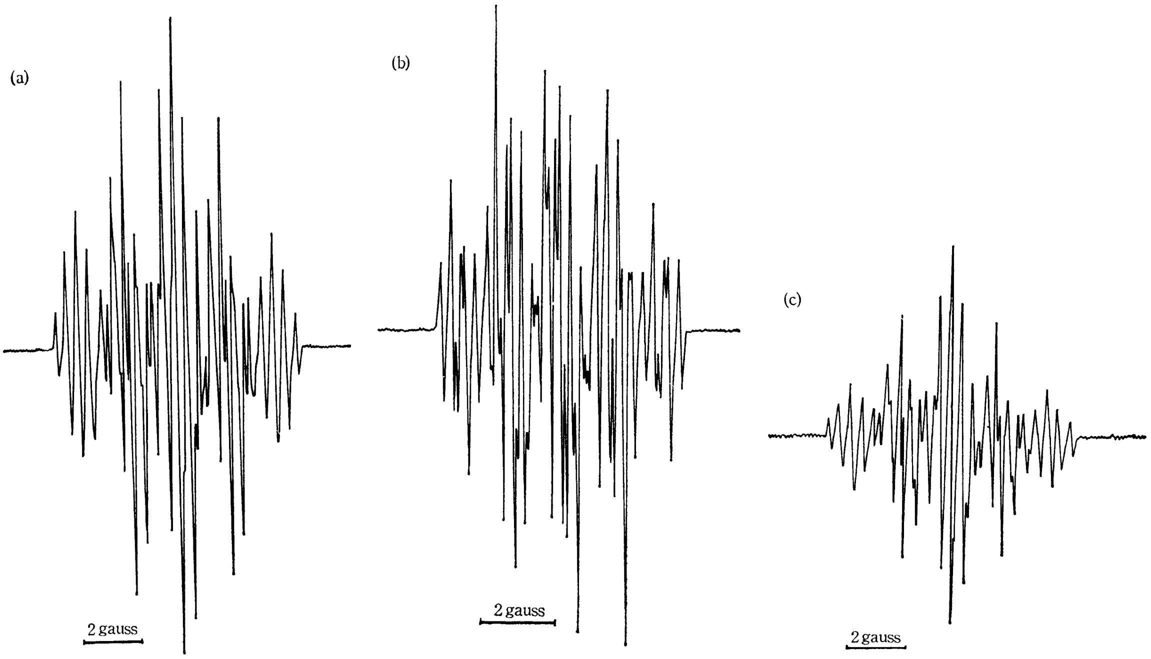


Fig. 1. (a) ESR spectrum of phenanthraquinone radical anion observed in the system phenanthraquinone-diethylamine-water (2H:1.73 gauss, 2H:1.69 gauss, 2H:0.41 gauss).
(b) ESR spectrum of potassium phenanthraquinone-2-sulfonate radical anion observed in the system potassium phenanthraquinone-2-sulfonate-diethylamine-water.
(c) ESR spectrum of radical anion produced by reduction of phenanthraquinone with metallic calcium-Hg in THF.

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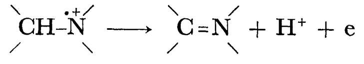
[1] E.M.Kosower "An Introduction to Physical Organic Chemistry", John Wiley & Sons, New York, (1968), p. 189.

[2] R.S.Davidson and R.Wilson, *J. Chem. Soc., B*, **1970,** 71.

[3] D. Walker and J. D. Hiebert, *Chem. Rev.*, **67,** 153 (1967); W. M. Horspool, *Quart. Rev.* (London), **23,** 204 (1969); Hans-Dieter Becker, *J. Org. Chem.*, **34,** 1198, 1203, 1211 (1969).

[4] A detailed chemical analysis of the products derived from amines is now being performed.



$$\rangle CH-\overset{\cdot +}{N}\langle \longrightarrow \rangle C=N\langle + H^{+} + e$$

(III)

The g-values of the radical anions are summarized in Table 1.

Table 1. g-Values of radical anions

Quinone	Reducing Reagent	g-Value
phenanthraquinone	diethylamine	2.0049[a)]
phenanthraquinone	Na	2.0050[b)]
phenanthraquinone	K	2.0051[b)]
acenaphthenequinone	triethylamine	2.0049[a)]
potassium phenanthraquinone-2-sulfonate	diethylamine	2.0050[a)]
potassium phenanthraquinone-2-sulfonate	triethylamine	2.0050[a)]

a) in water b) in tetrahydrofuran

For a comparison of the effect of the presence or absence of a counter cation around a radical anion molecule, the g-values of phenanthraquinone potassium and sodium ketyls have been determined; they are also tabulated in Table 1. However, although the distribution of the unpaired electron in radical anions is much affected by the presence or absence of a counter cation,[5)] no meaningful difference in g-value between a free radical anion and an ion-paired one is observed.

Procedure. Quinone, dissolved in pure water, and amine were each deaerated, mixed by means of the technique of a breakable seal in the dark, and left overnight. The characteristic color of the radical anion gradually appeared; thereupon the sample was submitted to ESR spectroscopy. An X-band ESR spectrophotometer with 100 Kc modulation manufactured by JEOL was used in this research.

[5)] K. Maruyama and R. Goto, *Rev. Phys. Chem. Jap.*, **34**, 30 (1964); K. Maruyama, M. Yoshida, and J. Osugi, *ibid.*, **39**, 117 (1969).