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Ionization of Some Quinones by the Interaction with Aliphatic Amines

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The interactions of alkylamines with *p*-benzoquinone and its chloro-derivatives in ethanol and ethyl ether were studied by the rapid scan spectrophotometric method. The formation of anion radicals was found spectroscopically for the *n*-butylamine-*p*-benzoquinone, *n*-butylamine-chloranil, dimethylamine-*p*-benzoquinone, and tri-*n*-butylamine-chloranil systems. The rates of ionization reactions were determined to be 0.30 $\mathrm{sec^{-1}\,mol^{-1}}$ (at 253.7°K), 0.89 $\mathrm{sec^{-1}mol^{-1}}$ (at 222.7°K), and 1.39 $\mathrm{sec^{-1}mol^{-1}}$ (223.2°K) for the tri-*n*-butylamine-chloranil, *n*-butylamine-chloranil, and *n*-butylamine-*p*-benzoquinone systems, respectively. The activation energy for ionization of the tri-*n*-butylamine-chloranil system in ethanol was estimated to be 0.57 kcal/mol.

The reactions of aromatic amines with *p*-benzoquinone and its derivatives are typical examples of interactions between electron donors and acceptors. Recent studies[1,2] showed that the inner (σ) and outer (π) complexes exist as reaction intermediates in this type of reactions. The reaction mechanism was clarified for the system including chloranil as electron acceptor and *m*-phenylenediamine or *s*-triaminobenzene[3] as electron donor, by detecting the intermediates spectrophotometrically at various temperatures. Another type of reaction between electron donor and acceptor may include ionization as an intermediate process. Nagakura and Tanaka[4] presented the electron-transfer theory for some aromatic substitution reactions and pointed out that ionized species may exist as intermediates for the reactions. Kosower[5] emphasized that ionization processes play an important role in various electron donor-acceptor reactions. Furthermore, in the reaction producing diethylaminovinyltrichloro-*p*-benzoquinone from triethylamine and chloranil, electron transfer was considered to be the first step of the reaction although the process was not directly observed.[6]

The existence of ionic species has been demonstrated for many systems including electron donors and acceptors.[7-12] Detailed experimental studies have been made in particular for systems including aromatic amines such as *N*,*N*-dimethyl- and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine as electron donors.[13,14]

In spite of many works on the formation of ionic species in systems including electron donors and acceptors, kinetic studies of the ionization process are scanty. In this paper, the existence of ionic species as reaction intermediates will be demonstrated by the rapid scan spectrophotometric technique for some quinone-

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[1] Z. Rappoport, *J. Chem. Soc.*, **1963**, 4498.

[2] T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura This Bulletin, **44**, 380 (1971).

[3] T. Yamaoka and S. Nagakura, *ibid.*, **43**, 355 (1970).

[4] S. Nagakura and J. Tanaka, *ibid.*, **32**, 735 (1959).

[5] E. M. Kosower, "Progress in Physical Organic Chemistry," Vol. 3, Interscience Publisher, New York (1965), p. 81.

[6] D. Buckley, S. Dunston, and H. B. Henbest, *J. Chem. Soc.*, **1957**, 4850.

[7] R. E. Miller and W. F. K. Wynne-Jones, *ibid.*, **1959**, 2375; *Nature*, **186**, 149 (1960).

[8] R. Foster, *J. Chem. Soc.*, **1959**, 3508.

[9] G. Briegleb, W. Liptay, and M. Cantner, *Z. Physik. Chem.* (Frankfurt), **26**, 55 (1960).

[10] H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron, Lett.*, **9**, 5 (1960).

[11] J. Weiss, *J. Chem. Soc.*, **1942**, 245.

[12] J. W. Eastman, G. Engelsma, and M. Calvin, *J. Amer. Chem. Soc.*, **84**, 1339 (1962).

[13] H. Kainer and A. Überle, *Chem. Ber.*, **88**, 1147 (1955).

[14] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

aliphatic amine systems. Furthermore, the rate of ionization process will be determined by the electric conductivity measurement.

Experimental

Materials. Chloranil was recrystallized three times from acetone. *p*-Benzoquinone and 2,5-dichloro-*p*-benzoquinone were purified by vacuum sublimation. Ethanol was distilled after refluxing with magnesium ethylate. Ethyl ether was dried with sodium metal and distilled. Commercially available *n*-butylamine and tri-*n*-butylamine of GR grade were used without further purification after their purities had been checked by gas chromatography. The alcoholic or ethereal solutions of the other amines were obtained by dissolving gaseous amines which were generated by heating their hydrochlorides with sodium hydroxide.

Measurement. A Hitachi rapid scan spectrophotometer RSP-2 located at the Institute of Industrial Science, The University of Tokyo, was used to measure visible and ultraviolet spectra. The apparatus is equipped with an automatically controlled mixing cell. Spectra could be measured every 1/3 second in the wavelength range from 200 mμ to 700 mμ. The electric conductivity and its time dependence were measured with a vibrating reed electrometer and an oscilloscope.

Results and Discussion

Change in Absorption Spectra Caused by the Ionization of Quinones. Reactions of primary, secondary, and tertiary amines with *p*-benzoquinone and its chloroderivatives were investigated spectroscopically in ethanol and ethyl ether. Most reactions were so rapid that the change in visible and ultraviolet absorption spectra was pursued only by the rapid scan spectroscopic method. Concentrations of quinones were adjusted to about 10^{-4} mol/*l*, and an excess amount of amines was used in order to keep their concentrations approximately constant throughout the reaction.

First, let us describe interactions of primary amines with quinones. When *n*-butylamine is mixed with chloranil in ethanol, the spectrum rapidly changes as is shown in Fig. 1. At 1/3 second after mixing, the spectrum with a couple of peaks due to a vibrational structure appears in the region of 420—450 mμ. It is undoubtedly ascribed to the chloranil anion radical from the peak positions and shapes.[8] With the gradual disappearance of these peaks the intensity of an absorption band at 360 mμ increases. This band coincides with that of 2,5-di-*n*-butylamino-3,6-dichloro-*p*-benzoquinone observed by Buckley *et al.*[15] The result shows that an electron transfer occurs from *n*-butylamine to chloranil prior to the substitution reaction.

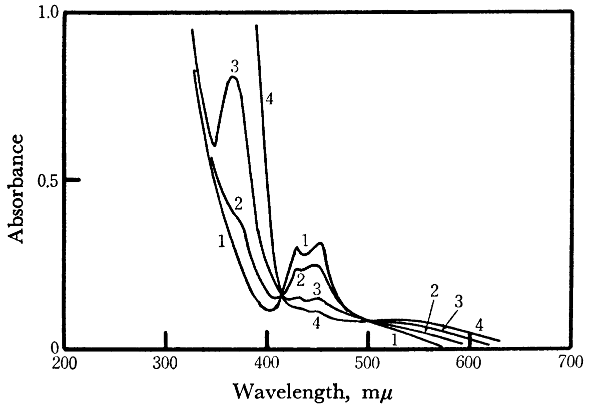

Fig. 1. The electronic absorption spectra of the *n*-butylamine - chloranil system in ethanol. Curves 1, 2, 3, and 4 are the spectra measured at 1/3 sec, 1 sec, 5 sec, and 30 sec, respectively, after the mixing.

A similar spectral change was observed for the methylamine - chloranil - ethanol system. The situation is the same for the systems including *p*-benzoquinone or 2,5-dichloro-*p*-benzoquinone instead of chloranil.

The ionization seems to be sensitive to the polarity of solvents and also the structure of electron acceptor. When *n*-butylamine and *p*-benzoquinone were mixed in ethyl ether, no absorption due to the *p*-benzoquinone anion radical was observed, only absorption bands due to the mono- and di-*n*-butylamino derivatives of *p*-benzoquinone appeared. This seems to mean that the ionic species is unstable in a weakly polar solvent like ethyl ether. When the electron affinity of the quinone is greater, the absorption of the anion radical appears even in ethyl ether. For instance,

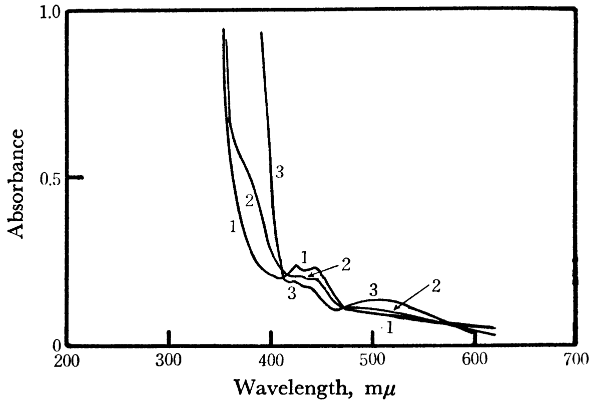

Fig. 2. The electronic absorption spectra of the *n*-butylamine - chloranil system in ethyl ether. Curves 1, 2, and 3 are the spectra measured at 1/3 sec, 1 sec, and 10 sec, respectively, after the mixing.

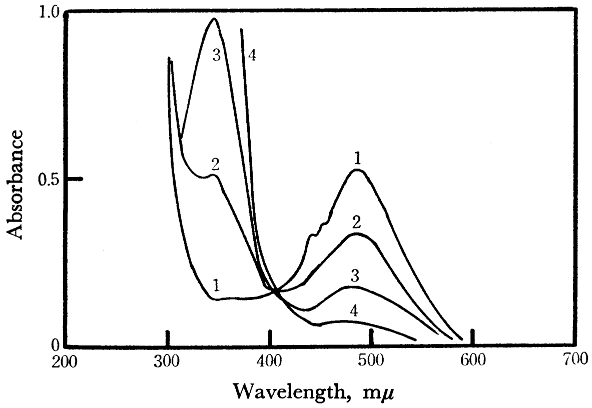

Fig. 3. The electronic absorption spectra of the dimethylamine - *p*-benzoquinone system in ethanol. Curves 1, 2, 3, and 4 are the spectra measured at 1/3 sec, 2 sec, 5 sec, and a few minutes, respectively, after the mixing.

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[15] D. Buckley, H. B. Henbest, and D. Slade, *J. Chem. Soc.*, **1957**, 4891.

the chloranil-*n*-butylamine system apparently shows an absorption due to the chloranil anion radical as is shown in Fig. 2, while the 2,5-dichloro-*p*-benzoquinone-*n*-butylamine system shows no such absorption.

In the interactions of secondary amines with quinones, the change in the absorption spectrum of the dimethylamine-*p*-benzoquinone-ethanol system takes place as shown in Fig. 3. At 1/3 second after mixing, an absorption band due to 2-dimethylamino-*p*-benzoquinone appears at 480 mμ for this system. Besides this band, there appears a shoulder due to the *p*-benzoquinone anion radical. This suggests that the anion exists as a precursor to 2-dimethylamino-*p*-benzoquinone. The dimethylamine-chloranil-ethanol system gives at 1/3 second after mixing, absorption peaks due to 2-dimethylamino-3,5,6-trichloro-*p*-benzoquinone but no peak due to the chloranil anion radical. It might be noted that the spectrum of the anion radical was not observed for the system containing dimethylamine as electron donor, while it was found for the system containing methylamine with the higher ionization potential. This seems to mean that the reaction rate of ionization is much lower than that of the successive process for the dimethylamine-chloranil-ethanol system.

The tri-*n*-butylamine-chloranil-ethanol system shows the absorption of the chloranil anion radical as seen in Fig. 4. In this system, the anion radical is stable and no further reaction occurs. The ionization of the system including tri-*n*-butylamine as electron donor largely depends on the electron affinity of quinone and also on the polarity of solvent. For example, in ethanol 2,5-dichloro-*p*-benzoquinone is ionized, though slowly, by the interaction with tri-*n*-butylamine but in the case of *p*-benzoquinone no ionization occurs. In ethyl ether neither quinones are ionized by the interaction with tri-*n*-butylamine.

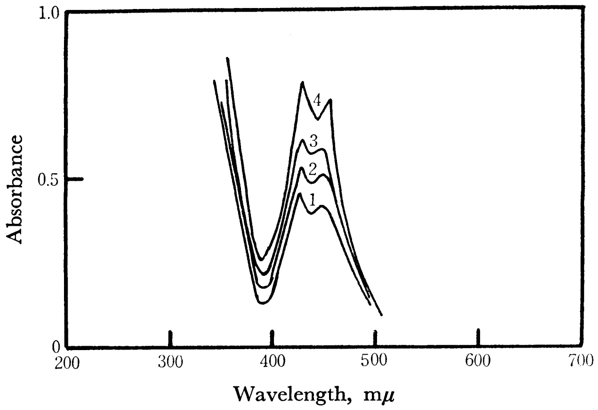

Fig. 4. The electronic absorption spectra of the tri-*n*-butylamine-chloranil system in ethanol. Curves 1, 2, 3, and 4 are the spectra measured at 1/3 sec, 1 sec, 5 sec, and a few minutes, respectively, after the mixing.

Rate of Ionization. Since the rapid scan spectrophotometric measurement could not be made at low temperatures, we undertook to use electric conductivity for the purpose of determining the rate of electron transfer from amine to quinone at various temperatures. In order to check the reliability of the measurement, the rate measured spectroscopically for the tri-*n*-butylamine-chloranil system at room temperature was compared with that obtained by aid of the conductivity measurement. The rate constants measured simultaneously by both methods coincide well with each other. Conductivity measurements were carried out at low temperatures at which the reactions succeeding the ionization actually stopped.

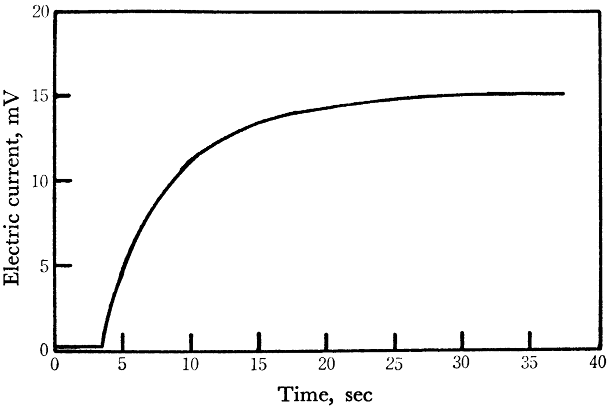

Fig. 5. Change in the electric conductivity of the ethanolic solution including tri-*n*-butylamine and chloranil.

Figure 5 shows the time dependence of conductivity of the ethanolic solution including tri-*n*-butylamine and chloranil. If the initial concentration of the amine, $[A_0]$, is excessively large compared with that of chloranil, $[Q_0]$, the electric current of the solution may change with time t as shown by the equation

$$I = \rho Q_0(1-e^{-[A_0]kt}) \tag{1}$$

where k is the rate constant for the reaction, Amine+Quinone→Amine$^+$+Quinone$^-$, and ρ is a constant determined by the electric charge and mobility of the ion, by the electrode voltage, and by the sizes of

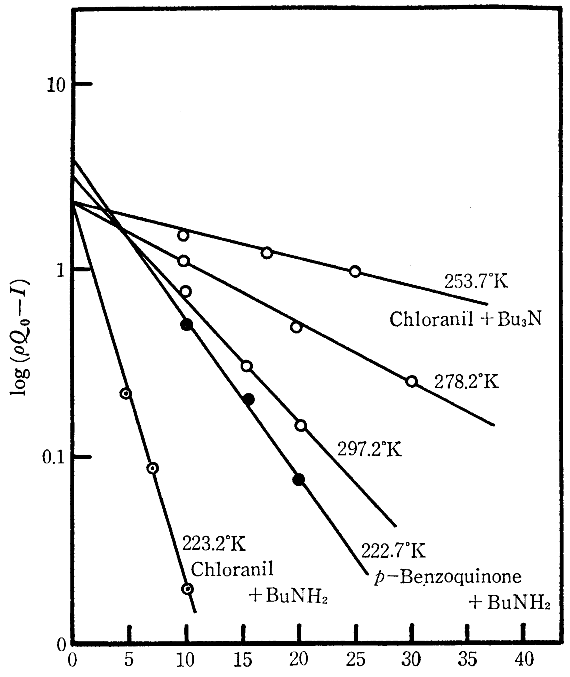

Fig. 6. Plots of log (ρQ_0-I) against the reaction time, *t*.

Table 1. IONIZATION RATE CONSTANTS FOR SOME ALIPHATIC AMINE QUINONE SYSTMES

Quinone	Amine	Rate constant ($sec^{-1}mol^{-1}$)
Chloranil	NBu_3	0.30 (253.7°K) 0.71 (278.2°K) 1.63 (297.2°K)
Chloranil	$BuNH_2$	0.89 (222.7°K)
p-Benzoquinone	$BuNH_2$	1.39 (223.2°K)

the electrodes. As is shown in Fig. 6, the plots of $\log(\rho Q_0\text{-}I)$ against t give a straight line for each system. This means that the observed rate of ionization fits well into Eq. (1). The rate constant of ionization was estimated from the slope of the straight line. The results are summarized in Table 1. This table shows that the rate of ionization is the smallest for the chloranil-tri-*n*-butylamine system. This is rather unexpected because tri-*n*-butylamine has the smallest ionization potential among the amines used in the present study, and suggests that the rate of ionization is sensitive to the steric factor of the amines.

The temperature dependence of the rate constant was measured for the system containing chloranil and tri-*n*-butylamine in ethanol; the result is shown in Fig. 6. The activation energy of ionization was estimated to be 0.57 kcal/mol. The activation energies for the other primary and secondary amine systems could not be measured because the succeeding chemical reactions are rapid at higher temperatures.

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