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Reactions of Aliphatic Amines with *p*-Benzoquinone and Its Chloro Derivatives

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The reactions of various aliphatic amines with *p*-benzoquinone and its chloro-derivatives were studied by detecting reaction intermediates by means of the rapid scan spectrophotometric method. A detailed kinetic study on the reaction intermediate and the final product was made for the system including *n*-butylamine and chloranil in ethanol; the result shows that the system produces 2,5-di-*n*-butylamino-3,6-dichloro-*p*-benzoquinone *via* the chloranil anion and the *n*-butylamine cation with the rate constant of 9.8×10^2 $sec^{-1}mol^{-1}l$ at 275.2°K. On the basis of reaction mechanisms, the reactions of various aliphatic amines with *p*-benzoquinone and its chloro-derivatives were classified into five types. Stabilization energies due to the amino-substitution of *p*-benzoquinone were calculated by the composite molecule method; the result shows that the 2,5-derivative is most stable among the disubstituted *p*-benzoquinones.

In previous papers,[1] we reported on the interactions of aniline and its *meta*-derivatives with chloranil and concluded that the substitution reactions occur through the outer(π)- and inner(σ)-complexes as reaction intermediates. In these cases, we could find no ion radical as a reaction intermediate. On the other hand, there are many systems consisting of electron donors and acceptors which are led to ionization and produce

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1) T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969); T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 380 (1971); T. Yamaoka and S. Nagakura, *ibid.*, **43**, 355 (1970).

the anion and cation radicals.[2] Furthermore, in some cases, the substitution or other reactions occur *via* these ion radicals. As an example, Eastman[3] reported that the reaction of *N,N*-dimethylaniline with chloranil proceeds through the ionized state to yield crystal violet.

In a previous paper[4] concerning the interactions of aliphatic amines with quinones, we demonstrated that ionization occurs and a quinone anion exists stably as a final product or transiently as a reaction intermediate. In the present paper, we focus our attention on reaction processes following ionization.

Studies have been carried out to clarify the mechanism of the reaction between alkylamine and quinone,[5] but details are not yet known. The S_N2 mechanism has hitherto been presented[5c] for the reactions of *p*-benzoquinone or its derivatives with alkylamines which act as nucleophilic reagents. In this mechanism, the ionization process is disregarded in the consideration of the reaction mechanism. However, the fact that the anion radicals of quinones exist transiently as a result of the interaction with alkylamines suggests that the reaction can proceed through ionized states. In view of this, we have undertaken to study the reaction mechanism with various systems including aliphatic amines as electron donors and *p*-benzoquinone or its chloro-derivatives as electron acceptors.

Experimental

Materials. *p*-Benzoquinone and chloranil were purified by recrystallization and sublimation at reduced pressure. Commercially available *n*-butylamine and tri-*n*-butylamine of GR grade were used without further purification. Their purities were checked by means of gas chromatography technique. Ethanol used as a solvent was refluxed with magnesium ethylate and was distilled. Ethyl ether was distilled after being kept with sodium metal.

Measurement. Electronic absorption spectra at various stages of a reaction path in solution were measured by a Hitachi rapid scan spectrophotometer RSP-2 located at the Institute of Industrial Science, The University of Tokyo. The apparatus is equipped with an automatically controlled mixing cell. Spectra could be measured every 1/3 sec in the wavelength range from 200 nm to 700 nm.

Results and Discussion

Rapid Scan Spectra of Systems Consisting of Alkylamines and Quinones. In order to clarify the mechanisms of reactions of aliphatic amines with *p*-benzoquinone and its chloro-derivatives in polar solvents, we measured the changes of absorption spectra with time by the rapid scan spectrophotometric method. First, let us explain the results obtained with the ethanol solution containing *p*-benzoquinone and *n*-butylamine ($BuNH_2$). As is seen in Fig. 1, the system shows a couple of peaks at 320 nm and 420—440 nm in the spectrum 1/3 sec after mixing. The peak intensities increase in parallel with each other up to 1 sec after mixing and afterward decrease gradually. As these peaks decrease in intensity, new absorption bands appear at 350 and 480 nm. The initial absorption spectrum is undoubtedly due to the *p*-benzoquinone anion radical judging from its position and shape in literature.[6] The final spectrum coincides with that of 2,5-dibutylamino-*p*-benzoquinone given in literature.[7] These facts show that electron transfer occurs from amine to quinone prior to the formation of 2,5-dibutylamino-*p*-benzoquinone. It should be noticed that the spectrum due to mono-butylaminated *p*-benzoquinone can not be observed. A similar time dependency of absorption spectra was also observed for the ethanol solutions including *n*-butylamine-2,5-dichloro-*p*-benzoquinone, *n*-butylamine-chloranil, and methylamine-*p*-benzoquinone. The reaction mechanism was studied in detail for the *n*-butylamine-chloranil system.

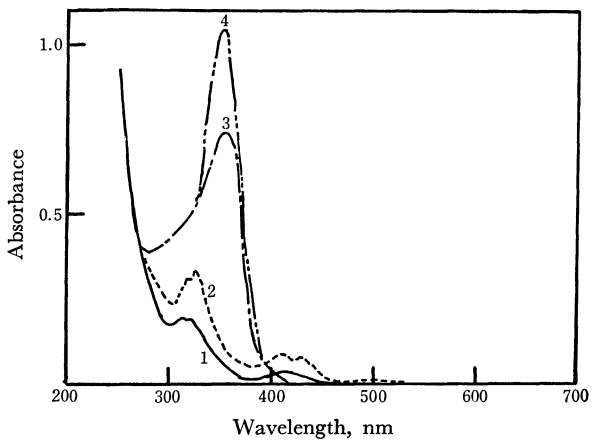


Fig. 1. Rapid scan spectra observed with the ethanol solution containing *n*-butylamine (5.1×10^{-2} mol/*l*) and *p*-benzoquinone (3.1×10^{-5} mol/*l*). Curves 1, 2, and 3 are the spectra measured 1/3 sec, 1 sec, and 10 sec, respectively, after the mixing, and curve 4 is the spectrum of the final product.

When trimethylamine is mixed with chloranil in ethanol, the absorption due to the chloranil anion radical rapidly appears. With the decrease of this absorption, an intense absorption occurs at 545 nm, which is due to 2-dimethylamino-3,5,6-trichloro-*p*-benzoquinone judging from its position and intensity.[7] As this absorption decreases in intensity, there appears the spectrum of the final product. This spectrum is the same as that of 2,5-bis(dimethylamino)-3,6-dichloro-*p*-benzoquinone given in literature.[7] This system is an example in which the absorptions due to the anion radical, the mono-alkylaminated quinone, and the final dialkylaminated product are separately observed with the progress of the reaction. Similar changes in ab-

2) Z. Rappoport, *J. Chem. Soc.*, **1963**, 4498; E. M. Kosower, "Progress in Physical Organic Chemistry," Vol. 3, ed. by S. G. Cohen *et al.*, Interscience Publisher, New York (1965), p. 81.

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

4) T. Yamaoka and S. Nagakura, This Bulletin, **44**, 1780 (1971).

5) a) B. K. Das and B. Majee, *J. Indian Chem. Soc.*, **45**, 1054 (1968); b) J. Kumanotani, F. Kagawa, A. Hikosaka, and K. Sugita, This Bulletin, **41**, 2118 (1968); c) L. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York (1961), p. 853.

6) R. Foster and J. V. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

7) D. Buckley, H. B. Henbest, and P. Slade, *J. Chem. Soc.*, **1957**, 4891.

sorption spectra were also observed for the ethanol solutions containing dimethylamine-*p*-benzoquinone and the diethylamine-*p*-benzoquinone, and for the ethereal solution of methylamine-*p*-benzoquinone.

Tri-*n*-butylamine is ionized by *p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone, and chloranil in such a polar solvent as ethanol but does not cause the substitution reaction.[4] However, trimethylamine reacts with chloranil gradually in ethanol to give 2,5-bis(dimethylamino)-3,6-dichloro-*p*-benzoquinone. This difference in the chemical reactivity between tri-*n*-butylamine and trimethylamine might be due to the great steric hindrance of the *n*-butyl group.

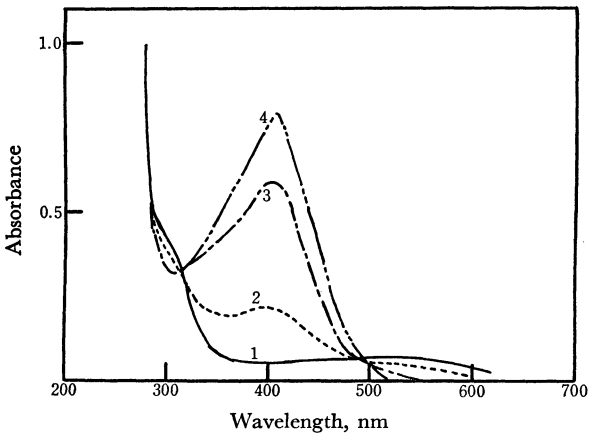


Fig. 2. Rapid scan spectra observed with the ethereal solution containing chloranil (7.9×10^{-5} mol/*l*) and an excess amount of dimethylamine. Curves 1, 2, and 3 are the spectra measured 1/3 sec, 2 sec, and 10 sec respectively, after the mixing, and curve 4 is the spectrum of the final product.

When we use ethyl ether as a solvent instead of ethanol, systems containing electron donors and acceptors show a general tendency for ionization to be difficult. When dimethylamine was mixed with chloranil in ethyl ether, the spectra shown in Fig. 2 were obtained. The absorption peaks appear at 300 and 500 nm in the spectrum 1/3 sec after mixing. These peaks are attributed to 2-dimethylamino-3,5,6-trichloro-*p*-benzoquinone.[7] As their intensities decrease, a new peak due to 2,5-bis(dimethylamino)-3,6-dichloro-*p*-benzoquinone[7] appears at 420 nm. In this case, the absorption of the chloranil anion radical could not be observed. A similar phenomenon was also observed for the ethereal solution containing *n*-butylamine and *p*-benzoquinone.

The ethereal solutions including methylamine-chloranil and *n*-butylamine-2,5-dichloro-*p*-benzoquinone give nothing but the absorption due to the final product, 2,5-dimethyl(or 2,5-di-*n*-butyl)aminated-*p*-benzoquinone.

Classification of the Amine-Quinone Reaction. The spectroscopic changes due to the progress in the reactions between alkylamines and quinones used as electron donors and acceptors, respectively, are greatly dependent on their properties as well as the polarity of the solvent. According to the present spectroscopic study, the reactions were phenomenologically[8] classified as shown in Table 1. The table clearly shows a general tendency for the spectra of the anion radicals of quinones to be easily observed in some stages of the reactions in ethanolic solutions, but not so in ethereal solutions. This may be due to the fact that the anion radical can be stabilized in such a polar solvent as ethanol. It may be noticed that the dimethylamine-chloranil system does not show the absorption of the

Table 1. Classification of the interactions of aliphatic amines with *p*-benzoquinone and its chloro-derivatives

Type of interaction[a]	System[b]
1) D+A→(D⁺)+A⁻ →(MS)→DS	$BuNH_2$-Q, QCl_2, QCl_4(EtOH)
	$MeNH_2$-Q(EtOH)
2) D+A→(D⁺)+A⁻ →MS→DS	Me_2NH-Q(EtOH)
	Me_3N-Q(EtOH)
	Et_2NH-Q(EtOH)
	$MeNH_2$-Q(Et_2O)
3) D+A→(D⁺)+A⁻	Bu_3N-Q, QCl_2, QCl_4(EtOH)(Et_2O)
4) D+A→MS→DS	$BuNH_2$-Q(Et_2O)
	Me_2NH-Q, QCl_2, (Et_2O)
	Me_2NH-QCl_4(EtOH)
5) D+A→(MS)→DS	Me_2NH-QCl_4(Et_2O)
	$BuNH_2$-QCl_2(Et_2O)

a) D, A, D^+, A^-, MS, and DS represent the electron donor, the electron acceptor, the donor cation, the acceptor anion, the monosubstituted species, and disubstituted species, respectively. The specimen in parentheses has not yet been observed directly by the spectrophotometric method.

b) Q, QCl_2, and QCl_4 indicate *p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone, and chloranil, respectively. (EtOH) and (Et_2O) indicate that ethanol and ethyl ether are used as solvents.

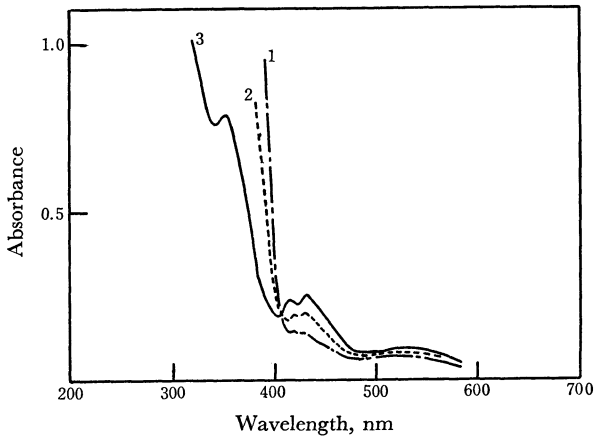
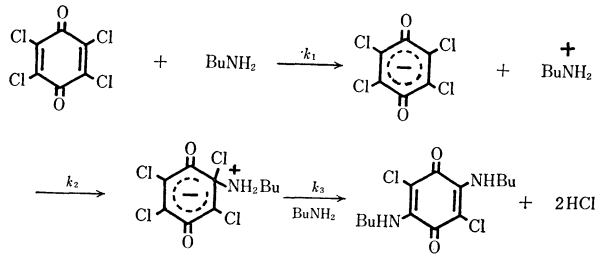


Fig. 3. Rapid scan spectra observed with the ethanol solution containing *n*-butylamine (5.1×10^{-2} mol/*l*) and chloranil (5.0×10^{-5} mol/*l*). Curves 1, 2, and 3 are the spectra measured 1/3 sec, 10 sec, and 40 sec respectively, after the mixing.

8) This classification is made on the basis of the spectroscopic behaviors observed for the systems containing aliphatic amines and *p*-benzoquinone or its chloro-derivatives. This is inevitable at the present stage when the reaction mechanism for the systems belonging to classes (4) and (5) is not yet clarified. Some minor modifications might be necessary when we succeed in clarifying it, though very difficult. For example, the Me_2NH-QCl_4(EtOH) system might move to class (2).

chloranil anion radical even in ethanol, in spite of the fact that the system containing dimethylamine and benzoquinone which is weaker as an electron acceptor than chloranil is ionized in ethanol. Although the reason for this is not clear, it may probably be due to the fact that the ionization process is slower than the succeeding substitution reaction process.

Reaction of n-*Butylamine and Chloranil.* Let us explain the reaction processes in detail, taking the ethanol solution containing *n*-butylamine and chloranil as an example. The time-dependence of the spectrum observed for this system is shown in Fig. 3. In the spectrum 1/3 sec after the mixing, the absorption of the chloranil anion radical[6] can clearly be observed at 420—450 nm. With the decrease in absorption intensity, a new peak due to 2,5-di-*n*-butylamino-3,6-dichloro-*p*-benzoquinone[7] appears, andthe isosbestic point is found at 410 nm. Thus, the following mechanism is proposed for the reaction of *n*-butylamine with chloranil. Here the first step of the reaction is



the electron transfer from *n*-butylamine to chloranil to form the anion radical. In the second step, the chloranil anion radical reacts with the *n*-butylamine cation to produce 2-*n*-butylamino-3,5,6-trichloro-*p*-benzoquinone,[7] which reacts further with *n*-butylamine to yield 2,5-di-*n*-butylamine-3,6-dichloro-*p*-benzoquinone.

In order to confirm the mechanism, we carried out a kinetic study for the *n*-butylamine-chloranil system. According to the above mechanism, the rate equation concerning the chloranil anion is given as follows:

$$\begin{aligned} d[Q^-]/dt &= k_1[A][Q] - k_2[Q^-]^2 \\ &= k_1'[Q] - k_2[Q^-]^2 \end{aligned} \quad (1)$$

where [A], [Q], and [Q^-] are the concentrations of *n*-butylamine, chloranil, and the chloranil anion radical, respectively. In our system, [A]>[Q] is satisfied and [A] may be regarded as constant during the reaction. From the time dependence of the peak intensity of the chloranil anion radical, the rate constant for the first step k_1, is known to be apparently much larger than that for the second step k_2. Therefore, after some stage of the reaction, the k_1[A][Q] term in Eq. (1) may be disregarded and we obtain the following equation:

$$k_2t = 1/[Q^-] - 1/[Q_0^-] \quad (2)$$

where [Q_0^-] is the apparent concentration of the chloranil anion radical at $t=0$, the reciprocal of which can be obtained by extrapolating the $1/[Q^-]-t$ relation to the initiation time of the reaction, and may be expected to be almost equal to the initial concentration of chloranil.[9] In the present system, [Q^-] can be determined spectroscopically with considerable accuracy. This is because its absorption spectrum in the 420—450 nm region is not overlapped with the absorptions of the other specimens in this system and the molar extinction coefficient is known.[10] Plotting the observed $1/[Q^-]$ values against reaction time t, we can obtain a straight line as is shown in Fig. 4. This means that Eq. (2) is satisfied and supports the proposed mechanism given by this equation. From the slope of the straight line, the value of k_2 was estimated to be $9.8(\pm0.5)\times10^2$ sec^{-1} mol^{-1} l at 275.2°K.[9]

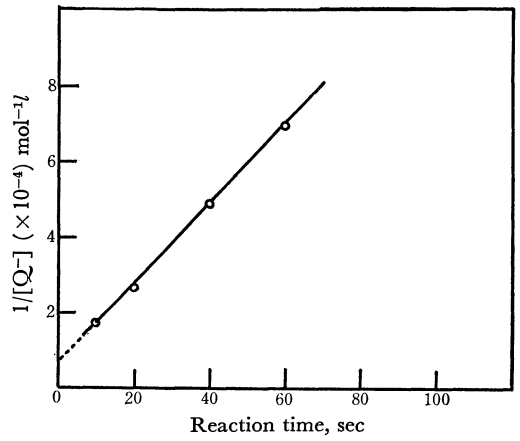


Fig. 4. Plots of the reciprocal of the concentration of the chloranil anion radical against the reaction time. The concentrations of *n*-butylamine and chloranil are 5.05×10^{-2} mol/l and 1.80×10^{-4} mol/l, respectively.

The value of k_2 was also obtained from the rate of the formation of the final product by the aid of the following equation:

$$k_2t = [P]/([Q_0^-]^2-[Q_0^-][P]) \quad (3)$$

where [P] is the concentration of the final product. Equation (3) can be derived by combining Eq. (2) with the relation $[Q^-]=[Q_0^-]-[P]$ which is reasonable from the reaction mechanism presented by us. The value of k_2 obtained from the time dependence of the observed [P]'s by the aid of Eq. (3) is $8.5(\pm0.4)\times10^2$ sec^{-1} mol^{-1} l at 275.2°K and is consistent with the value obtained by the aid of Eq. (2) within experimental errors.

It is concluded that the replacement reaction observed for the chloranil-*n*-butylamine system proceeds through the ionic species, the chloranil anion and the *n*-butylamine cation, as reaction intermediates. Thus it may be said that the present study gives experimental support to the electron transfer mechanism for the substitution reaction proposed by one of the authous (S.N.) and Tanaka from the consideration of the molecular orbitals of substrates and reagents.[11]

9) The [Q^-] value obtained from the intercept of the straight line with the ordinate is almost equal to the initial concentration of chloranil. This shows the adequateness of the present treatment and supports the reaction mechanism.

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11) S. Nagakura and J. Tanaka, This Bulletin, **32**, 734 (1959).

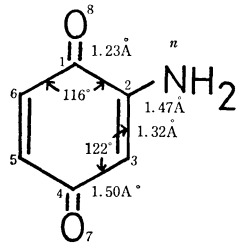

Fig. 5. Geometrical structure and numbering of 2-amino-benzoquinone.

Stabilization Energies of the Aminated p-*Benzoquinones.* The stabilization energies of aminated *p*-benzoquinones were calculated by the composite molecule method.[12] Let us explain the calculation procedure taking 2-amino-*p*-benzoquinone as an example. The system was divided into two components; *p*-benzoquinone and the amino group. The numbering of the atoms and geometry of the molecule are shown in Fig. 5. The Hückel orbitals of *p*-benzoquinone were taken as the component orbitals[13] since they do not differ appreciably from the SCF MO's evaluated by the P-P-P method.[14] The interaction between *p*-benzoquinone and the amino group was taken into account by the configuration interaction between the ground (G), several locally-excited (LE), and charge-transfer (CT) configurations.

The energy of the ground configuration was taken to be standard. The energies of the lowest two locally excited configurations (LE_1, LE_2) were taken to be equal to the observed transition energies corresponding to the first and second bands of *p*-benzoquinone. The energies of CT configurations were calculated by the relation, $I-A+\Delta C$, where I, A, and ΔC represent the ionization potential of amino group (8.40 eV),[15] the electron affinity of *p*-benzoquinone (2.02 eV),[16] and the electrostatic interaction energy between the positive and negative charges caused by an electron transfer from the amino group to *p*-benzoquinone, respectively. The Pariser-Parr approximation[17] was used for evaluating the two center Coulomb repulsion integrals necessary for the evaluation of ΔC. The energies of the configurations are shown in Fig. 6.

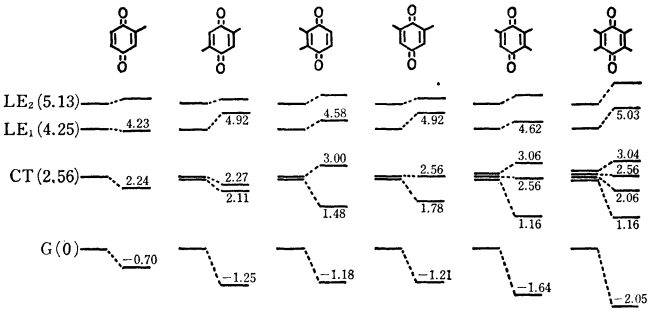

Fig. 6. Configurations used for the composite molecule calculation and the calculated energies (eV) of amino-substituted *p*-benzoquinones. For example, the configurations for 2-amino-*p*-benzoquinone are represented as follows:
$G=|1\,\bar{1}\,2\,\bar{2}\,3\,\bar{3}\,n\,\bar{n}|$ $LE_1=0.9794\,\Phi\,(3\to5)-0.2021\,\Phi(4\to6)$
$LE_2=\Phi\,(3\to6)$
$CT=\Phi\,(n\to4)$
where, $\Phi\,(a\to b)=\{|1\ldots a\bar{b}\ldots\bar{n}|+|1\ldots b\bar{a}\ldots\bar{n}|\}/\sqrt{2}$
and 1, 2,... are the Hückel MO's of *p*-benzoquinone, and n is the 2p AO of amino-nitrogen.

The non-zero off-diagonal matrix elements for each of the interactions between the CT configurations and the G or LE configurations can be represented by the aid of the resonance integral β_{CN} between the neighboring nitrogen and carbon atoms. The value was taken to be −2.0 eV after several trial calculations.

The stabilization energies of *p*-benzoquinone caused by the amino substitutions were evaluated as the difference in energy between the ground configuration and the calculated lowest state. The results are shown in Fig. 6. We see that the 2,5-isomer is most stable among diaminobenzoquinones. This may be related to the fact that the substitution reaction preferably occurs on the 2,5-positions of *p*-benzoquinone.

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17) P. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).