High-pressure Kinetics of the Reactions of *p*-Benzoquinone with Aliphatic Amines in Aprotic Solvents

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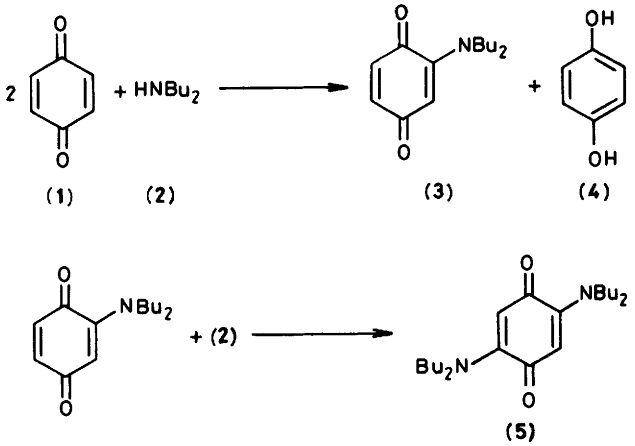
The rates of substitution reaction between *p*-benzoquinone and dibutylamine and of the electron-transfer reaction between chloranil and tripropylamine were examined spectrophotometrically, under pressure, in dichloromethane, 1,2-dichloroethane, chloroform, and acetonitrile. For the substitution to produce 2-dibutylamino-*p*-benzoquinone the reaction rate obeyed a third-order kinetic equation: first order with respect to *p*-benzoquinone and second order with respect to dibutylamine. The activation volume was as large as *ca.* -60 cm^3 mol^{-1} in the solvents used, and a negative activation energy of -31 kJ mol^{-1} was observed in acetonitrile. A reaction scheme has been proposed where an electron-transfer reaction to form the *p*-benzoquinone anion radical occurs prior to the rate-determining step, which is the second attack by the amine. By taking into account the result that the electron transfer from chloranil to tripropylamine accompanied the activation volume of *ca.* -30 to -45 cm^3 mol^{-1}, the reaction volume of this process was estimated to be *ca.* -45 cm^3 mol^{-1}. Thus, in the *p*-benzoquinone–dibutylamine system we may reasonably assign the activation volume of -10 to -15 cm^3 mol^{-1} to the second bimolecular attack by the amine.

It is known that *p*-benzoquinone and chloranil, electron acceptors, react with mono- and di-alkylamines, electron donors, to give mono- and di-substituted *p*-benzoquinones.[1–3] With tertiary amines only the radical anion of *p*-benzoquinone was formed. Nagakura and co-workers studied extensively the electronic spectra of these reaction systems and found that, even with primary and secondary amines, the radical anion of the quinone was tentatively formed in alcoholic solution. However, the role of the radical anion in the course of the substitution reaction is not yet obvious. Some cases were reported that the interaction between electron donor and acceptor leads to their ionization.[4–6] For one of the possiblities, it may be assumed that the process of electron transfer between *p*-benzoquinone and amine exists as a precursory step of the substitution. In a previous paper,[7] we suggested that the electron-transfer process was likely to occur in the first stage. In order to make the reaction mechanism clear we carried out extensive kinetic studies of the substitution reaction between *p*-benzoquinone and dibutylamine and the electron-transfer reaction from tripropylamine to chloranil in some aprotic solvents.

The study of reaction rates in solution at high pressure is well recognized as giving a great deal of important information on the role of the solvent in activation and reaction dynamism.[8] Since an electron-transfer reaction between neutral molecules is not accompanied by a drastic rearrangement of the reactant molecules, but the charge generation significantly affects the degree of solute–solvent interaction, the pressure effect on the reaction rate reflects, very approximately, only the charge in solvation upon activation. However, to our knowledge, an experimental study focused on this viewpoint has never been made for organic molecules, so we also examined the kinetics of the reaction between chloranil and tripropylamine under pressure as well as the substitution reaction.



Scheme 1.

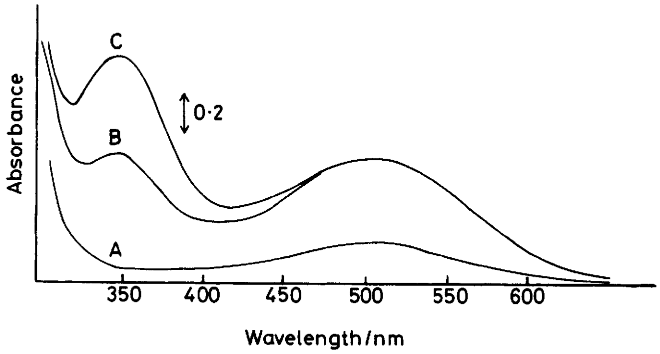


Figure 1. Absorption spectra of a *p*-benzoquinone–dibutylamine mixture in acetonitrile. $[(1)]_0$ = 0.5 mmol dm^{-3}, $[(2)]_0$ = 38 mmol dm^{-3}. Minutes after mixing at 2 500 bar: A, 10; B, 60; and C, 120

Results and Discussion

Reaction of p-*Benzoquinone with Dibutylamine.*—With dichloromethane, 1,2-dichloroethane, and acetonitrile as solvents, chosen because the reaction rates suited the measurement at high pressure and there was no complication due to autoprotolysis, the reaction of *p*-benzoquinone (1) with dibutylamine (DBA) (2) produced only 2-dibutylamino-*p*-benzoquinone (3) and hydroquinone (4) at 1 bar and 25 °C over several hours. But as the reaction proceeded further, the formation of 2,5-bis(dibutylamino)-*p*-benzoquinone (5), which is a disubstituted product, became noticeable (Scheme 1). The change in the electronic absorption spectrum of the reaction mixture shows that the appearance of (5) ($\lambda_{max.}$ 350 nm in acetonitrile, 360 nm in dichloromethane and 1,2-dichloroethane) is preceded by the formation of (3) ($\lambda_{max.}$ 503 nm in acetonitrile, 508 nm in 1,2-dichloroethane, and 510 nm in dichloro-

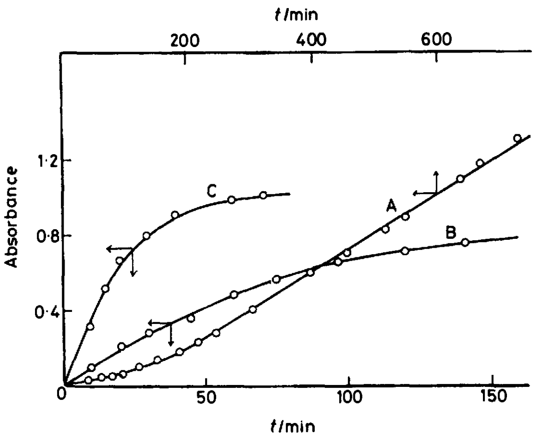


Figure 2. The increase in absorbance at 508 nm due to formation of (3) in 1,2-dichloroethane at 25 °C. A, 1 bar, $[1]_0$ = 3 mmol dm^{-3}, $[2]_0$ = 30 mmol dm^{-3}; B, 2 000 bar, $[1]_0$ = 0.6 mmol dm^{-3}, $[2]_0$ = 40 mmol dm^{-3}; C, 3 000 bar, $[1]_0$ = 0.6 mmol dm^{-3}, $[2]_0$ = 40 mmol dm^{-3}

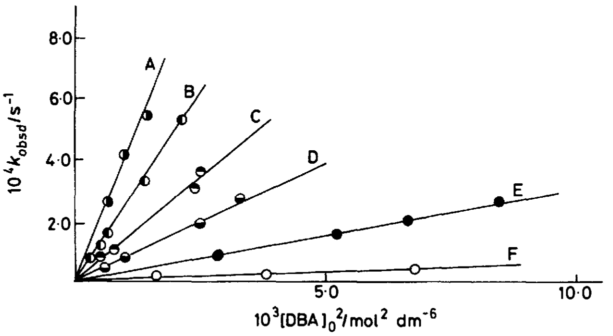


Figure 3. Plot of $k_{obsd.}$ against dibutylamine concentration in acetonitrile at 25 °C, at different pressures. A, 2.5 kbar; B, 2.0 kbar; C, 1.5 kbar; D, 1.0 kbar; E, 0.5 kbar; F, 1 bar

methane) as seen in Figure 1, and the formation of (5) is much more enhanced by pressure than is the formation of (3). The stoicheiometry was in accord with a polarographic study in alcoholic solvents.[9] In this work we focused on the formation of (3).

Figure 2 shows that in 1,2-dichloroethane at 1 bar the amount of (3) becomes significant only after an induction period, and the rate of formation increases with increasing pressure. However, in dichloromethane and acetonitrile this feature was not observed. When $HNBu_2$ existed in a large excess over *p*-benzoquinone the apparent rate of the formation of (3) obeyed a first-order kinetic equation. The slope of the Guggenheim plot then gave the observed pseudo-first-order rate constant $k_{obsd.}$. As shown in Figure 3 the plot of $k_{obsd.}$ against the square of the concentration of $HNBu_2$ was a straight line in each solvent, under the present experimental conditions. It is concluded that the rate of monosubstitution is third order: first order with respect to *p*-benzoquinone and second order with respect to $HNBu_2$ (2). The numerical values of the third-order rate constants *k* are listed in Tables 1—3. Activation energy E_a and activation entropy $\Delta S^{\ddagger}$ were obtained from the dependence of *k* on temperature. It is noticeable that, in acetonitrile, *k* decreased with increasing temperature.

Pressure greatly enhanced the rate of this reaction. The activation volume $\Delta V^{\ddagger}$ was calculated from equation (1). For

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^{\neq}}{RT} \qquad (1)$$

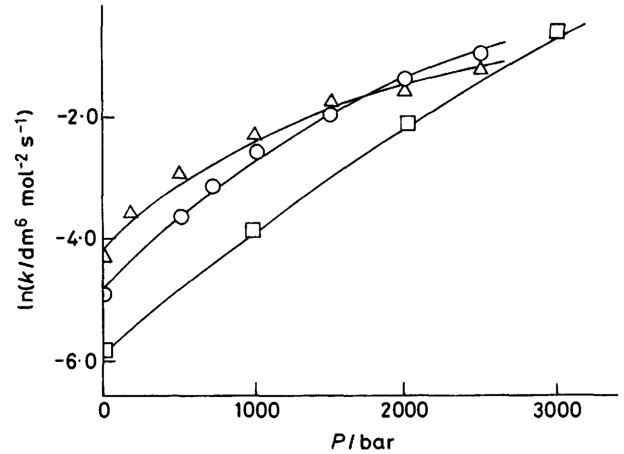


Figure 4. Pressure dependence of the rate constant for the monosubstitution reaction of *p*-benzoquinone–dibutylamine at 25 °C. □, 1,2-Dichloroethane; ○, acetonitrile; △, dichloromethane

Table 1. Third-order rate constants $10k(dm^6\ mol^{-2}\ s^{-1})$ for the *p*-benzoquinone–dibutylamine monosubstitution reaction (25 °C) at different pressures[a]

	p/bar						
Solvent	1	500	1 000	1 500	2 000	2 500	3 000
CH_2Cl_2	0.118	0.630	1.32	1.62	2.88	3.37	
$ClCH_2CH_2Cl$	0.029		0.208		1.29		5.95

[a] Experimental uncertainty is ±3%.

Table 2. Third-order rate constants $10^3\ k(dm^6\ mol^{-2}\ s^{-1})$ for the *p*-benzoquinone–dibutylamine monosubstitution reaction (1 bar) at different temperatures[a]

	T/°C			
Solvent	15	20	25	30
CH_2Cl_2	6.95	9.23	11.8	14.4
$ClCH_2CH_2Cl$	2.53	2.73	2.90	3.20

[a] Experimental uncertainty is ±3%.

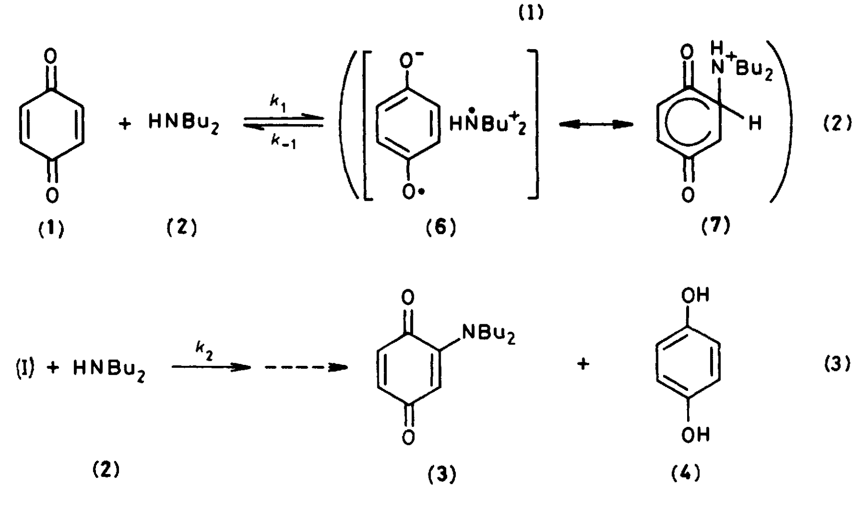
Table 3. Third-order rate constants $10^2k(dm^6\ mol^{-2}\ s^{-1})$ for the *p*-benzoquinone–dibutylamine monosubstitution reaction in acetonitrile at different pressures and temperatures

	p/bar					
T/°C	1	500	1 000	1 500	2 000	2 500
15	1.11	3.38				
20	1.00	3.30				
25	0.715	2.93	8.23	14.4	24.5	35.7
30	0.583	2.77				

[a] Experimental uncertainty is ±3%.

the solvent used, this equation gave, as shown in Figure 4, a slightly curved plot. By representing the logarithm of *k* by a quadratic function of pressure,[7] $\Delta V^{\ddagger}$ was calculated from the differential coefficient at 1 bar. The activation parameters E_a, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ at 1 bar and 25 °C are given in Table 4. The magnitude of $\Delta V^{\ddagger}$ is such that it is not associated with a single reaction step.

These results strongly suggest that the substitution consists of



Scheme 2.

Table 4. Activation parameters for the *p*-benzoquinone–dibutylamine monosubstitution reaction

Solvent	E_a kJ mol^{-1}	$\Delta S^‡$ J mol^{-1} K^{-1}	$\Delta V^‡$ cm^3 mol^{-1}
CH_3CN	-31 ± 2	-390	-67 ± 3
CH_2Cl_2	39 ± 2	-160	-63 ± 3
$ClCH_2CH_2Cl$	11 ± 2	-260	-54 ± 2

several reaction steps. A probable reaction involved in the course of formation of (3) is an electron transfer from $HNBu_2$ to *p*-benzoquinone. The electronic absorption spectrum of the mixture in dichloromethane showed the tentative formation of a *p*-benzoquinone radical anion in the early stage of the reaction. The characteristic absorption of this radical, *ca.* 420—450 nm, though weak, was found.[10] The e.s.r. spectrum also gave evidence for the existence of the radical: a quintet of intensity ratio 1:4:6:4:1 and $a_H = 0.235$ mT[11] was found for *ca.* 10 min after the mixing.

Hence the reaction given in Scheme 2 may be proposed. First, either the radical ion pair (6) or a zwitterionic σ-complex (7),[2,12] which is a result of combination of the radical pair, may be formed as an intermediate (I). Second, the fact that the rate is of second order with respect to (2) means that the over-all reaction is base catalysed, and the rate-determining step would be the proton abstraction by the second amine molecule. If the steady-state approximation is applied to an intermediate (I), the pseudo-first-order rate constant $k_{obsd.}$ is expressed by equation

$$k_{obsd.} = \frac{k_1 k_2 [DBA]_0^{\,2}}{k_{-1} + k_2[DBA]_0} \tag{4}$$

(4), where $[DBA]_0$ denotes the initial concentration of (2). Furthermore, if $k_{-1} > k_2[DBA]_0$ equation (5) is obtained,* and

$$k_{obsd.} = \frac{k_1}{k_{-1}} k_2 [DBA]_0^{\,2} \tag{5}$$

thus it is understood that the reaction has the second-order dependence on the amine concentration. Based on Scheme 2 and equation (5), the apparent activation energy of the substitution, E_a, is represented by the sum of the enthalpy change of reaction (2), $\Delta H_1{}^0$ [$= E_{a(1)} - E_{a(-1)}$], and the activation energy of reaction (3), $E_{a(2)}$. The negative value of E_a in acetonitrile is explicable by supposing $-\Delta H_1{}^0 > E_{a(2)}$. In the same way the activation volume $\Delta V^‡$ is represented by the sum of $\Delta V_1{}^0$ and $\Delta V_2{}^‡$. We could not evaluate $\Delta H_1{}^0$ and $E_{a(2)}$ separately since the early stage of the reaction was concealed by the subsequent substitution reaction, as described in the next section. However, it seems likely that reaction (2) is fairly exothermic because the radical ions produced will be strongly solvated in dipolar solvents. The variation of the activation energy with solvent seems to reflect the electrostatic solvent–transition state interaction; the solvent of higher dielectric constant lowers E_a and $\Delta S^‡$. However, $\Delta V^‡$ does not follow these lines. At present we cannot explain the variation of all the activation parameters with solvent, and more studies on other bases may help to solve this problem.

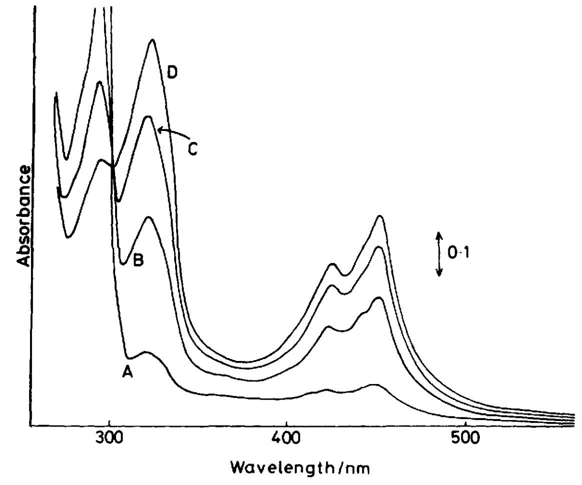


Figure 5. Absorption spectra of the chloranil–tripropylamine mixture in dichloromethane at 25 °C and 1 bar, at different times. A, 0.5; B, 10; C, 25; and D, 55 min

Electron Transfer from Tripropylamine to Chloranil.—In order to estimate the volumetric contribution from each reaction step based on Scheme 2, it is necessary to study the

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* This assumption means that reaction (2) is in a preliminary equilibrium. The backward electron transfer k_{-1} within a solvent cage is expected to be faster than the bimolecular attack requiring bond cleavage, particularly at low concentrations of DBA.

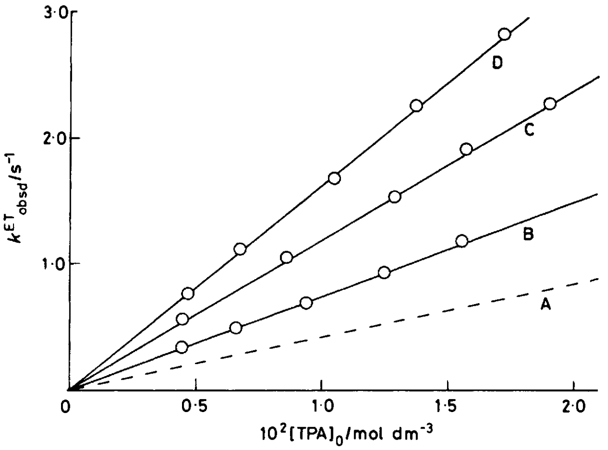

Figure 6. Dependence of $k_{obsd.}^{ET}$ on the tripropylamine concentration at 25 °C in dichloromethane. The dashed line (A) for 1 bar is from the results of spectrophotometry using a quartz cuvette cell: B, 250; C, 500; D, 750 bar

electron-transfer process at high pressure. In a *p*-benzoquinone–dibutylamine system the electronic spectrum showed an absorption at *ca.* 420—450 nm at first, and though weak, its growth rate obeyed second-order kinetics: first order with respect to both (**1**) and (**2**). However, since the subsequent substitution masked the quantitative analysis of this absorption, we chose, analogous to *p*-benzoquinone–dibutylamine, the chloranil (**8**)–tripropylamine (**9**) system in which no other appreciable reactions took place in *ca.* 1 h, other than electron transfer.

With chloroform, dichloromethane, and 1,2-dichloroethane as solvents, characteristic absorptions of the chloranil radical anion appeared at 323, 424, and 450 nm (Figure 5) corresponding to a singlet e.s.r. spectrum.[10,13] When the concentration of amine (**9**) is excessively large compared with that of (**8**), the rate of radical formation obeyed a first-order rate equation. A plot of the observed pseudo-first-order rate constant k_{obsd}^{ET} against the amine concentration was a straight line, as shown in Figure 6. The second-order rate constant, k^{ET}, obtained from Figure 6 is given in Table 5. A plot of lnk^{ET} *versus* p gave a straight line up to 750 bar in all solvents used; the activation volume $\Delta V_{ET}^{\ddagger}$ is given in Table 6 along with E_a^{ET} and $\Delta S_{ET}^{\ddagger}$. The large negative value of $\Delta V_{ET}^{\ddagger}$, -30 to -45 cm^3 mol^{-1}, seems attributable to the electrostriction brought about by generation of the electric charge at the transition state. Although there has been no study, to our knowledge, on the activation volume of a purely electron-transfer process in non-aqueous solvents, examples involving the effect of charge separation on activation parameters may be comparable. The activation volumes for Menschutkin reactions[8] are -30 to -60 cm^3 mol^{-1}. However, the proton–deuteron transfer reaction from carbon acid to aliphatic amines has a less negative value, -10 to -20 cm^3 mol^{-1}.[14—16]

The change of $\Delta S_{ET}^{\ddagger}$ with solvent parallels that of $\Delta V_{ET}^{\ddagger}$. Such a tendency is often observed in other reactions and indicates that the coupling of the solvent molecule at the transition state is important.[17,18] In this case an equilibrium study was impossible because the radical decayed slowly after about 1 h. The enthalpy change associated with the reaction could not be determined, but it seems fairly exothermic, considering the large equilibrium constant suggested by the plot of Figure 6 and the strong solvation of the radical ion.

Table 5. Second-order rate constant 10^2k^{ET}(dm^3 mol^{-1} s^{-1}) for the chloranil–tripropylamine reaction[a]

		p/bar			
Solvent	*T*/°C	1	250	500	750
CH_2Cl_2	15	2.49			
	20	3.92			
	25	4.53	7.72	11.9	17.6
	30	5.77			
$ClCH_2CH_2Cl$	20	4.29			
	25	6.14	8.17	12.6	17.2
	30	7.94			
	35	10.0			
$CHCl_3$	15	2.04			
	20	2.79			
	25	3.87	5.19	7.38	9.70

[a] Experimental uncertainty is ±3%.

Table 6. Activation parameters for electron-transfer reaction between chloranil and tripropylamine

Solvent	E_a^{ET} kJ mol^{-1}	$\Delta S_{ET}^{\ddagger}$ J mol^{-1} K^{-1}	$\Delta V_{ET}^{\ddagger}$ cm^3 mol^{-1}
CH_2Cl_2	39 ± 2	−150	−44 ± 3
$ClCH_2CH_2Cl$	42 ± 2	−130	−35 ± 2
$CHCl_3$	45 ± 2	−130	−31 ± 2

Since neither bond cleavage nor formation takes place in the electron-transfer process, the structural contribution to ΔV_{ET}° or $\Delta V_{ET}^{\ddagger}$ is negligible; the activation volume depends almost entirely on the degree of rearrangement of the solvent molecules and the degree of charge generation at the transition state. Hence the reaction volume is supposed to be smaller (a more negative value) than the activation volume: $\Delta V_{ET}^{\circ} < \Delta V_{ET}^{\ddagger}$. We can estimate ΔV_{ET}° approximately on the basis of Born's equation as given by equation (6).[19] $\Delta V_{solv.}^{\circ}$ denotes the reaction

$$\Delta V_{ET}^{\circ} = \Delta V_{solv.}^{\circ} = -\frac{1}{2}Ne^2\left(\frac{1}{a_Q}+\frac{1}{a_A}\right)\frac{\partial}{\partial p}\left(1-\frac{1}{\varepsilon}\right) \qquad (6)$$

volume due to the difference in the degree of solvation. The radii a_Q and a_A are of chloranil and tripropylamine radicals, respectively. N denotes Avogadro's constant, e the unit charge, and ε the dielectric constant of solvent. The radii were estimated from the rate of self-exchange reaction to be *ca.* 5—6 Å each.[20] The value of $\Delta V_{solv.}^{\circ}$ was calculated to be -40 to -45 cm^3 mol^{-1} in dichloromethane and 1,2-dichloroethane.* Considering that $\Delta V_{ET}^{\circ} < \Delta V_{ET}^{\ddagger} < 0$ and the calculated value of ΔV_{ET}° is comparable to $\Delta V_{ET}^{\ddagger}$ it seems likely that the electron will be almost completely transferred in the transition state. Consequently ΔV_{ET}° can be regarded to be *ca.* -45 cm^3 mol^{-1}. This estimated value is also comparable with the reaction volume for a Menshutkin reaction,[8] *ca.* -50 cm^3 mol^{-1}, but it is less than that of proton/deuteron transfer,[15] -15 to -35 cm^3 mol^{-1}.

Pressure Effect on the p-*Benzoquinone–Dibutylamine System.*—As was discussed for equation (5), the activation volume of the monosubstitution, $\Delta V^{\ddagger}$, is composed of two components, equation (7). The reaction volume ΔV_1, which is for the first

$$\Delta V^{\ddagger} = \Delta V_1 + \Delta V_2^{\ddagger} \qquad (7)$$

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* The change in dielectric constant with pressure was cited from the following literature: L. G. Schornack and C. A. Eckert, *J. Phys. Chem.*, 1970, **74**, 3014; J. F. Skinner, F. L. Clusser, and R. M. Fuoss, *ibid.*, 1968, **72**, 1057.

electron-transfer process, is estimated to be *ca.* -45 cm^3 mol^{-1}; this is also the case for the *p*-benzoquinone–dibutylamine system, by taking into account that $\Delta V_{ET}°$ for the chloranil–tripropylamine reaction holds approximately for this system. For the second reaction between the intermediate (I) and $HNBu_2$ the activation volume $\Delta V_2^{\ddagger}$ is considered, in a similar way to the proton transfer from a carbon acid to a base,[14–16] to be -10 to -20 cm^3 mol^{-1}. Thus we can reasonably explain the overall activation volume being as large as -50 to -60 cm^3 mol^{-1} for the substitution reaction. In conclusion, the reaction scheme in which the electron transfer takes place prior to the rate-determining proton abstraction is reasonable when we consider the activation volume as well as other activation parameters.

Experimental

Materials.—*p*-Benzoquinone (**1**) (m.p. 115—116 °C) was recrystallized from light petroleum. Chloranil (**8**) (m.p. 289—290 °C) was recrystallized a number of times from acetone. They were stored away from the light, and purification was repeated frequently. Dibutylamine (**2**) (b.p. 159—160 °C) and tripropylamine (**9**) (b.p. 156—157 °C) were dried (NaOH or KOH) and distilled after being refluxed over CaH_2. Acetonitrile was refluxed over Na_2CO_3 and P_2O_5, then distilled (b.p. 81—82 °C). 1,2-Dichloroethane (b.p. 83—84 °C) and dichloromethane (b.p. 39—40 °C) were refluxed over CaH_2 and then distilled. Chloroform (spectrograde) was used without further purification.

Apparatus and Procedure.—Absorption spectra at 1 bar were recorded by a Shimadzu UV-200S spectrophotometer. The reaction rate was followed spectrophotometrically by monitoring the absorbance of the product.

At high pressure the kinetic measurement was carried out as follows. For the substitution reaction of the *p*-benzoquinone–dibutylamine system, we used a piston–cylinder-type high-pressure apparatus.[21] A Teflon capsule with thin walls (less than 0.1 mm) is filled with *ca.* 4 cm^3 of the reaction solution and put into the high-pressure cylinder, which is preheated to the desired temperature. The pressure-transmitting fluid is silicone oil and the pressure was measured by a manganin wire gauge, calibrated for a free piston pressure balance. After the desired reaction time, the pressure was relaxed to 1 bar, then the absorbance of the mixture was recorded. For the chloranil–tripropylamine reaction, the *in-situ* method for optical measurement was applied.[22] Using a high-pressure bomb equipped with two sapphire windows the absorbance at a particular wavelength was recorded after thermal equilibrium had been attained at a desired pressure. Temperature was regulated to within ±0.1 °C by circulating thermostatted fluid around the high-pressure bomb.

The concentration of amine was 50—300 fold as high as the *p*-benzoquinones. The concentration prepared at 1 bar was corrected for compression on the basis of density data of Srinivasan and Kay[23] for acetonitrile and of Newitt and Weale[24] for the other solvents.

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