# High-pressure Kinetics of the Reaction of *p*-Benzoquinone with Di-n-butylamine in Some Aprotic Solvents

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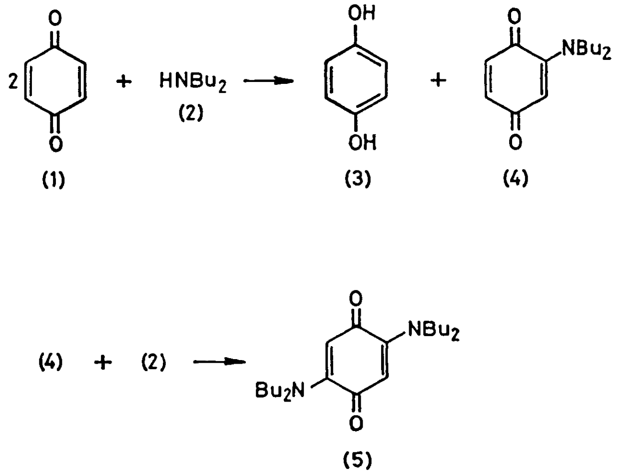
*Summary* The kinetics and the volume of activation of the title reaction to form 2-dibutylamino-*p*-benzoquinone in 1,2-dichloroethane and acetonitrile, $-54 \pm 2$ and $-67 \pm 2$ cm$^3$/mol respectively, strongly support a reaction scheme in which ionic species are formed prior to the rate-determining step which is the second attack by the amine.

The reaction of *p*-benzoquinone and chloranil with some aliphatic amines has been studied extensively by Nagakura and his co-workers;[1] in alcoholic solvents mono- and/or di-substituted *p*-benzoquinones are formed in the reactions with primary and secondary amines, while only radical anions are produced with tertiary ones.

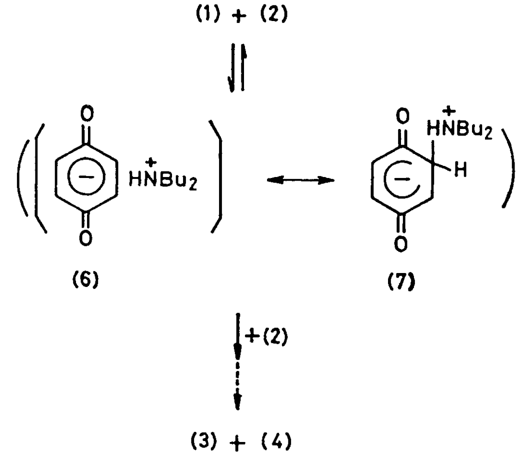
We have carried out a kinetic study at high pressure in order to elucidate the mechanism of the substitution of *p*-benzoquinone (**1**) by di-n-butylamine (**2**) which was chosen because the butyl hydrogen atoms were not eliminated in the reaction, in contrast with the case of ethylamines.[2,3]

In 1,2-dichloroethane and acetonitrile as solvent, which were chosen because the reaction rate suited the measurement at high pressure and there were no complications due to autoprotolysis, hydroquinone (**3**) and 2-dibutylamino-*p*-benzoquinone (**4**), ($\lambda_{max}$ 508 and 500 nm in 1,2-dichloroethane and acetonitrile, respectively) were the only products at a pressure of 1 bar and 25 °C over several hours. The stoicheiometry was in accordance with a polarographic study in alcoholic solvents[4] (Scheme 1). At high pressure the rates of formation of both (**4**) and 2,5-bis(dibutylamino)-*p*-benzoquinone (**5**), ($\lambda_{max}$ 360 and 350 nm in 1,2-dichloroethane and acetonitrile, respectively) increased greatly, although the formation of (**5**) was preceded by the appearance of (**4**). It is noteworthy that the formation of (**5**) was markedly enhanced by pressure; when a solution containing 0·1 mmol/dm$^3$ of (**1**) and 0·02 mol/dm$^3$ of (**2**) was compressed at 3 kbar for *ca.* 100 min, only a little (**5**) was produced, with $< 3\%$ of (**4**), while at 7 kbar the product was mostly (**5**) even after 100 min of pressurization. It has been confirmed that (**5**) arises from the reaction of (**4**) with (**2**), and pressure favours the reaction very much, but the kinetic data have not yet been quantified sufficiently for a reliable pressure dependence to be determined.



Scheme 1

At present, the kinetic work has focused on the formation of (**4**) which was monitored spectrophotometrically at its u.v. absorption maximum. In 1,2-dichloroethane at lower pressure, the amount of (**4**) became significant only after an induction period, the duration of which decreased with increasing pressure and which could hardly be detected at 1 kbar. We could not discover what reactions were occurring within the induction period in either dichloroethane or acetonitrile but the most probable reaction (Scheme 2) is an electron transfer to form the ion pair (**6**) or the zwitterionic $\sigma$-complex (**7**).[1,5] In fact, in ethanol and acetone, the formation of the anion radical of (**1**) was evident in the first stage from the e.s.r. and electronic spectra. After the induction period the observed rate obeyed a third-order kinetic equation at pressures up to 3 kbar: first-order with respect to (**1**) and second-order with respect to (**2**). The third-order rate constant *k* at 25 °C can be represented well by the quadratic function (1) of pressure (*p*/bar).



Scheme 2

$$\ln (k/\mathrm{dm^6\,mol^{-2}\,min^{-1}}) = -a + bp - cp^2 \qquad (1)$$

in ClCH$_2$CH$_2$Cl, $a = 1{\cdot}759$, $b = 2{\cdot}119 \times 10^{-3}$, $c = 1{\cdot}130 \times 10^{-7}$

in MeCN, $a = 0{\cdot}2159$, $b = 2{\cdot}673 \times 10^{-3}$, $c = 4{\cdot}292 \times 10^{-7}$

From the relationship $\Delta V^{\ddagger} = -RT(\delta \ln k/\delta p)_T$, the volume of activation $\Delta V^{\ddagger}$ was determined at 1 bar and 25 °C to be $-54 \pm 2$ cm$^3$/mol in 1,2-dichloroethane and $-67 \pm 2$ cm$^3$/mol in acetonitrile. Such remarkably negative values of $\Delta V^{\ddagger}$ cannot be reasonably explained by a single reaction step; ionic species must be involved before the rate-determining step. Although, to our knowledge, there have been no studies on the volume of activation of a purely electron-transferring process in nonaqueous solvents, examples involving point charge separation upon activation may be comparable. For example, the volumes of activation for many Menschutkin reactions are $-25$ to $-45$ cm$^3$/mol in nonaqueous solvents,[6] and those for proton-transfer reactions from some carbon acids to aliphatic amines[7] are $-10$ to $-20$ cm$^3$/mol. Hence, if (**6**) or (**7**) is an intermediate, the volume contraction upon activation at the rate-determining step in passing from (**6**) or (**7**) to (**4**) is estimated to be 15—30 cm$^3$/mol, which is reasonable for a bimolecular step.[6] Together with the fact that the reaction rate has a second-order dependence on the amine, this is strong support for Scheme 2 in which an electron-transfer step takes place prior to the second attack by the amine.

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