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Reactions of Aromatic Radical Anions with Benzhydryl Chloride Studied by Pulse Radiolysis

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Reactions of the aromatic radical anions with benzhydryl chloride have been investigated by pulse radiolysis. The second-order rate constants were determined for the reactions of benzhydryl chloride with various aromatic radical anions. On the basis of the linear relationship between the free energy and the activation energy, an irreversible electron transfer with an early transition state was elucidated.

Electron transfer reactions (ET) to generate radical-ion intermediates have been of wide-spread interest, especially in the photochemistry connected with solar energy storage. Of particular importance is a system where an endergonic and irreversible ET step is followed by a rapid chemical reaction. In such a system, chemical reactions *via* the radical ions of a substrate can be initiated by a mediator (radical ion) which possesses a lower redox potential than that of the substrate. The system is, thus, of great value for organic synthesis.¹⁾ The interpretation of the kinetics for the system has been carried out by Schuster,²⁾ based upon the model proposed by Rehm and Weller.³⁾

We report herein the measurement of the absolute rate constants for the reactions of aromatic radical anions with benzhydryl chloride and the mechanism of the irreversible ET by a pulse radiolysis technique. The reactions of aromatic radical anions with alkyl and aromatic halides have been investigated by using electrochemical reactions,⁴⁾ organometallic compounds,⁵⁾ and also pulse radiolysis technique.⁶⁾ The currently accepted reaction mechanism includes an initial ET, producing an alkyl radical, and immediately following competitive reactions of the alkyl radical, such as reduction to carbanions, addition to aromatic radical anions, and radical-radical reacaions.⁷⁾

However, we have observed that in the case of intramolecular reactions of biphenyl radical anions with a terminal alkyl chloride which is linked to biphenyl moiety by a methylene chain, an intramolecular S_N2 reaction occurs.⁸⁾ Therefore, it seems essential to investigate the initial step of each respective reaction system, to determine whether it is an ET or S_N2 reaction.

Experimental

Materials. Benzhydryl chloride (Tokyo Kasei) was recrystallized twice from the ethanol solution and dried under high vacuum. The white crystal was stored in a refrigerator with silica gel as a drying agent (mp 16 °C). Biphenyl, phenanthrene, *trans*-stilbene, pyrene, and anthracene were purified by recrystallization or sublimation in the usual method. 2-Methyltetrahydrofuran (Wako Pure Chemicals) was distilled over $LiAlH_4$ three times.

Pulse Radiolysis. The L-band linear accelerator at Osaka University was used as the source of electron pulses.⁹⁾ The energy was 28 MeV and a 10 ns pulse width was selected for the present experiments. A detector (1P28 photomultiplier) and analyzing light produced by a 450W-Xenon pulse lamp (OPG-450, Osram) were used, and signals were monitored by a storage oscilloscope (Tektronix 7843) and a programmable digitizer (Tektronix 7912AD).

Fresh MTHF solutions were prepared just before irradiation and degassed under high vacuum. The following absorption bands were used in order to monitor the decay rate of the various aromatic radical anions: biphenyl (410 nm), phenanthrene (450 nm), *trans*-stilbene (500 nm), pyrene (495 nm), and anthracene (670 nm).

Results and Discussion

2-Methyltetrahydrofuran (MTHF) solutions of biphenyl containing benzhydryl chloride (BC) were irradiated with a 10 ns electron pulse of a 35 MeV L-band linear accelerator at room temperature. The transient absorption spectra were recorded at various times after the pulse; these are presented in Fig. 1.

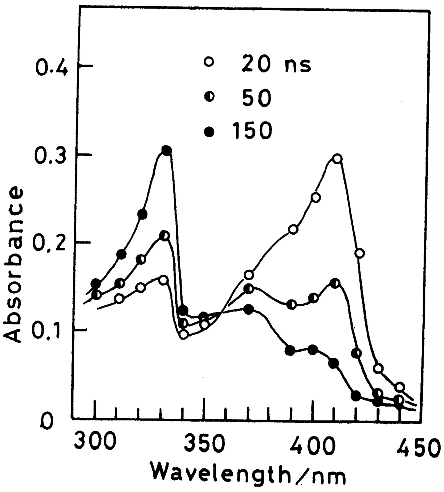

Fig. 1. Transient absorption spectra obtained at various times after a 10 ns pulse irradiation of a MTHF solution of biphenyl (50 mM) and BC (11 mM) mixture. Absorbed dose: 8.8 krad per pulse.

The spectrum observed immediately after the pulse has an absorption maximum at 410 nm, which is assigned to the biphenyl radical anions.¹⁰⁾ The 410-nm band decays according to the pseudo-first-order kinetics with the simultaneous formation of a 330-nm band. This latter band is assigned to a benzhydryl radical, by comparison with the spectrum obtained by the pulse radiolysis of a MTHF solution of BC.¹¹⁾ The rate of formation of the 330-nm band is fully consistent with

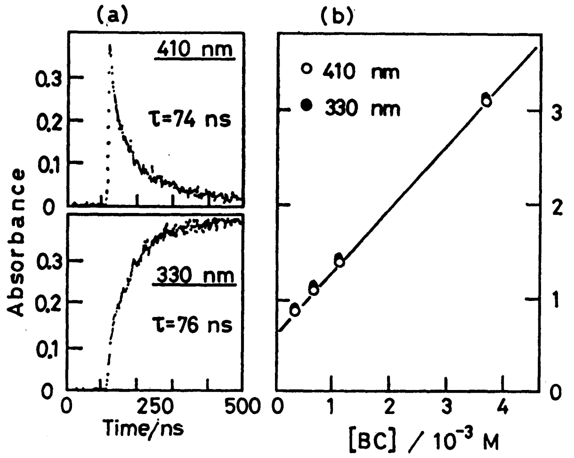

Fig. 2. Kinetic behavior of each band in Fig. 1 (a) The time dependency of transient absorption at 410- and 330-nm bands in Fig. 1. (b) The plot of the pseudo-first-order rate constant obtained from the 330-nm band formation and from the 410-nm band decay *vs.* BC concentration.

the decay rate of the 410-nm band, as shown in Fig. 2a. The plot of the pseudo-first-order rate constant *vs.* the BC concentration is linear; its slope results in the second-order rate constant: $k_S=7.0\times10^9\ M^{-1}\ s^{-1}$ ($1\ M=1\ mol\ dm^{-3}$). The two slopes obtained from the 330-nm band formation and the 410-nm band decay are in fair agreement within experimental error (Fig. 2b). Thus, the following equation is supported [M: biphenyl, BC: benzhydryl chloride]:

$$M^{\cdot-} + BC \xrightarrow{k_s} M + Ph_2CH\cdot + Cl^-.$$

In order to clarify the reaction mechanism, the second-order rate constants for the reaction of BC with aromatic radical anions of varying reduction potentials have been determined by a similar method to that described above. The plot of ln k_S as a function of the electrochemical half-wave potentials of the aromatic hydrocarbon (M)[12] yields a linear correlation, except for biphenyl, where the rate constant reaches the diffusion-controlled region, as shown in Fig. 3. The slope of the straight line is −9.45 in the units used here,[†] which corresponds to $-0.25/RT$.

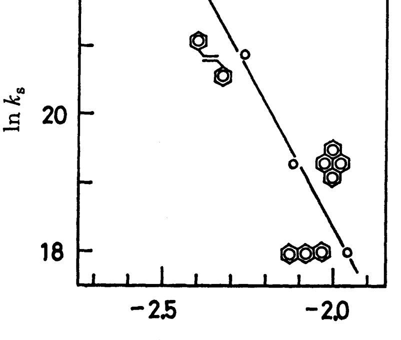

Fig. 3. Dependence of k_s on the reduction potential of various aromatic hydrocarbons.

According to Rehm and Weller,[3] the electron transfer mechanism can be described by the following reaction scheme.

$$M^{\cdot-} + BC \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (M^{\cdot-}\cdots BC) \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} (M\cdots BC^{\cdot-})$$

$$\xrightarrow{k_{30}} M + Ph_2CH\cdot + Cl^-$$

In the present system, it is presumed that the ET step (k_{23}) is endergonic and that, even so, the $BC^{\cdot-}$ radical anion formed undergoes an irreversible bond cleavage at a rate faster than the back ET: thus, $k_{23}\ll k_{21}$ and $k_{32}\ll k_{30}$. Under such a circumstance, the following equation for the rate constant is obtained, applying a steady-state approximation:[2)]

$$\ln k_s = \ln K_{12}k_i + \frac{\alpha E_{1/2}^{red}(BC)}{RT} - \frac{\alpha E_{1/2}^{red}(M)}{RT}, \qquad (1)$$

where $K'_{12}=k_{12}/k_{21}$ and k_i is the rate constant for the reaction where $\Delta G_{23}=0$ and the activation barrier is $\Delta G_0^{\neq}$. $E_{1/2}^{red}$ is the electrochemical half-wave reduction potential of BC and M. The transfer coefficient α is defined as $\Delta G^{\neq}=\Delta G_0^{\neq}+\alpha\Delta G_{23}$ (see Ref. 2). The present observation appears to be in accord with the relationship expressed in Eq. 1, provided $\alpha=0.25$. If we presume the reversible ET step, the slope of the straight line should be $-1/RT$; this is incompatible with the present results.

Although a simple linear correlation between reactivities and the ionization potentials or the redox potentials of the substrates has been observed in many chemical reactions,[13] there is surprisingly little quantitative information and few discussions on the transfer coefficient. It is, however, worthwhile to mention that a reversible ET system affords a straight line with a slope of $-1/RT$, but a net α value is not obtained in such a system. The idea of the parameter α has been originally proposed by Horiuchi-Polanyi.[14] It is reasonable to accept that α reflects the position of the transition state, along with the reaction coordinate.[15]

Bank and Juckett reported a similar low α value (0.22) for the reaction of aromatic radical anions with alkyl bromides,[5] while $\alpha=0.72$ is calculated from the data presented for the reaction with chlorobenzene by Lund and coworkers.[4] On the basis of these observations, it seems that, when the C–X bond cleavage proceeds very rapidly, α becomes low. Such a low α value indicates an early transition state in which electrons localize mainly upon the aromatic hydrocarbon (M). Thus, it becomes questionable whether a full electron transfer from $M^{\cdot-}$ to BC goes to completion prior to the successive C–Cl bond cleavage in such a labile halide.

A simple estimation suggests that if α is less than one-half, ΔG should be negative.[15] Therefore, our interpretation is that in such a system where α is very low, an irreversible ET proceeds with an early transition state and this, therefore, closely correlates with a rapid C–Cl

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[†] The slope is −9.45 when $E_{1/2}^{red}$ is expressed in V.

bond cleavage; a distinct discrimination between ET (k_{23}) and the successive bond cleavage (k_{30}) steps is difficult. The value of α would be considered as a parameter reflecting the extent of the ET in such a system.

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