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Mechanistic Evaluation of Dissociative Electron-Transfer and Nucleophilic Substitution Reactions

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The relationship between electron-transfer (ET) and S_N2 reactions has been extensively studied to clarify the role of the donor–acceptor combination.[1] One important observation was obtained from the intramolecular reactions of aromatic radical anions with terminal alkyl halides,[1n-p] in which the approach of a donor to an acceptor is spatially controlled by a methylene chain and the ET and S_N2 reactions provide clearly different products. The previous observation suggested that the mode of reaction, ET or S_N2, correlates with the decay rate of the aromatic radical anion. The results of this study provide clear evidence for the presence of a common mechanism, especially in a controlled reaction system such as substituted 1-benzoyl-ω-haloalkane (RBZ_X-*n*).

The intramolecular reactions of the radical anions of RBZ_X-*n* (**1**, R = *p*-MeO, *p*-Me, *p*-Et, H, *p*-F, *m*-F, *p*-Cl; X = Cl, Br, I; *n* = 3, 4;[2] λ_{max} = 330 and 490 nm) were observed using a pulse radiolysis technique in hexamethylphosphoric triamide (HMPA).[3] The initial intensities of these bands (RBZ_X-*n*, 10 mM) were almost the same as that of the band of acetophenone radical anion measured under the same reaction conditions. The results indicate that the solvated electrons generated in the HMPA solutions (*G*-value = 2.3)[4] are preferentially captured in the benzoyl moiety of RBZ_X-*n*. The ET and S_N2 reactions that occurred competitively with each radical anion gave quite different compounds, such as an alkyl aryl ketone (**4**) and an adduct (**5**) of a cyclic ether radical (**3**, λ_{max} = 300 nm)[5] with a solvent radical (S•; $((CH_3)_2N)_2P(O)N(CH_3)CH_2^•$) which is derived by loss of H^+ from $HMPA^{•+}$ generated by irradiation (Scheme 1), as final products.[6]

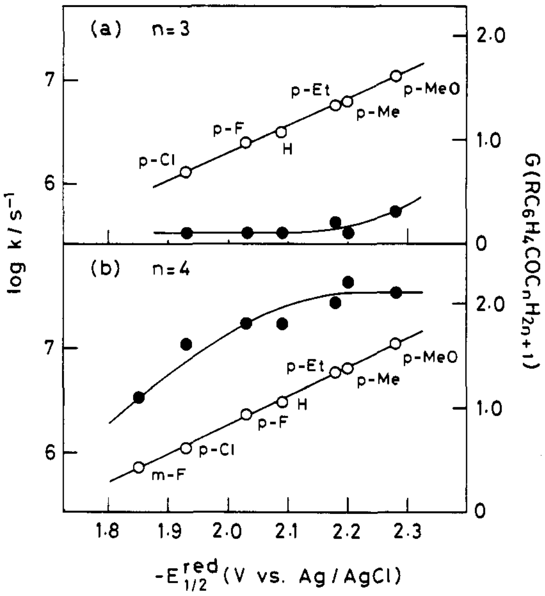

Figure 1. Variation of the decay rate constants (log *k*) of the radical anions of RBZ_{Br}-*n* (○; *n* = 3, 4) and the *G*-values of the formation of alkyl aryl ketone (4; ●) with the half-wave reduction potential ($E_{1/2}$) of the corresponding acetophenones.

Scheme 1

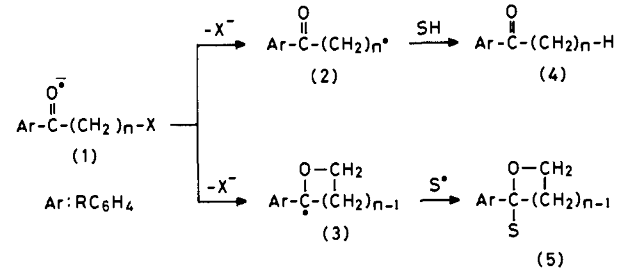

Figure 1 illustrates the variation in the decay rate constants (log *k*, s^{-1}) of the radical anions of RBZ_{Br}-*n* with the half-wave reduction potential ($E_{1/2}$, V) of the corresponding acetophenones,[7] together with the yields of **4** formed (*G*-values), which show the relative fraction of the ET reaction in the overall reaction of **1** (total *G*-value of the formation of **4** and **5** should be equal to that of the solvated electron,[8] i.e., $G(e^-)$ = 2.3 in HMPA). There is a good correlation between the rate constant and the reduction potential. This trend is similar to that observed for the dissociative ET reaction of aromatic radical anions with alkyl halides.[1h,l] In the same manner, the *G*-values of **4** are dependent on the electron donor ability of the radical anion as well as the methylene chain length. A good correlation was also obtained with Hammett's σ constants. The ρ values calculated by the Hammett equation indicated a considerably large negative value, i.e., −1.81 ± 0.01 for RBZ_{Br}-3 and −1.87 ± 0.02 for RBZ_{Br}-4. The distinct similarity of reaction kinetics in both systems (*n* = 3 and 4) in spite of their different modes of reaction (ET or S_N2) suggests that the ET and S_N2 reactions are governed by the same activation–driving force–free energy relationship.

On the other hand, a good correlation between the rate constants, log *k*, and the fraction of the ET reaction in various systems including HBZ_{Cl}-3, RBZ_{Cl}-4 (R = H, *p*-MeO), HBZ_I-3,

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[1] (a) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 8303. (b) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (c) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702. (d) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 21. (e) Lund, T.; Lund, H. *Acta Chem. Scand. B* **1986**, *40*, 470. (f) Lund, T.; Lund, H. *Acta Chem. Scand. B* **1988**, *42*, 269. (g) Bordwell, F. G.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5470. (h) Lexa, D.; Saveant, J. M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617. (i) Eberson, L.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4484. (j) Daasbjerg, K.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1991**, *45*, 424. (k) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. (l) Saveant, J. M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (m) Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205. (n) Kigawa, H.; Takamuku, S.; Toki, S.; Kimura, N.; Takeda, S.; Tsumori, K.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 5176. (o) Kimura, N.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2433. (p) Kimura, N.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1668.

[2] RBZ_{Cl}-*n* and RBZ_{Br}-*n* were prepared by a Grignard reaction of RC_6H_4-MgBr with $NC(CH_2)_nX$ (X = Cl, Br; *n* = 3, 4). HBZ_I-*n* (*n* = 3, 4) was prepared by the reaction of the corresponding bromides with KI.

[3] The sample solutions were irradiated with an 8-ns pulse of 28 MeV electrons. The apparatus for the pulse radiolysis experiments was described in a previous paper.[1o]

[4] Yield of the solvated electron at energy absorption of 100 eV: Shaede, E. A.; Dorfman, L. M.; Flynn, J.; Walker, D. C. *Can. J. Chem.* **1973**, *51*, 3905.

[5] The 300-nm band formed with the decay of the initial absorption bands was assigned to a cyclic ether radical (**3**) because of the similarity of the spectrum to that of an α-methoxybenzyl radical (λ_{max} = 300 nm) formed by one-electron reduction of benzaldehyde dimethyl acetal.

[6] Product analysis was carried out by GLC (Shimazu GC-7A, using a 1-m × 3-mm glass column packed with 5% Silicon OV-1 on Chromosorb WAW-DMCS, 60–80 mesh) and GLC–MS (JEOL JMS-D300). The mass spectra of the main products (yields: 60–70% based on the amount of substrate that disappeared) from HBZ_{Cl}-3, RBZ_{Br}-3, and RBZ_{Cl}-4 showed the formation of an adduct (**5**) of a cyclic ether radical (**3**) with a solvent radical (S•; see text). For example, the results for HBZ_X-3 (X = Cl, Br) were as follows: adduct **5**, $(MeN)_2P(O)N(Me)CH_2\overline{C(Ph)(CH_2)_3O}$, *m*/*e* 325 ($M^{•+}$), 281 ($M^{•+} - Me_2N$), 178 ($M^{•+} - 147$), 147 ($(Ph\overline{C(CH_2)_3O})^+$), 135 ($((Me_2N)_2PO)^+$, major peak), 105 ($(PhCO)^+$), 77 ($Ph^+$), 44 ($Me_2N^+$).

[7] Loutfy, R. O.; Loutfy, R. O. *Tetrahedron* **1973**, *29*, 2251. $E_{1/2}$ values for *p*-Et, *p*-F, and *m*-F derivatives were obtained from the linear correlation between $E_{1/2}$ values of other acetophenones and Hammett's σ constants.

[8] The *G*-values (2.2–2.5) of the substrate that disappeared were close to the *G*-value of the solvated electron.

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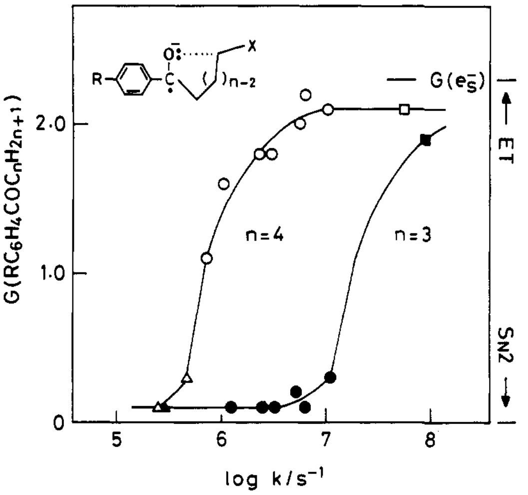

Figure 2. Variation of the *G*-values of alkyl aryl ketone (**4**) (and the ratio of the ET and S_N2 reactions) with the rate constants (log *k*) measured with HBZ_{Cl}-3 (▲), RBZ_{Br}-3 (●), HBZ_I-3 (■), RBZ_{Cl}-4 (△), RBZ_{Br}-4 (○), and HBZ_I-4 (□).

and HBZ_I-4 was obtained, as shown in Figure 2. It is apparent that the fraction of the ET reaction increases with an increase in the reaction rate.

When the nucleophile or the substrate is modified so as to make the reaction faster, the electron transfer takes place earlier during the reaction, and the transition-state geometry becomes more reactant-like.[1d,m] The transition state consequently becomes less able to satisfy the S_N2 conditions, which allows an attack of the central carbon in the axis of the C–X bond and a partial bond formation in the transition state. It is clear that the spatial distribution of the radical pair (distance) initially formed is an important factor for the following bond formation. For this reason, the fraction of the S_N2 reaction decreased with an increase in the rate.

A second important factor for the intramolecular S_N2 reaction is the contribution of a cyclic structure for back-side attack. The structure of tetrahydrofuran is nearly planar, while tetrahydrofuran has a chair ring.[9] Thus, it appears that the six-membered ring transition state of RBZ_X-4 is less able, compared with the five-membered ring transition state of RBZ_X-3, to satisfy the S_N2 conditions previously described, because the bond formation process requires a structural change to form a chair ring. The importance of the three-center (D–C–X) angle was also noted by Saveant and co-workers for intermolecular reactions, and they have shown that the transition-state geometry determining the reaction mechanism is governed by activation energy–entropy balance.[1h,l] Present results indicate that the second important factor is the orientation of the orbitals of the radical pair (angle) formed by the concerted electron-transfer and bond-breaking processes.

Aromatic radical anions ($A^{\bullet-}$) have a delocalized electronic system, hence an interaction between $A^{\bullet-}$ and alkyl halides (RX) in the transition state should be small. The reaction of $A^{\bullet-}$ with RX consequently brings about only their dissociation into A, $R^\bullet$, and X^-. In the present intramolecular system, the transition-state geometry (O–C distance and O–C–X angle) is approximately fixed by means of the methylene chain length. The S_N2 reaction that competitively occurred with the ET reaction is mainly controlled by these factors.

The present research gives the first example for a continuous ET–S_N2 mechanistic spectrum, which shows a systematic change in the reaction mechanism as a function of the donor–acceptor combination.

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[9] Eckert, J. M.; Le-Fevre, R. J. W. *J. Chem. Soc. B* **1969**, 855.