1668 © 1992 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **65**, 1668—1671 (1992) [Vol. 65, No. 6

Competitive Intramolecular Electron Transfer and S_N2 Reactions of Radical Anions. Effects of Solvent Polarity on the Reaction Mechanism

Norio KIMURA* and Setsuo TAKAMUKU
The Institute of Scientific and Industrial Research,
Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567

(Received December 18, 1991)

The solvent effects on the chemical reactivities of the radical anions of 1-(4-biphenylyl)-ω-chloroalkane have been investigated by using a pulse radiolysis technique. The reaction rates and reaction mechanism (intramolecular electron transfer and S_N2) were found to change as a function of the polarity of the solvent used. On the basis of these results, it is discussed how their dichotomy takes place.

Since the pioneering studies of Kornblum,[1] Russell,[2] and Bunnett,[3] electron transfer (ET) has become one of the most fundamental processes in organic reactions.[4] One of the major subjects in modern physical organic chemistry is a mechanistic evaluation of ET processes in various well-known organic reactions. For example, in nucleophilic substitution reactions, one unresolved question is the relationship between ET and S_N2 mechanisms,[5] i.e., how their dichotomy takes place? And, do alkyl halide radical anions exist as discrete intermediates?

In a previous investigation concerning the intramolecular reaction of the radical anions of 1-(4-biphenylyl)-ω-haloalkane, an S_N2 reaction yielding a spirocyclic radical occurred competitively to an ET reaction, leading to a terminal carbon radical.[6]

It is well known that organic reactions involving dipolar activated complex such as S_N1 and S_N2 are subject to solvent influence.[7,8] Therefore, in the present paper, in order to make the relationship between the ET and S_N2 reactions clear, solvent effects on the competitive intramolecular ET and S_N2 reactions in the radical anions of 1-(4-biphenylyl)-ω-chloroalkane (BP_{Cl}-*n*; $n=3$, 4) have been investigated by using a pulse radiolysis technique.

Experimental

1-(4-Biphenylyl)-3-chloropropane (BP_{Cl}-3) and 1-(4-biphenylyl)-4-chlorobutane (BP_{Cl}-4) were synthesized by a previously described procedure.[6]

N,N-Dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), and *N*-methyl-2-pyrrolidone (NMP) used as a solvent were distilled over CaH_2 under reduced pressure. The solutions were degassed in a vacuum line and sealed into Suprasil quartz cells.

The samples were irradiated with a 3-ns pulse of 28 MeV electrons from a linear accelerator at Osaka University. The procedure and apparatus for pulse radiolysis experiments were described in a recent paper.[9]

Results and Discussion

In a previous investigation concerning a one-electron reduction of 1-(4-biphenylyl)-ω-chloroalkane (BP_{Cl}-*n*; $n=3$, 4) in HMPA by pulse radiolysis,[6] it was shown that an initial absorption band with λ_{max} at 410 nm due to the corresponding biphenyl radical anion (**1**) decayed by a first-order kinetics along with a simultaneous formation of a new band with λ_{max} at 330 nm (Fig. 1), which was assigned to a spirocyclic radical (**3**) generated by an intramolecular S_N2 reaction. This reaction occurred competitively with an intramolecular ET reaction, leading to a terminal carbon radical (**2**), as shown in Scheme 1.

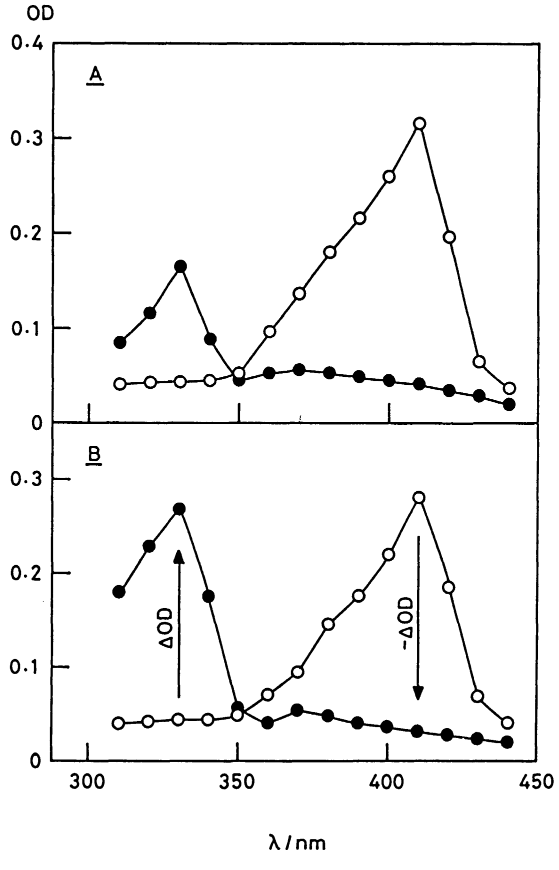
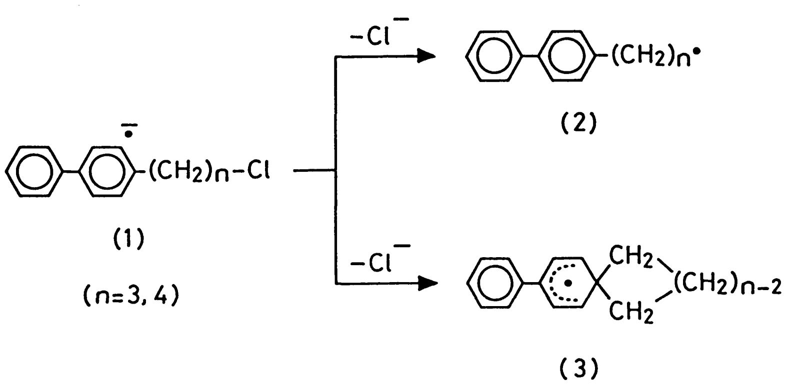


Fig. 1. Transient absorption spectra observed with BP_{Cl}-*n* ($n=3$, 4) in HMPA solution (1×10^{-2} mol dm^{-3}): (A) BP_{Cl}-3 (○) end of the pulse, (●) 8 μs after the pulse; (B) BP_{Cl}-4 (○) end of the pulse, (●) 4 μs after the pulse. Absorption dose was 190 Gy/pulse.



Scheme 1.

The rate constants for BP$_{Cl}$-3 and BP$_{Cl}$-4 were 5.5×10^5 and $1.2\times10^6\,s^{-1}$ from the decay of the 410 nm band, and 5.4×10^5 and $1.1\times10^6\,s^{-1}$ from the formation of the 330 nm band, respectively. The relative fraction of the S$_N$2 reaction in the overall reaction of the radical anion (**1**) indicated a $\Delta OD_{330}/-\Delta OD_{410}$ ratio (see Fig. 1; a detailed description is found in Ref. 6) of 0.45 and 0.92 for BP$_{Cl}$-3 and BP$_{Cl}$-4, respectively.

In various solvents such as DMA, DMF, DMSO, and NMP (*N*-methyl-2-pyrrolidone), pulse radiolysis of BP$_{Cl}$-3 and BP$_{Cl}$-4 were carried out with a 3-ns electron pulse at room temperature. The initial absorption spectra (λ_{max}=410 nm) were quite similar to that observed in HMPA. The decay of the 410 nm bands followed first-order kinetics and the rates were independent of the solute concentration in the 1×10^{-3}—1×10^{-2} mol dm^{-3} range. These results indicate that the decay reaction of the radical anion (**1**) proceeds unimolecularly.

However, the decay rate constants of the 410 nm bands (k_{410}/s^{-1}) were dependent on the nature of the solvent used. The correlation of the rate constants, $\log k_{410}$, with empirical parameters reflecting the solvent polarity was examined. Of the various parameters, a rather good correlation was found with an acceptor number (AN), which is a measure of electrophilic properties of the solvent.[10] Plots of $\log k_{410}$ vs. AN are shown in Fig. 2, together with that for the formation rate constants (k_{330}/s^{-1}) of the 330 nm bands. It is apparent that the rate constants increase with increasing AN, namely the solvent polarity. Similar correlations were also obtained when the Reichardt–Dimroth polarity parameter, $E_T(30)$,[11] was used.

The degree of solvation is related to the charge density on the anion,[7] i.e., small anions with localized charge are subject to more solvation than large anions with dispersed charge. Such a different solvation for anions in the transition state, reactants, or products causes either a retardation or acceleration of the reaction rate.

The present results indicate that the radical anion (**1**) in which negative charge is delocalized in the biphenyl moiety is subject to moderate solvation, while at the end of the reaction, the negative charge is localized in a dissociated chlorine atom. Therefore, stronger solvations are expected for the leaving chloride ion than for the biphenyl radical anion. Thus, an increase in the solvent polarity resulted in an increase in the reaction rate.

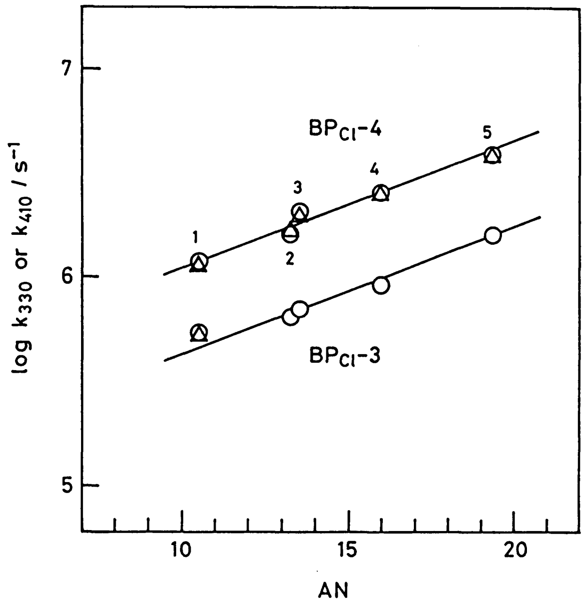


Fig. 2. Relationship between the rate constants, $\log k_{410}$ (○) and k_{330} (△), measured with BP$_{Cl}$-3 and BP$_{Cl}$-4 and the acceptor number (AN) of the solvent: 1, HMPA; 2, NMP; 3, DMA; 4, DMF; 5, DMSO.

Contrary to the rate, a ratio of $\Delta OD_{330}/-\Delta OD_{410}$ (see Fig. 1), which shows a relative fraction of an S$_N$2 reaction in the overall reaction of the radical anion (**1**), decreases with increasing the solvent polarity, as shown in Fig. 3. It, thus, appears that the S$_N$2 reaction becomes unfavorable in a more polar solvent in which the reaction proceeds faster.

The two rate constants, k_{410} and k_{330}, measured in each solvent are, nevertheless, in good agreement within the experimental error, and the decay rate constants, k_{410}, measured with BP$_{Cl}$-3 and BP$_{Cl}$-4 increased (as parallel lines) with an increase in the solvent polarity (Fig. 2). These results suggest that the bond-breaking

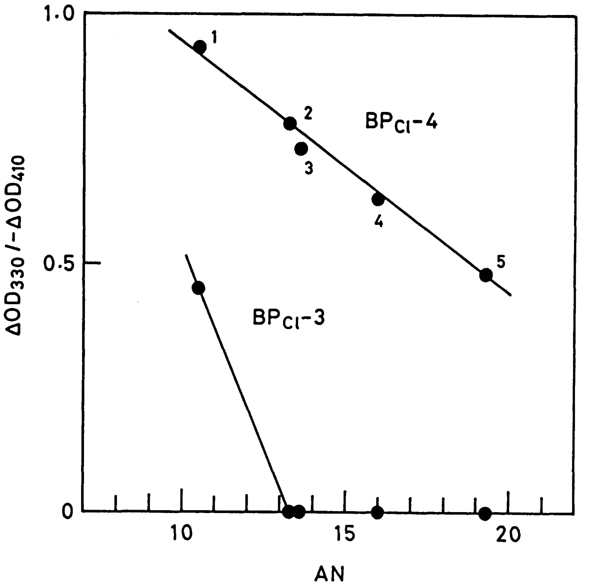


Fig. 3. Relationship between a ratio of ΔOD$_{330}$/$-\Delta$OD$_{410}$ (see Fig. 1) measured with BP$_{\rm Cl}$-3 and BP$_{\rm Cl}$-4 and the acceptor number (AN) of the solvent: 1, HMPA; 2, NMP; 3, DMA; 4, DMF; 5, DMSO. This ratio is the average of three measurements with an error less than 5%.

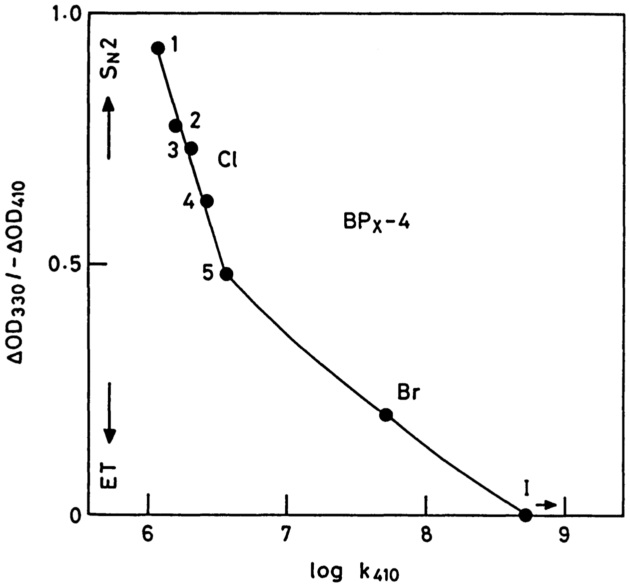


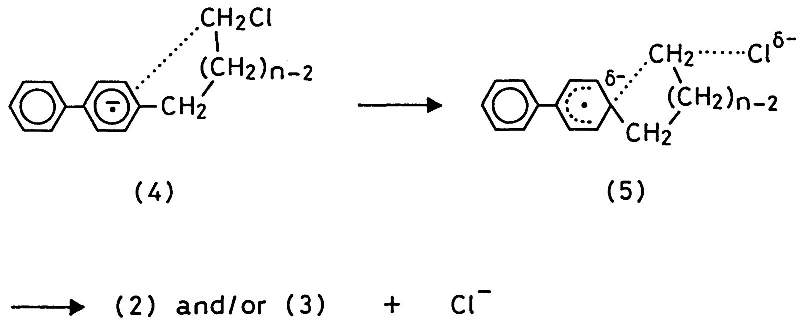
Fig. 4. Relationship between the rate constants, log k_{410}, and a ratio of ΔOD$_{330}$/$-\Delta$OD$_{410}$ (see Fig. 1) measured with 1-(4-biphenyl)-4-iodobutane (BP$_{\rm I}$-4) and 1-(4-biphenylyl)-4-bromobutane (BP$_{\rm Br}$-4) in HMPA and BP$_{\rm Cl}$-4 in HMPA (1), NMP (2), DMA (3), DMF (4), and DMSO (5).

process, concerted with an electron shift which is involved in both ET and S$_N$2 reactions, occurs as the rate-determining step.

If a terminal chloride radical anion, -CH$_2^{\cdot-}$-Cl, is formed as a discrete intermediate in an ET reaction, leading to a terminal carbon radical (**2**), its rate is not affected by the solvation of the leaving chloride ion. In such a case, a first-order kinetic plot of the decay of the radical anion (**1**) accompanied by the formation of radicals (**2**) and (**3**) should not give a straight line. However, in all radical anions (**1**) a straight line was obtained. Accordingly, it is clear that the ET and S$_N$2 reactions involve a common mechanism in which an electron is transferred from a biphenyl radical anion to a terminal carbon accompanied by the simultaneous release of a chloride ion, as shown in Scheme 2.

For nucleophilic substitution reactions, Pross and Shaik[5,12] have proposed that, at the transition state, one half of the negative charge on the nucleophile anion is transferred to the substrate, and that a negative charge is localized in the leaving group, regardless of the position of the transition state along the reaction coordinate. However, when the nucleophile, leaving group, or solvent is modified so as to make the reaction faster, the energy barrier for the reaction becomes lower, and the transition state occurs earlier, in accord with the Leffler–Hammond postulate.[13,14]

According to the proposed theory,[5,12] a negative charge is distributed to the biphenyl moiety and the leaving chlorine atom in equal amounts in the transition state (**5**). However, in a more polar solvent, which increases the reaction rate, the transition state occurs earlier, and the energy barrier for the reaction becomes lower; hence, the elimination of the chloride ion becomes faster. The transition state (**5**), consequently, becomes harder to satisfy the S$_N$2 conditions, which



Scheme 2.

allows an attack of the central carbon in the axis of the C–X bond and a partial bond formation in the transition state. That is, the probability of the formation of the S_N2 transition state becomes lower. For these reasons, an increase in the solvent polarity resulted in a decrease in the fraction of the radical (**3**) generated by the S_N2 reaction.

Consistent with these solvent effects, a good correlation between the rate constants, $\log k_{410}$, and the fraction of the S_N2 reaction in various systems including BP_{Br}-4 and BP_I-4 was obtained, as shown in Fig. 4. It is apparent that the fraction of the S_N2 reaction decreases monotonously with increasing reaction rate [1-(4-biphenylyl)-4-halobutane (BP_X-4); k_{410}: I>Br>Cl (DMSO>DMF>DMA>NMP>HMPA)].[6] This trend is consistent with the ease of reducing the alkyl halides.[15] Therefore, the S_N2 reaction seems to require a reaction system in which an efficient release of a halide ion does not occur.

On the basis of these results, we conclude that the ET and S_N2 reactions involve a common mechanism, and that the fundamental mechanistic difference between the ET and S_N2 reactions is whether new bond formation is synchronized to the concerted electron-transfer and bond-breaking processes or not.

References

1) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Am. Chem. Soc.*, **88**, 5660 (1966).

2) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966).

3) J. A. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).

4) L. Eberson, "Electron Transfer Reactions in Organic Chemistry," Springer-Verlag, Berlin (1985).

5) A. Pross, *Adv. Phys. Org. Chem.*, **21**, 99 (1985).

6) H. Kigawa, S. Takamuku, S. Toki, N. Kimura, S. Takeda, K. Tsumori, and H. Sakurai, *J. Am. Chem. Soc.*, **103**, 5176 (1981).

7) A. Parker, *Chem. Rev.*, **69**, 1 (1969).

8) C. Reichardt, "Solvent Effects in Organic Chemistry," Verlag Chemie, Weinheim (1979).

9) N. Kimura and S. Takamuku, *Bull. Chem. Soc. Jpn.*, **64**, 2433 (1991).

10) V. Gutmann, *Electrochim. Acta*, **21**, 661 (1976).

11) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **19**, 98 (1979).

12) A. Pross and S. S. Shaik, *Tetrahedron Lett.*, **1982**, 5467.

13) J. F. Leffler, *Science*, **117**, 340 (1953).

14) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

15) C. P. Andrieux, I. Gallard, J. M. Saveant, and K. B. Su, *J. Am. Chem. Soc.*, **108**, 638 (1986).