

Intramolecular Electron Transfer and S_N2 Reactions in the Radical Anions of 1-(4-Biphenyl)- ω -haloalkane Studied by Pulse Radiolysis

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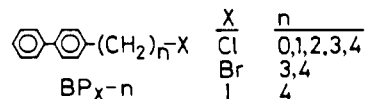
Abstract: One-electron reduction of 1-(4-biphenyl)- ω -haloalkane (BP_{X-n}) by solvated electrons and the intramolecular reactions of the radical anion thus formed have been investigated using the pulse-radiolysis technique. The spectrum observed immediately after the pulse has an absorption maximum at 410 nm which is assigned to the corresponding biphenyl radical anion. The decay behavior of all these 410-nm bands follows first-order kinetics and the rates are dependent on the methylene chain length, n . With BP_{Cl-0} and BP_{Cl-2}, which provide large rate constants (7.5×10^7 and 1.7×10^8 s⁻¹, respectively) and large G values of 4-alkylbiphenyl formation, an intramolecular electron transfer from a biphenyl radical anion to a C-Cl bond is presumed. The rate constants of the radical anions decrease in the order BP_{Cl-1} > BP_{Cl-2} > BP_{Cl-0} which is roughly parallel to the C-Cl bond energy of these compounds and does not correlate with the chain length n , which corresponds to the distance required for the electron transfer. On the other hand, in the case of BP_{Cl-3} and BP_{Cl-4}, the decay of the 410-nm band decreased about two orders of magnitude (5.5×10^5 and 1.2×10^6 s⁻¹, respectively) and was characterized by a simultaneous formation of a 330-nm band which is assigned to a spirocyclic radical. The G values of the corresponding 4-alkylbiphenyl formation were low for these compounds. On the basis of these observations, an intramolecular carbanionic displacement of the biphenyl radical anion on the chlorine center, which is a novel type of intramolecular S_N2 reaction, has been concluded. Intramolecular reactions of bromo and iodo derivatives were also investigated and compared with those of corresponding chlorides.

Introduction

The reactions of aromatic radical anions with alkyl halides have attracted considerable attention, especially the initial step, whether it is electron transfer (ET) or S_N2.¹⁻³ A reaction mechanism which 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 reactions is currently accepted.⁴⁻⁹

On the other hand, intramolecular reactions of aromatic radical anions with a terminal alkyl halide which is linked to the aromatic moiety by a methylene chain have been investigated by several groups by using organoalkali compounds,¹⁰⁻¹⁴ electrochemical reduction,^{15,16} and pulse radiolysis.¹⁷ However, the reaction mechanism of the intramolecular reaction is complex owing to several competitive reactions and still not clearly elucidated.

In the present paper, we have investigated one-electron reduction of 1-(4-biphenyl)- ω -haloalkane (BP_{X-n}) by solvated electrons,



and the intramolecular reactions of the radical anions thus formed have been elucidated using the pulse-radiolysis technique.

Experimental Section

Materials. 4-Chlorobiphenyl (BP_{Cl-0}) (Tokyo Kasei) and 4-chloromethylbiphenyl (BP_{Cl-1}) (Aldrich) were recrystallized from ethanol and dried under vacuum. 4-Methylbiphenyl (BP-Me) (Aldrich) was used without further purification.

1-(4-Biphenyl)-2-chloroethane (BP_{Cl-2}). This compound was synthesized by a procedure similar to that of Grovenstein et al.¹¹ After the usual workup, 0.6 g of BP_{Cl-2} was obtained by vacuum transfer at 100 °C under 0.1 Torr: NMR (CDCl₃) δ 7.0-7.6 (9 H, m), 3.5-3.8 (2 H, t), 2.9-3.3 (2 H, t).

1-(4-Biphenyl)-3-chloropropane (BP_{Cl-3}). 3-(4-Biphenyl)-2-propenoic acid which was synthesized by reaction of *p*-biphenylcarboxaldehyde with malonic acid¹⁸ was hydrogenated to the corresponding propanoic acid by Raney-Ni catalyst.¹⁹ mp 147-149 °C; NMR (CDCl₃) δ 7.0-7.7 (9 H, m), 2.6-3.2 (4 H, m). This acid was reduced to the corresponding alcohol by LiAlH₄ and then chlorinated by PCl₅ in chloroform: bp 130-135 °C (0.01 Torr); NMR (CDCl₃) δ 7.0-7.6 (9 H, m), 3.4-3.7 (2 H, t), 2.6-3.0 (2 H, t), 1.8-2.3 (2 H, m). Anal. Calcd for C₁₅H₁₅Cl: C, 78.08; H, 6.55; Cl, 15.37. Found: C, 77.98; H, 6.51; Cl, 15.51.

1-(4-Biphenyl)-4-chlorobutane (BP_{Cl-4}). This compound was synthesized by a procedure similar to that of Grovenstein et al.¹³: bp 140-145 °C (0.01 Torr); NMR (CDCl₃) δ 7.0-7.6 (9 H, m), 3.4-3.7 (2 H, t), 2.4-2.8 (2 H, t), 1.5-2.0 (4 H, m).

1-(4-Biphenyl)-3-bromopropane (BP_{Br-3}). A mixture of 0.9 g (4 mmol) of 3-(4-biphenyl)propanol, 2.5 mL (9 mmol) of PBr₃, and 20 mL of CCl₄ was refluxed for 1 h. After the usual workup, evaporation of the solvent and recrystallization from *n*-pentane gave 0.6 g (52%) of BP_{Br-3}: mp 42 °C; NMR (CDCl₃) δ 7.1-7.6 (9 H, m), 3.3-3.6 (2 H,

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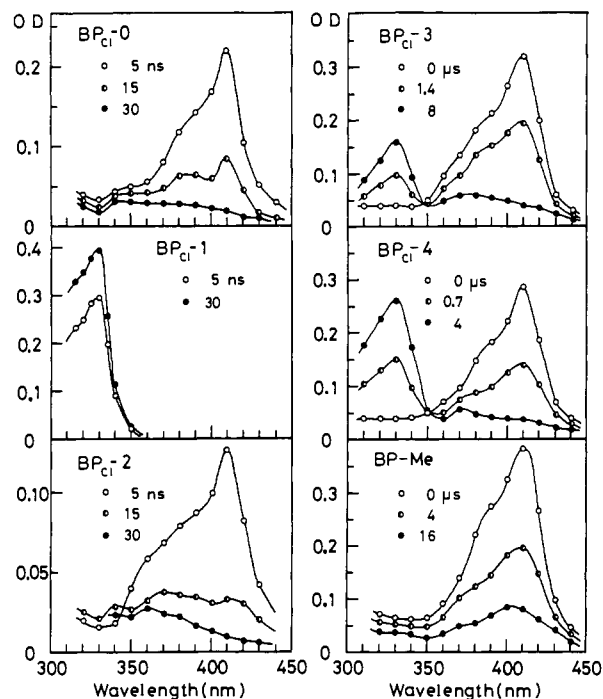


Figure 1. Transient absorption spectra obtained at various times after a 3-ns pulse irradiation of HMPA solutions of BP_{Cl-n} and BP-Me (1.1×10^{-2} M) at room temperature. Absorbed dose was 19 krad/pulse for BP_{Cl-0} – BP_{Cl-2} and BP-Me and 14 krad/pulse for BP_{Cl-3} and BP_{Cl-4} , respectively.

t), 2.7–3.0 (2 H, t), 2.0–2.5 (2 H, m). Anal. Calcd for $C_{15}H_{15}Br$: C, 65.47; H, 5.49; Br, 29.04. Found: C, 65.85; H, 5.44; Br, 28.64.

1-(4-Biphenyl)-4-bromobutane (BP_{Br-4}). This compound was synthesized by a procedure similar to that of BP_{Br-3} described above. The yield was 50%: bp 150–155 °C (0.01 Torr); NMR ($CDCl_3$) δ 7.0–7.6 (9 H, m), 3.3–3.6 (2 H, t), 2.6–2.9 (2 H, t), 1.6–2.1 (4 H, m).

1-(4-Biphenyl)-4-iodobutane (BP_{I-4}).²⁰ A mixture of 4-(4-biphenyl)butanol, sodium iodide, and trimethylsilyl chloride in dry acetonitrile was refluxed; after the usual workup, BP_{I-4} was formed in 90% yield: NMR ($CDCl_3$) δ 7.0–7.6 (9 H, m), 3.0–3.3 (2 H, t), 2.3–2.6 (2 H, t), 1.5–2.0 (4 H, t).

Apparatus. The L-band linear accelerator at Osaka University was used as the source of electron pulse. The energy was 28 MeV and the pulse width was selected as 40 ps, 3 ns, or 10 ns. The dose was 19 krad per 3-ns pulse (the beam diameter, ca. 4 mm). A 450W xenon pulse lamp (OPG-450, Osram), a monochromator (Nikon G-250), a photomultiplier (R843), and a programmable digitizer (Tektronix 7912 AD) were used. For the picosecond pulse radiolysis, an R843 photomultiplier and special circuit with subnanosecond time response were used according to Beck.²¹

Hexamethylphosphoric triamide (HMPA) used as a solvent was distilled over CaH_2 twice. Solutions were prepared freshly before irradiation and were degassed under high vacuum. Product analysis was carried out by GLC after γ -irradiation.

Results and Discussion

Chloro Derivatives with a Different Chain Length. Hexamethylphosphoric triamide (HMPA) solutions of BP_{Cl-n} and 4-methylbiphenyl (BP-Me) were irradiated with 3-ns electron pulses, and the transient absorption spectra recorded at various times after the pulse are presented in Figure 1. Except for BP_{Cl-1} , the spectrum observed immediately after the pulse has an absorption maximum at 410 nm which is assigned to the corresponding biphenyl radical anion by comparison with that of BP-Me and biphenyl.²² These observations indicate that the excess electron is predominantly present initially in the aromatic part of the molecule and not in the σ^* (C–Cl) bond. This is consistent

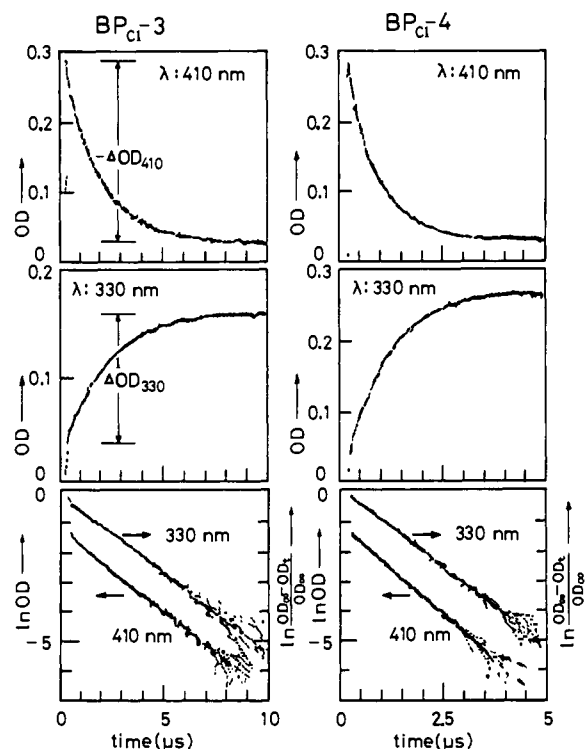


Figure 2. Decay and formation curves for 410- and 330-nm bands, and their kinetic behavior (first-order plot) obtained with HMPA solutions of BP_{Cl-3} and BP_{Cl-4} (1.1×10^{-2} M): pulse width, 3 ns; dose, 14 krad/pulse. The rate constants for BP_{Cl-3} and BP_{Cl-4} are 5.5×10^5 and 1.2×10^6 s^{-1} from the decay of the 410-nm band, and 5.4×10^5 and 1.1×10^6 s^{-1} from the 330-nm band, respectively.

Table I. Pulse Radiolysis^a and γ -Radiolysis^b of BP_{Cl-n} and BP-Me in HMPA at Room Temperature

n	OD_{410}	$k(s^{-1})$	$\frac{\Delta OD_{330}}{-\Delta OD_{410}}$	$G(BP\text{-alkane})^c$
0	0.22	7.5×10^7	≈ 0	2.10^d
1				0.36^d
2	0.13	1.7×10^8	0.05	2.08^d 2.06
3	0.40	5.5×10^5	0.45	0.97
4	0.35	1.2×10^6	0.92	0.05
BP-Me	0.39	e	≈ 0	

^a Pulse width was 3 ns and the absorbed dose was 19 krad/pulse. Substrate concentration: 1.1×10^{-2} M. ^b ^{60}Co γ -radiolysis; dose, 1.5×10^5 rad. Products were analyzed by GLC. Substrate concentration: 5.0×10^{-2} M. ^c 100-eV yield of 4-alkylbiphenyl. ^d MTHF was used as the solvent because the reaction products from BP_{Cl-0} and BP_{Cl-1} were not clearly isolated from HMPA on GLC. ^e Second-order rate constant: 1.2×10^{10} $M^{-1} s^{-1}$.

with available competitive data for solvated electrons which indicate that electron attachment to biphenyl is favored over that to alkyl chloride.²³ In the case of BP_{Cl-1} , the 410-nm band was weakly observed only during a 10-ns pulse with a high dose. The 330-nm band formed immediately after the pulse is assigned to the 4-phenylbenzyl radical.²⁴ Such a short lifetime of the radical anion of BP_{Cl-1} may be due to very fast C–Cl bond cleavage.

The decay behavior of all these 410-nm bands except for BP-Me follows first-order kinetics, and the rates are dependent on the

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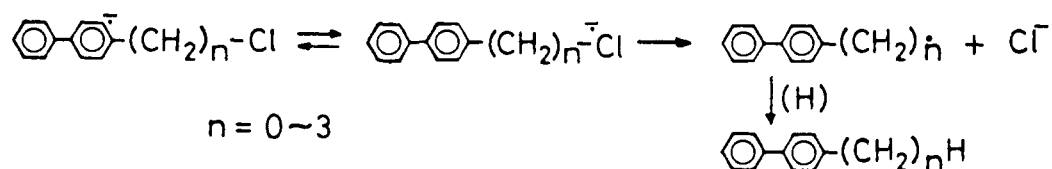
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(23) Bimolecular reaction of BP-Me and *n*-butyl chloride (*n*-BuCl) in HMPA was carried out by pulse irradiation. The initial optical density of BP-Me radical anion decreased with increasing of *n*-BuCl concentration. The plots of reciprocal optical densities vs. reciprocal *n*-BuCl concentrations provided a straight line, the slope and intercept of which gave $k(e^- + BP\text{-Me})/k(e^- + n\text{-BuCl}) = 11.0$. Moreover, the decay of BP-Me radical anion followed pseudo-first-order kinetics, and the plots of the rate constants vs. *n*-BuCl concentrations gave $k(BP\text{-Me}^- + n\text{-BuCl}) = 1.6 \times 10^5$ $M^{-1} s^{-1}$.

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Scheme I



methylene-chain length n . The rates for BP_{Cl}-0 and BP_{Cl}-2, which show very rapid decays, were measured by a 40-ps single electron-pulse irradiation with a detection system of a subnanosecond time response. The rate constants thus obtained are 7.5×10^7 and $1.7 \times 10^8 \text{ s}^{-1}$, respectively.

On the other hand, BP_{Cl}-3 and BP_{Cl}-4 followed rather slow decay rates (μs order) and were characterized by a simultaneous formation of a 330-nm band, which is more extensive in BP_{Cl}-4 than in BP_{Cl}-3. The rate of formation of the 330-nm band is fully consistent with the decay rate of the 410-nm band in both compounds as shown in Figure 2. The former band coincides with that of a phenylcyclohexadienyl radical produced by protonation of a biphenyl radical anion in the shape and λ_{max} of the spectrum.²⁵ These results obtained by the pulse radiolysis are summarized in Table I, together with the product yields obtained by the γ -radiolysis. The main reaction product, which was analyzed by GLC after γ -irradiation of HMPA or 2-methyltetrahydrofuran (MTHF) solutions of BP_{Cl}- n , was the corresponding 4-alkylbiphenyl. BP_{Cl}-0 and BP_{Cl}-2 gave rather high G values which are close to that of the solvated electrons, i.e., $G(e_s^-) = 2.3$ in HMPA²⁶ and 2.6 in MTHF,²⁷ respectively. A low value observed in BP_{Cl}-1 is reasonably explained by the formation of dimer on the analogy that benzyl chloride yields bibenzyl as a main product on the γ -radiolysis,²⁸ while a pronounced decrease in the G value was observed in the case of BP_{Cl}-3, especially in BP_{Cl}-4, and appeared to correspond to the formation of the 330-nm band which is indicated in Table I as a ratio of $\Delta\text{OD}_{330}/-\Delta\text{OD}_{410}$ (see Figure 2; the ratio is presumed as a measure of an intramolecular S_N2 reaction discussed later).

On the basis of these observations, the reaction mechanism will be discussed in some detail. With BP_{Cl}-1 and BP_{Cl}-2, which result in large rate constants and also large product G values, an intramolecular ET from a biphenyl radical anion (electron donor) into a C-Cl bond (electron acceptor) is presumed. Such an ET would be affected by the difference in the reduction potential between electron donor and electron acceptor, and by the distance required to the electron transfer (r). It has been shown that such an ET proceeds very slowly in a bimolecular system; a rather low rate constant, $1.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, was obtained for the reaction of a BP-Me radical anion with n -butyl chloride,²³ consistent with the endothermicity of the reaction. The present intramolecular reaction proceeds rather rapidly when n is less than or equal to 2, that is, $r < \text{ca. } 8 \text{ \AA}$. However, the rate constants of the radical anions decrease in the order BP_{Cl}-1 > BP_{Cl}-2 > BP_{Cl}-0 which is roughly parallel to the C-Cl bond energy of these compounds and does not correlate with r . Thus, the reactions in Scheme I, in which the cleavage of the C-Cl bond is the rate-determining step, are presumed for BP_{Cl}-0-BP_{Cl}-2 and also a part of BP_{Cl}-3 as mentioned below.

On the other hand, in the case of BP_{Cl}-3 and BP_{Cl}-4, the decay rates of the biphenyl radical anions decreased about two orders of magnitude. Concurrent formation of the 330-nm band which is assigned to the phenylcyclohexadienyl radical is significant, while the G value of 4-alkylbiphenyl formation becomes low; instead of this, dimers were obtained as a main product. On the basis of these observations, intramolecular carbanionic displacement of the biphenyl radical anion on the chlorine center, that is, an

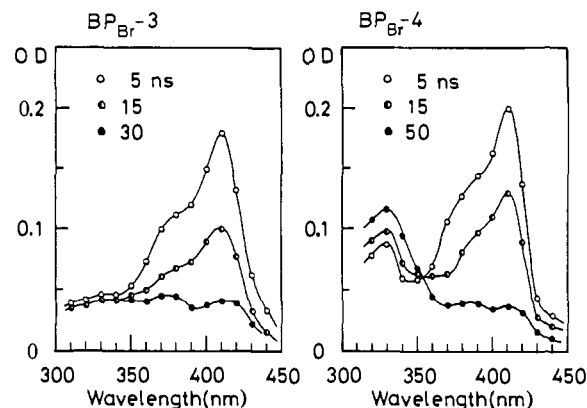
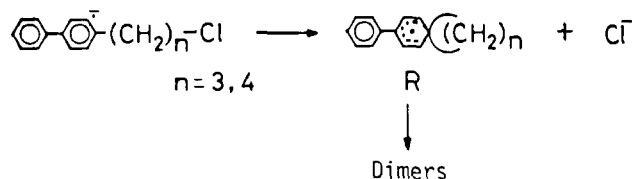


Figure 3. Transient absorption spectra obtained at various times after a 3-ns pulse irradiation of HMPA solutions of BP_{Br}-3 and BP_{Br}-4 ($1.1 \times 10^{-2} \text{ M}$) at room temperature. Absorbed dose was 19 krad/pulse.

Scheme II



intramolecular S_N2 reaction, is presumed.

Simultaneous formation of a spirocyclic radical (R) via a cyclic transition state would explain the 330-nm band formation. Although the reaction products of the intermediate radical, R, are not confirmed yet, such a spirocyclic radical is known to be present as a stable intermediate²⁹ and possesses an absorption band similar to that of the corresponding cyclohexadienyl radical.³⁰ The formation of a spirocyclic product from the reaction of BP_{Cl}-4 with alkali metals, reported by Grovenstein and Akabori,¹³ also supports the presence of R although their reaction mechanism is inconsistent with the present observation. By consideration of the spectral data and the G value of the product, BP_{Cl}-4 seems to proceed by the intramolecular S_N2 reaction preferentially while in the case of BP_{Cl}-3, S_N2 and ET are competitive. It is reasonable that the intramolecular S_N2 reaction of BP_{Cl}-4 is favored over BP_{Cl}-3 which produces a more strained four-membered intermediate.

Bromo and Iodo Derivatives. Comparison with the Data of Corresponding Chlorides. HMPA solutions of BP_{Br}-3 and BP_{Br}-4 were irradiated with a 3-ns pulse, and the transient absorption spectra were recorded at various times after the pulse. The spectra are presented in Figure 3. Those radical anions observed immediately after the pulse show a maximum at 410 nm, similarly to those of BP_{Cl}- n , but the intensity of the bands is weaker than those of the corresponding chlorides. This would be explained by the fact that the C-Br moiety is more reactive with solvated electrons than chlorides and competes with the biphenyl moiety for electrons, leading to the direct formation of biphenyl-alkyl radicals. Indeed, the G values of 4-alkylbiphenyl formation were larger in these bromides than those in the corresponding chlorides. The spectral characteristics of these bromides are that the 410-nm

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Table II. Pulse Radiolysis^a and γ -Radiolysis^b of BP_X-*n* in HMPA at Room Temperature

<i>n</i>	X	OD ₄₁₀	<i>k</i> (s ⁻¹)	$\frac{\Delta OD_{330}}{-\Delta OD_{410}}$	<i>G</i> (BP-alkane)	ΔE (V) ^c
3	Cl	0.40	5.5×10^5	0.45	0.97	0
3	Br	0.18	8.5×10^7	≈0	2.14	-0.62
4	Cl	0.35	1.2×10^6	0.92	0.05	0
4	Br	0.20	4.8×10^7	0.17	1.07	-0.62
4	I	0.04		≈0	1.74	-1.03

^a Pulse width was 3 ns and the absorbed dose was 19 krad/pulse. Substrate concentration: 1.1×10^{-2} M. ^b ⁶⁰Co γ -radiolysis; dose, 1.5×10^5 rad. Products were analyzed by GLC. Substrate concentration: 5.0×10^{-2} M. ^c $\Delta E = E_{1/2}^{\text{red}}(\text{BP}) - E_{1/2}^{\text{red}}(\text{CH}_3\text{CH}_2\text{X})$ (vs. SCE).

band decays very rapidly while the formation of the 330-nm band is observed rather weakly (BP_{Br}-4) or not at all (BP_{Br}-3). This effect of bromides becomes more significant in the iodide. These results are summarized in Table II, together with those of BP_{Cl}-3 and BP_{Cl}-4 for comparison.

With BP_{Br}-3 and BP_I-4, which provide large rate constants (in the case of iodide, the decay kinetics could not be followed by the present time response) and the large product *G* values, an intramolecular ET is presumed as described in Scheme I. In the case of the iodide, of course, solvated electrons are mainly going to the C-I bond which leads to the direct formation of biphenyl-alkyl radicals. The fact that the 330-nm band still does not build up in BP_{Br}-3 and BP_I-4, where the biphenyl-alkyl radicals are formed, excludes an alternative possibility that in Scheme II, R would be formed by the cyclization of the biphenyl-alkyl radicals once formed by an ET mechanism.³¹

In the case of BP_{Br}-4, the formation of the 330-nm band and the *G* value of the reaction product suggest that the both mechanisms are competitively taking place.

The rates of the intramolecular ET are found to change with the halide, as well as with the methylene-chain length, *n*. The rate constant decreases in the order iodide > bromide > chloride. This trend is readily explicable in terms of the ET mechanism, in which the rate constant is expected to be parallel to the difference in reduction potential between electron acceptor (alkyl halide) and electron donor (biphenyl) (ΔE in Table II).

On the other hand, the intramolecular S_N2 proceeded predominantly in BP_{Cl}-4 and competitively in BP_{Cl}-3 and BP_{Br}-4. Thus, the S_N2 reaction seems to require a reaction system where an efficient ET does not occur because the S_N2, forming a new chemical bond, cannot compete with such a long-range ET reaction. Another important factor for the S_N2 is the contribution of the cyclic structure to stabilize the transition state. Indeed, in a bimolecular reaction between biphenyl radical anion and butyl chloride an intermolecular S_N2 reaction could not be observed by the pulse radiolysis.

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(31) A referee pointed out the possibility that the biphenyl-alkyl radicals initially formed from the iodide might be reduced further faster than they cyclize because the formation of the radicals, especially in the iodide, completes immediately after the pulse. However, the initial concentration of the reducing species, e_s⁻, produced by a 3-ns pulse irradiation is very low (4×10^{-5} M). Therefore, the concentration of the biphenyl-alkyl radical is also very low, compared to that of the iodide (1×10^{-2} M). Under these reaction conditions, the possibility of further reduction of the radical by e_s⁻ may be excluded.

Oxidative C-C Bond Cleavage of 1,2-Diols by Silver(II)¹

Anil Kumar

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556. Received February 27, 1981

Abstract: Oxidation of ethylene glycol and related compounds by Ag(II) has been investigated. Complexation of these substrates by Ag(II) precedes their oxidation. Oxidation occurs through electron transfer from an OH group to the Ag(II) within the complex resulting in the formation of alkoxy-type radicals. The radicals thus formed undergo β -scission to give cleavage products. For ethylene glycol a complexation rate $1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and oxidation rate $\sim 3 \times 10^3 \text{ s}^{-1}$ were observed. A general trend for the type of the substrates which would undergo C-C bond scission by Ag(II) is discussed.

The role of Ag⁺ as a catalyst in redox reactions of peroxydisulfate ion is well-known and has been reviewed by several workers.²⁻⁴ Its selective mode in the oxidation of 1,2-diols which results in the C-C bond scission was first pointed out by Greenspan and Woodburn.⁵ The reactions of different diols with this redox system have been the subject of numerous studies in attempts to elucidate the mechanism.⁶⁻¹⁴

In the recent past Huyser and Rose¹³ in their study of Ag⁺-catalyzed oxidation of the straight chain and cyclic 1,2-diols by S₂O₈²⁻ proposed two mechanistic paths involving either Ag(II) or Ag(III) or both depending on the experimental conditions. Recently, Walling and Camaioni¹⁵ on the basis of their studies on alcohols ruled out the possibility of participation of Ag(III) and suggested a possible pathway for cleavage of glycol by Ag(II). So far no information has appeared on the exclusive Ag(II) reactions in the absence of S₂O₈²⁻ with diols. The available literature on Ag(II) reactions with other type of organics is also quite scanty.¹⁶⁻²²

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2225 from the Notre Dame Radiation Laboratory.

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