

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

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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

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It has been pointed out earlier²² that the presence of $S_2O_8^{2-}$, which would cause $SO_4^{\cdot-}$ to be involved in two competitive reactions with Ag^+ and with the substrate, might affect considerably the course of reaction. Therefore, to gain insight into the mechanism, the oxidation of ethylene glycol has been carried out by producing $Ag(II)$ radiolytically without having $S_2O_8^{2-}$ in the system. Indeed, $Ag(II)$ was found to cleave the C-C bond of 1,2-diols, and in agreement with previous findings with amino acids,²² complexation precedes the oxidation.

Experimental Section

Chemicals. The organic compounds were from Fisher (ethylene glycol, ethylenediamine, and formaldehyde), Aldrich (ethanolamine, 1-phenyl-1,2-ethanediol, propane-1,3-diol, and tetranitromethane), Eastman (propane-1,2-diol), B.D.H. (erythritol), calbiochem (glycolic acid), and Baker (methanol, benzaldehyde, and glycerol) and were used as received. Silver perchlorate was from Alfa. All other reagents used were of certified analytical grade and were used without further purification.

Water was purified by Millipore Milli-Q system. Fresh solutions were prepared before each irradiation. The solutions were bubbled either by N_2 or N_2O to remove the oxygen. N_2O also served to convert e_{aq}^- to $\cdot OH$ ($e_{aq}^- + N_2O \rightarrow N_2 + \cdot OH + OH^-$).

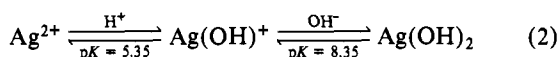
Kinetics. The kinetics were followed by using the pulse radiolysis technique. Details of the technique and the computer-controlled apparatus are reported earlier.^{23,24} Pulse irradiations were carried out by an ARCO LP-7 linear accelerator using generally 10–20-ns pulses which produced $\sim 2\text{--}4 \mu M$ of the radicals. KSCN was used for dosimetry.²⁵ Steady-state radiolysis experiments were performed in $CO^{60}\gamma$ source with a dose rate of $2.9 \times 10^{17} \text{ eV g}^{-1} \text{ min}^{-1}$.

Analyses. Formaldehyde was estimated by using chromotropic acid,²⁶ and benzaldehyde was measured directly by its intense absorption at 249 nm ($\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The yield of Ag^0 was determined by adding a drop of tetranitromethane²⁷ to the irradiated solutions which results in the formation of nitroform anion $C(NO_2)_3^-$ in the presence of Ag^0 . The yield of $C(NO_2)_3^-$ was determined spectrophotometrically at 350 nm ($\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

Results and Discussion

Pulse Radiolysis Experiments. For the kinetic details of the processes involved to be worked out, pulse radiolysis experiments were performed.

$Ag(II)$ was produced by irradiation of N_2O -saturated aqueous solution of $AgClO_4$. The $Ag(OH)^+$ thus produced and its acid-base equilibria have been reported earlier²⁸ and can be summarized briefly in the following two steps



The reaction of $Ag(II)$ with different substrates can be followed in two ways: either by monitoring the decay of $Ag(II)$ ²² absorption or the buildup of the resulting radicals.^{19,21} In the present study the progress of the reaction has been followed by measuring the decay of the absorption of $Ag(II)$ species since the organic radicals formed do not exhibit intense absorption above 250 nm. The spectra of the transients were recorded by irradiating N_2O -saturated aqueous solution of $AgClO_4$ ($\sim 1 \text{ mM}$) and ethylene glycol ($\sim 1 \text{ mM}$) at pH 4.6 and 5.2. The spectra obtained at different time intervals after the pulse at pH 4.6 are shown in Figure 1.

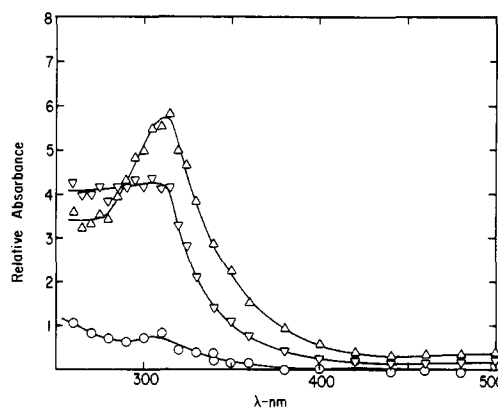


Figure 1. Transient absorption spectra observed with irradiated N_2O -saturated aqueous solution of Ag^+ ($1.1 \times 10^{-3} \text{ M}$) and ethylene glycol ($1.1 \times 10^{-3} \text{ M}$) at pH 4.6: Δ , $\sim 1 \mu s$ after the pulse; ∇ , $\sim 14 \mu s$ later; O , 2.3 ms after the pulse. Ordinate represents relative absorbance, and each unit marked on this scale is equivalent to an extinction coefficient of $1000 \text{ M}^{-1} \text{ cm}^{-1}$ for a species produced with a yield of $G = 6$.

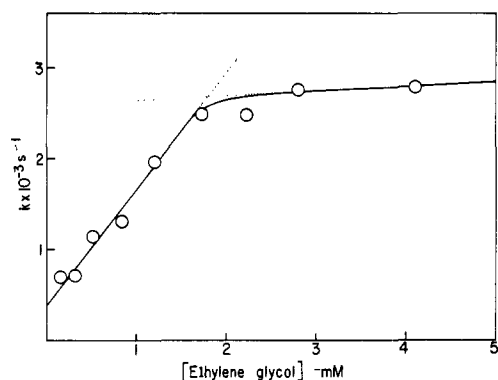


Figure 2. Effect of concentration of ethylene glycol on the decay of $Ag(II)$ absorption monitored at 300 nm at pH 4.7. All solutions up to $2.8 \times 10^{-3} \text{ M}$ glycol concentration contain $1.1 \times 10^{-3} \text{ M}$ Ag^+ . At $4 \times 10^{-3} \text{ M}$ glycol a higher concentration of Ag^+ was added, in order to avoid direct $\cdot OH$ reaction with glycol. All solutions were saturated with N_2O .

The spectrum observed $\sim 1 \mu s$ after the pulse is not identical with but quite similar to the spectrum of $Ag(OH)^+$ and could be assigned to the mixture of $Ag(OH)^+$ and $Ag^{II}OH$ glycol. The initial spectrum was found to change with time. The spectrum recorded $\sim 14 \mu s$ later is different from that obtained from irradiated Ag^+ solution alone.²⁹ Taking into consideration the pK of conversion of $Ag(OH)^+$ to Ag^{2+} and the corresponding spectral shift, the spectrum may be attributed to the contribution of three species, namely, $Ag^{II}OH$ glycol, Ag^{II} glycol, and partly uncomplexed Ag^{2+} . This spectrum was found to decay in all wavelengths region recorded without any further spectral change. Similar types of spectral changes were observed at pH 5.2.

It should be pointed out here that the decay of the latter species mentioned above at both pHs studied results in a small absorption in 250–350-nm wavelength range. This absorption cannot be interpreted as the spectrum of the resulting radicals as the expected radicals formed (e.g., alkoxy, $\cdot CH_2OH$) are known to have a comparatively short lifetime. It could be the absorption of a small concentration of Ag^{3+} formed by the disproportionation of the uncomplexed Ag^{2+} .

The kinetics of the latter spectral decay was followed as a function of ethylene glycol concentration at pH 4.7 at various wavelengths (Figure 2). Initially, with an increase in glycol in the range of 1.5×10^{-4} – $1.6 \times 10^{-3} \text{ M}$ an increase in the rate of decay of $Ag(II)$ absorption was observed. Decay curves were found to follow first-order kinetics and the decay rate was practically unaffected by change in the dose per pulse. A threefold increase in dose rate caused only 20% increase in the decay rate at $\sim 1 \text{ mM}$ glycol. This small contribution seems to be of partly uncomplexed $Ag(II)$ species which would be decaying by a sec-

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Table I. Product Analysis Data with Irradiated N₂O Saturated Aqueous Solutions of Ag⁺ with Different Substrates

substrate	[substrate], M	10 ³ [Ag ⁺], M	pH	G(CH ₂ O)	G(Ag ⁰)
ethylene glycol	9 × 10 ⁻⁴	0	5.7	0.5	
ethylene glycol	9 × 10 ⁻⁴	1.2	5.2	6.2	
ethylene glycol	1.1 × 10 ⁻³	1.1	5.0		2.8
ethylene glycol	2.3 × 10 ⁻³	1.3	5.4	5.2	
methanol	2.5 × 10 ⁻³	0	5.5	0.3	
methanol	1.0	1.3	5.3	6.0	
methanol	1.0	1.5	5.5		4.8
methanol	1.2 × 10 ⁻³	1.2	5.5	3.4	
ethanolamine	8.3 × 10 ⁻⁴	0	9.1	1.5	
ethanolamine	6.6 × 10 ⁻⁴	1.3	8.1	6.5	
ethanolamine	8.3 × 10 ⁻⁴	1.2	5.2	0.4	
glycolic acid	7.8 × 10 ⁻⁴	1.3	5.3	6.0	
ethylenediamine	7.5 × 10 ⁻⁴	1.2	8.3	~0.1	
ethylenediamine	1.1 × 10 ⁻³	1.0	5.4	≤0.3	
propane-1,2-diol	1.1 × 10 ⁻³	0	5.9	≤0.2	
propane-1,2-diol	1.1 × 10 ⁻³	1.2	5.4	3.3	
glycerol	6.2 × 10 ⁻⁴	0	6.2	0.6	
glycerol	6.2 × 10 ⁻⁴	1.2	5.3	4.2	
erythritol	1.1 × 10 ⁻³	0	5.7	0.6	
erythritol	9 × 10 ⁻⁴	1.0	5.5	2.4	
1-phenyl-1,2-ethanediol	1.0 × 10 ⁻⁴	1.2	5.0	1.7 ^a	
propane-1,3-diol	1.1 × 10 ⁻³	1.2	5.5	0.4	

^a Benzaldehyde was produced with G = 2.5.

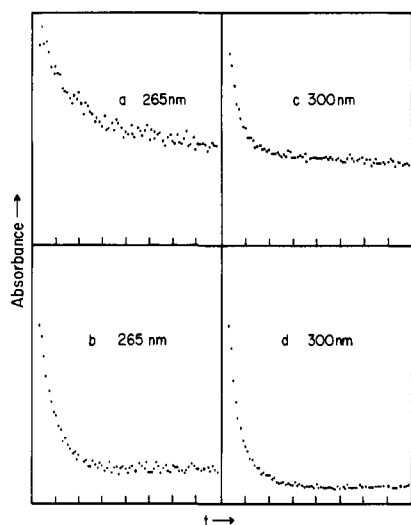
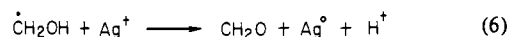
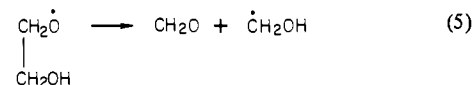
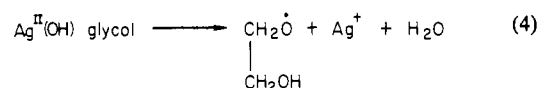
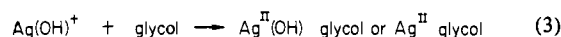


Figure 3. Kinetic traces at 265 and 300 nm with N₂O-saturated irradiated solution containing 1.1 × 10⁻³ M Ag⁺: (a and c) no ethylene glycol; (b) 1.1 × 10⁻³ M ethylene glycol; (d) 1.2 × 10⁻³ M ethylene glycol. Each division on the time scale is equivalent to 1 ms.

ond-order process on the same time scale. Few kinetic traces are shown in Figure 3. A further increase in glycol up to 4 mM did not seem to change the decay rate appreciably. The second-order rate constant for the initial process which is assigned to a complexation step of Ag(II) with glycol was evaluated as (1.3 ± 0.3) × 10⁶ M⁻¹ s⁻¹. The limiting rate constant equal to (2.8 ± 0.8) × 10³ s⁻¹ can be ascribed as the oxidation rate which is taking place most likely through electron transfer from OH groups to Ag(II) within the complex to result in the formation of alkoxy radicals. From the kinetic data it is evident that for the formation of alkoxy radicals, complexation is the rate-determining step at low glycol concentrations while electron transfer is the rate-determining step at higher concentrations.

Thus, pulse radiolysis experiments show that complexation of Ag(II) with glycol takes place in the first step followed by oxidation in the next step. Moreover, these results ruled out the participation of Ag(III) species in the oxidation process since the complexation and oxidation processes occur at the time scale shorter than that required for Ag(III) formation²⁹ and do not result in the production of any other spectrum which absorbs in the

Scheme I



vicinity of Ag(III) absorption. This finding is in agreement with the study of Walling and Camaioni.¹⁵ However, in those cases, where the complexation rates of Ag(II) with the substrates are slow such that the appreciable amount of uncomplexed Ag(II) can disproportionate to Ag(III), the possibility of participation of Ag(III) in the oxidation process cannot be neglected.

On the basis of the above results Scheme I can be suggested for the oxidation.

The validity of the above postulated steps has further been explored by carrying out the analyses of the oxidation products of glycol and related compounds by Ag(II) under various conditions.

Product Analyses. The yield of the oxidation products was determined by carrying out steady-state radiolysis experiments. The experimental conditions in most cases were adjusted in such a way that all ·OH generated in the radiolysis and by the reaction $e_{\text{aq}}^- + \text{N}_2\text{O} \rightarrow \cdot\text{OH} + \text{N}_2 + \text{OH}^-$ react mainly with Ag⁺. The details of the conditions and the yields of the products with different systems are mentioned in Table I.

The main product of oxidation of glycol by Ag(II) was found to be formaldehyde. With Ag⁺-ethylene glycol system formaldehyde yield of G = 6.2 was observed in contrast to G = 0.5 in the absence of Ag⁺. Apparently, Ag(II) is involved in the oxidation process via C-C bond cleavage. The fate of the resulting ·CH₂OH radicals in the presence of Ag⁺ was checked in a separate experiment.³⁰ Thus the yield observed is lower than that expected

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(30) It has been reported earlier by Tausch-Treml, Henglein, and Lillie³¹ that CH₂OH can not simply transfer an electron to Ag⁺ to form Ag⁰. To find out the efficiency of this step, a steady-state radiolysis experiment with methanol-Ag⁺ system was made. The [CH₂OH] was adjusted in such a way so that all ·OH produced react with methanol to give CH₂OH. Almost, quantitative conversion of CH₂OH to formaldehyde and Ag⁰ was observed (Table I).

by nearly a factor of 2, if it were the only reaction. However, the lower yield of formaldehyde can be accounted for by the lack of complete complexation between Ag(II) and glycol. When the [ethylene glycol] was increased to 2.34 mM and $[Ag^+]$ was 1.27 mM, the formaldehyde yield of $G = 5.2$ was observed. Under these conditions nearly 27% of $\cdot OH$ would directly react with glycol³² and one could expect a $G = 8.8$ for formaldehyde formation.

Similar experiments were performed with Ag^+ -ethanolamine system where the complexation ability of Ag(II) though the amino group could be varied considerably with pH. At pH 8.1 a formaldehyde yield of $G = 6.5$ was estimated while a substantial decrease in the yield to $G = 0.4$ was observed at pH 5.2. This experiment clearly reveals two facts. First, the aminoethoxy radicals produced undergo β -scission to result formaldehyde and CH_2NH_2 , and second, the protonation of amino group which prevents complexation of Ag(II) through this group causes a remarkable decrease in the cleavage product. It should be specified here that only 50% of the resulting $\cdot CH_2NH_2$ radicals get oxidized by Ag^+ to produce formaldehyde.²² Virtually, a yield of $G \approx 10$ might have reached with this system if this oxidation would have been quantitative. It is worth mentioning that in the above depicted reaction the formation of $NH_2CH_2CH_2O\cdot$ has been preferred over the equally possible $HOCH_2CH_2\dot{N}H$ on the basis of the formation of formaldehyde as the oxidation product since amino radicals do not appear to undergo β -scission as is discussed below for ethylenediamine. Quantitative oxidation through C-C bond cleavage could clearly be observed with Ag^+ -glycolic acid, where Ag(II) can efficiently complex via carboxyl group.

The significance of complexation of Ag(II) with these substrates for oxidative cleavage is quite obvious from the above illustrated experiments. Attempts were made to clarify whether complexation is the only condition for the C-C bond cleavage. Oxidation of ethylenediamine at pH 8.3 and 5.4 by Ag(II) did not result in

cleavage products, which indicates that besides complexation another condition like formation of alkoxy radicals is also required for C-C bond scission.

Cleavage products were also observed with propane-1,2-diol glycerol, erythritol, and 1-phenyl-1,2-ethanediol (Table I). However, no appreciable cleavage product could be detected with Ag^+ -propane-1,3-diol system. This observation matches the previous finding with Ag^+ -catalyzed oxidation of propane-1,3-diol by $S_2O_8^{2-}$ ¹⁴ where hydroxypropanal was found to be the only product of oxidation. The non formation of cleavage product appears to be due to separation of two OH groups by one C atom in propane-1,3-diol and indirectly reflects for the requirement of cyclic complexation of Ag(II) with substrate.

On the basis of the results with Ag^+ -ethanolamine (pH 5.2) and Ag^+ -propane-1,3-diol the requirement of the formation of cyclic complex between Ag(II) and substrate for cleavage to occur can be argued. But, on the other hand the inductive effect of NH_3^+ group in ethanolamine which would cause a decrease in electron density at -OH group and the difference in the behavior of the radicals produced from propane-1,3-diol which might not undergo C-C bond scission could be the contributing factors for unaccomplishment of C-C bond cleavage.

Conclusion

Product analyses data suggest that any compound containing one -OH group on one carbon and another efficient complexing group on the adjacent carbon would lead to C-C bond cleavage by Ag(II). In other words the formation of the alkoxy-type radicals, which are known to undergo β -scission, is a requirement for accomplishing C-C bond cleavage. From the present study, however, it was not possible to conclude whether complexation of Ag(II) with glycol involves one -OH group or a cyclic complex. Nevertheless, this study rules out the possibility of participation of Ag(III) in such a system. Moreover, it also leads to generalization of the view, in accord to the previous findings,²² that oxidation by Ag(II) takes place through complexation with the substrate as the first step.

Acknowledgment. The Author is grateful to Professor R. H. Schuler and Professor P. Neta for their valuable comments and suggestions.

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