

chemical data to benefit our understanding of the chemistry of metal-cation species. The development of the pulsed-laser volatilization/ionization source has greatly facilitated ICR studies of atomic metal cations.⁴ Freiser and co-workers have recently reported studies on reaction of Cu⁺ with esters and ketones²⁰ and solvation of Cu⁺ by various molecules.²¹ Work in our laboratory has resulted

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in quantitative determination of relative ligand binding energies for complexes with Cu⁺,⁷ Al⁺,² Mn⁺,³ Co⁺,⁷ Ni⁺,²² and FeBr⁺ (ref 22) as well as other mechanistic and thermochemical studies of the chemistry of atomic metal cations.^{2,5-8,12,22}

Acknowledgment. Acknowledgment is made to the National Science Foundation for support of this work by Grant CHE-76-17304.

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Kinetics of Complexation and Oxidation of Ethanolamine and Diols by Silver(II)¹

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The oxidation of ethanolamine (EtA), ethylene glycol, and several other diols by Ag(II) has been studied at pH ~8.5. In the basic pH range, complexation of the substrate by Ag(II) has been found to take place in two steps by successive ligand uptake. Complexation rates are higher by 1 order of magnitude in the basic pH range as compared to the acidic pH range. Oxidation then takes place through intramolecular electron transfer from substrate to Ag(II) within the complex. Oxidation rates for *cis*- and *trans*-1,2-cyclohexanediols are quite similar.

Introduction

In 1954 Greenspan and Woodburn² reported the Ag⁺-S₂O₈²⁻ system as a C-C bond cleaving reagent for 1,2-diols. Later, in a mechanistic investigation for oxidation of aliphatic and cyclic 1,2-diols, Huyser and Rose^{3,4} proposed the involvement of both Ag(II) and Ag(III) species in these oxidations. Walling and Camaioni⁵ more recently suggested a mechanism with the participation of only Ag(II). We have found⁶ that Ag(II) oxidizes ethylene glycol, ethanolamine, and other polyhydric alcohols through C-C bond cleavage. On the basis of product analysis data, the types of substrates which might undergo C-C bond cleavage by Ag(II) were suggested. For these substrates the importance of an efficient complexing group on one carbon atom and the presence of an alcoholic group on the vicinal carbon atom was demonstrated. To further explore the role of complexation in these oxidations, I carried out pulse radiolysis experiments with ethanolamine in both acidic and basic pH ranges. Ethanolamine was selected as a substrate because of the reversal of its complexing nature through changes in the protonation of the amino group at high and low pH. Furthermore, in an attempt to obtain an explanation for the observed similarity in the oxidation rates with *cis*- and *trans*-1,2-cyclohexanediols by Ag⁺-S₂O₈²⁻,² a study of the oxidation of these substrates by Ag(II) was also undertaken. The present work supplements the kinetic and spectral evidence for the complexation of Ag(II) with these substrates

in the initial step prior to oxidation.

Using the pulse radiolysis technique with optical and conductometric detectors, I obtained kinetic data which allowed a mechanism for the complexation of these substrates by Ag(II) to be proposed. Interestingly, Ag(II) has been found to cleave the C-C bond of 2,2-dimethylpropane-1,3-diol, while no cleavage product was obtained with propane-1,3-diol.⁶

Experimental Section

All studies have been carried out in an aqueous medium. Water was purified by a Millipore-Milli-Q system. Fresh solutions were prepared before each irradiation.

The organic compounds used were ethanolamine and *cis*-1,2-cyclohexanediol (Alfred Bader Chemicals) (Aldrich), ethylene glycol and formaldehyde (Fisher), *trans*-1,2-cyclohexanediol (Matheson Coleman and Bell), and 2-hydroxycyclohexanone (Pfaltz and Bauer). NMR spectra of *cis*- and *trans*-1,2-cyclohexanediols show that the two do not contain any traces of each other. All of these chemicals were used as received, without further purification. Silver perchlorate was obtained from Alfa, and all other chemicals used were either Baker analyzed or certified analytical reagents. The pHs of the solutions were adjusted by using sodium hydroxide and perchloric acid. Sodium borate was used as a buffer for maintaining the basic pH.

In the radiolysis of N₂O-saturated aqueous solutions ·OH radicals are produced with *G* = 6. Ag(II) was produced by the reaction of ·OH radicals with Ag⁺.



Its acid-base equilibria have been discussed earlier.⁷ At

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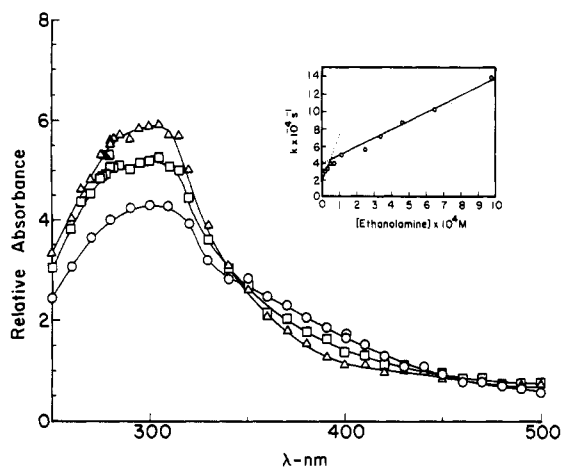
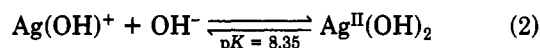


Figure 1. Transients absorption spectra observed with irradiated N_2O -saturated aqueous solution of silver perchlorate (1.2×10^{-3} M) containing ethanolamine (6.3×10^{-4} M) at pH 8.9: (Δ) 2.5 μ s after the pulse; (\square) ~ 14 μ s after the pulse; (O) ~ 70 μ s after the pulse. Each unit on the relative absorbance scale, in this and the other figures, represents an extinction coefficient of $1000 \text{ M}^{-1} \text{ cm}^{-1}$ for transients produced with a yield of $G = 6$. Insert: Effect of the concentration of ethanolamine on the buildup rate at 400 nm. All of these solutions were saturated with N_2O and contained $\sim 1.2 \times 10^{-3}$ M silver perchlorate. The pH was maintained at ~ 8.5 .

pH 8.5, where most of the experiments have been performed, the following equilibrium would be important:



In general, $\text{Ag}(\text{II})$ is known to have a coordination number of 4.⁸ The coordination number requirement of the species considered herein can be satisfied by considering water molecules as ligands.

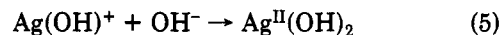
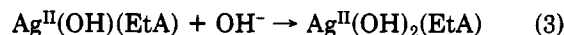
The kinetics of transients formation, interconversion, and decay were studied by using the pulse radiolysis setup described earlier.^{9,10} Pulse irradiations were carried out by using generally 5–10-ns pulses which produced ~ 2 – 3 μM of radicals. KSCN was used for dosimetry.¹¹ Kinetics for the ligand uptake by $\text{Ag}(\text{II})$ has been followed by monitoring the buildup in the region of 400 nm, as the complexation and oxidation processes could easily be resolved at these wavelengths. Oxidation rates in all cases were measured by following the decay of $\text{Ag}(\text{II})$ absorption.^{6,12} Pulse conductivity experiments were carried out by the device described elsewhere by Janata.¹³

Steady-state radiolysis experiments were performed in a ^{60}Co γ source at a dose rate of $2.8 \times 10^{17} \text{ eV g}^{-1} \text{ min}^{-1}$. Yields of formaldehyde were determined by using chromotropic acid.¹⁴

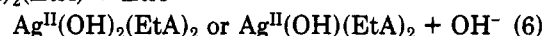
Results and Discussion

Ethanolamine. The spectra of the intermediates in a silver perchlorate and ethanolamine (EtA) solution (pH 8.9) are shown in Figure 1 at difference time intervals after the pulse. The assignment of the different species, in general, has been made to parallel that in previous studies.^{6,12,15} The spectrum scanned nearly 2.5 μ s after the

pulse is different from that of $\text{Ag}(\text{OH})^+$ and seems to manifest contributions from both $\text{Ag}(\text{OH})^+$ and $\text{Ag}^{\text{II}}(\text{OH})(\text{EtA})$. Nearly 14 μ s later a spectral change was observed. Though the spectral shift was in the same direction as that observed with Ag^+ solution alone, the spectrum as such was different. Taking into consideration the pK of the conversion of $\text{Ag}(\text{OH})^+$ to $\text{Ag}^{\text{II}}(\text{OH})_2$, can attribute this spectrum mainly to the transients $\text{Ag}^{\text{II}}(\text{OH})_2(\text{EtA})$ with a little contribution of uncomplexed $\text{Ag}^{\text{II}}(\text{OH})_2$.



Nearly 70 μ s after the pulse a still different spectrum was observed, and this could be assigned mainly to the mixture of the species $\text{Ag}^{\text{II}}(\text{OH})_2(\text{EtA})_2$ and $\text{Ag}^{\text{II}}(\text{OH})(\text{EtA})_2$.



The absorption thus produced decays to result in a very weak absorption in the 250–400-nm region without any spectral shift. This absorption could be due to the $\text{Ag}(\text{III})$ species formed by the disproportionation of partially uncomplexed $\text{Ag}^{\text{II}}(\text{OH})_2$ on the same time scale.

The above-proposed transients after 14 and 70 μ s of the pulse have been considered to possess five and a mixture of five and six coordinates, respectively, unlike the previous study.¹² The support for this could be procured by the pulse conductivity experiments, discussed later. However, it would not have been possible to conduct these experiments with the previously reported ligands like amino acids.¹² The assignment of the transients present 70 μ s after the pulse with two ethanolamine molecules has been made on the basis of the kinetic data which are described below. In a similar way the uptake of the two ligands by $\text{Ag}(\text{II})$ in the basic pH range has been reported for ammonia¹⁵ and amino acids.¹²

Kinetics for the observed spectral changes as well as for the later decay of the transients were followed as a function of ethanolamine concentration. Rates of the buildup at 400 nm and nearby wavelengths were found to increase with an increase in ethanolamine concentration. A plot of the rate vs. ethanolamine concentration (Figure 1) shows that this reaction is composed of two independent consecutive processes occurring with second-order rate constants of $(5.5 \pm 1.3) \times 10^8$ and $(1 \times 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively. These two processes indicate the uptake of ethanolamine in two successive steps resulting in the formation of $\text{Ag}^{\text{II}}(\text{OH})_2(\text{EtA})$ and a mixture of $\text{Ag}^{\text{II}}(\text{OH})_2(\text{EtA})_2$ and $\text{Ag}^{\text{II}}(\text{OH})(\text{EtA})_2$ species, respectively. A few representative kinetic traces for this step with different substrates have been depicted in Figure 2A.

The kinetic traces for the latter decay of the $\text{Ag}(\text{II})$ absorption at pH 8.5 followed first-order behavior in the presence of ethanolamine (Figure 2, B and C). The decay rate ($\sim 2 \times 10^3 \text{ s}^{-1}$) was found to be almost independent of ethanolamine concentration within the range of 4.8×10^{-4} – 2.8×10^{-3} M. This process can be assigned to the oxidation step which is taking place by intramolecular electron transfer within the complex. At low concentrations, however, a slight decrease in the decay rate of $\text{Ag}(\text{II})$ was observed with increasing ethanolamine. Slightly higher rates at low concentrations could be due to the involvement of monomeric species $\text{Ag}^{\text{II}}(\text{OH})_2(\text{EtA})$ in the oxidation process.

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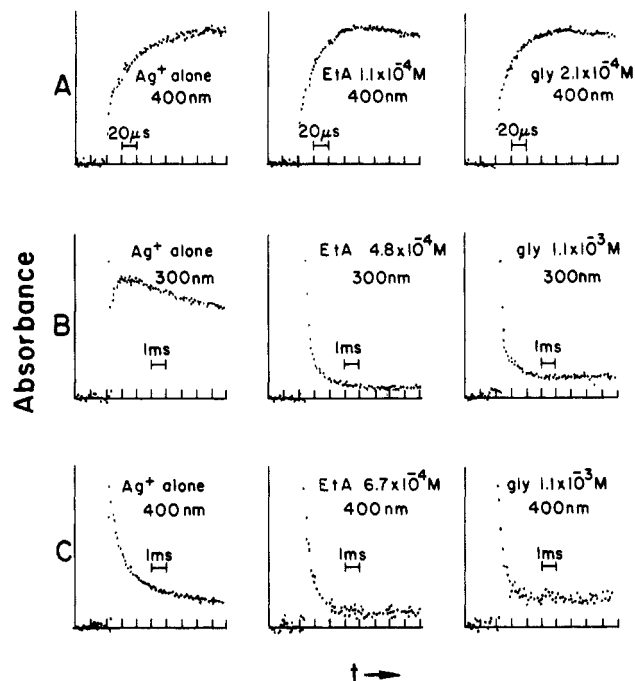
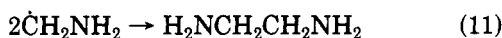
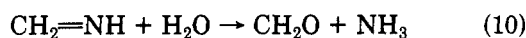
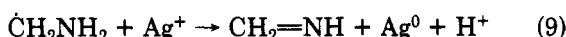
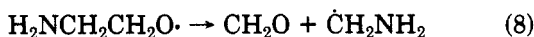
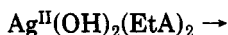


Figure 2. Kinetic traces observed in the pulse radiolysis study with N_2O -saturated irradiated aqueous solution of $\sim 1.2 \times 10^{-3}$ M silver perchlorate at pH 8.5 containing various substrates on the time scale indicated in the traces.

In steady-state radiolysis experiments, formaldehyde was found to be the main product of oxidation of ethanolamine by $Ag(II)$ at pH 8.3.⁶



No complexation was observed with Ag^+ -ethanolamine at pH 4.7. The spectral changes at this pH were almost similar to those of irradiated solution containing only silver perchlorate. Kinetic and spectral studies indicated less reactivity of $Ag(II)$ toward protonated ethanolamine. This observation lends further support to the interpretation made earlier on the basis of the product analysis data with this system.⁶ There, the absence of cleavage product was explained in terms of the noncomplexing and electron-attracting nature of the protonated amino group.

Ethylene Glycol. The apparent kinetic and spectral differences in the acidic and basic pH ranges with ethanolamine prompted us to investigate the reaction of ethylene glycol (gly) at basic pH also. The results obtained with Ag^+ -glycol at pH 8.6 are quite similar to those of Ag^+ -ethanolamine at this pH. With this system also the formation of three intermediates was noted prior to the oxidation. The spectra shown at nearly 2.5, 14, and 56 μs after the pulse (Figure 3) can be assigned to the species $Ag^{II}(OH)(gly)$, $Ag^{II}(OH)_2(gly)$, and a mixture of $Ag^{II}(OH)(gly)_2$ and $Ag^{II}(OH)(gly)_2$, respectively. Complexation of glycol by $Ag(II)$ could be kinetically differentiated to take place in two steps by the successive uptake of glycol. Second-order rate constants of $(1.5 \pm 0.3) \times 10^8$ and $(3 \pm 1) \times 10^7 M^{-1} s^{-1}$ were measured for these two processes, respectively. Oxidation of glycol by electron transfer from its OH group to $Ag(II)$ within the complex occurs at a rate of $\sim 2.5 \times 10^9 s^{-1}$. In steady-state radiolysis, the main

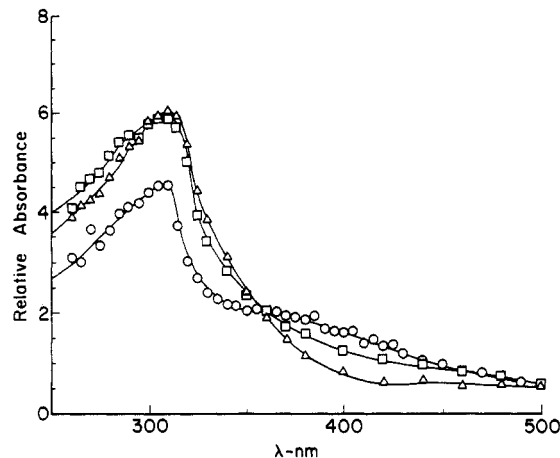


Figure 3. Transients absorption spectra observed with irradiated aqueous N_2O -saturated solution of silver perchlorate (1.2×10^{-3} M) and glycol (~ 2.5 and $14 \mu s$ after the pulse, 5.4×10^{-4} M; $56 \mu s$ after the pulse, 1.1×10^{-3} M) at pH 8.5: (Δ) 2.5 μs after the pulse, (\square) $\sim 14 \mu s$ after the pulse, (\circ) $\sim 56 \mu s$ after the pulse.

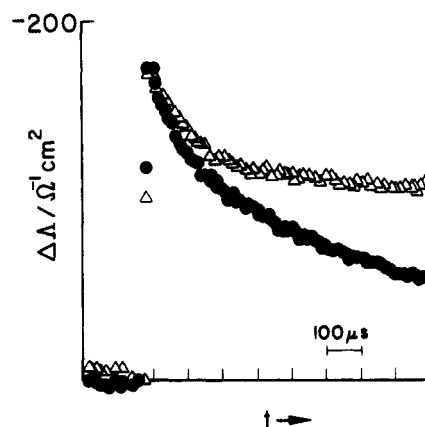


Figure 4. Kinetic traces observed in pulse conductivity experiments with N_2O -saturated solution of silver perchlorate (4.6×10^{-4} M) at pH 9.1 containing no substrate (Δ) and glycol (2.2×10^{-4} M) (\bullet). The ordinate represents the relative change in conductivity.

product of oxidation of glycol by $Ag(II)$ was found to be formaldehyde ($G = 5.4$).¹⁶

Pulse Conductivity Experiments. From the previous^{6,12} and present studies it is apparent that the complexation of $Ag(II)$ with different substrates notably takes place by one-ligand uptake when $Ag(OH)^+$ and Ag^{2+} are the reactive species and in two steps by two successive ligands uptake when $Ag(OH)^+$ and $Ag^{II}(OH)_2$ are the predominant species. It indirectly indicates that complexation could be taking place mainly through OH^- substitution by the ligand. In order to ascertain this possibility, I undertook pulse conductivity experiments with Ag^+ -glycol.

A change in conductivity was followed on a 1-ms time scale with a solution of silver perchlorate (4.6×10^{-4} M) at pH 9.1 by adding increasing concentrations of glycol. A typical trace in Figure 4 shows the change in conductivity in the presence and the absence of glycol on a 1-ms time scale. Change in the conductance with and without glycol seems to follow the same path in the beginning. Thus, in parallel to the study of Asmus et al.⁷ with Ag^+ solution, the first step would be leading to the formation of $Ag^{II}(OH)_2(gly)$ in the presence of glycol. In optical pulse studies this species has been assigned at nearly 14 μs after

(16) Steady-state radiolysis experiments were performed with reaction mixture containing silver perchlorate (1.2×10^{-3} M); ethylene glycol (9.0×10^{-4} M) at pH 8.5. All solutions were saturated with N_2O .

TABLE I: Rate Constants for Complexation and Oxidation by Ag(II)

| substrate | pH | $k_{\text{complexation}}, \text{M}^{-1} \text{s}^{-1}$ | | $k_{\text{oxidation}}, \text{s}^{-1}$ |
|-----------------------------------|-----|--|---------------------------|---------------------------------------|
| ethanolamine | 8.5 | $(5.5 \pm 1.3) \times 10^8$ | $(1 \pm 0.3) \times 10^8$ | $(2 \pm 1) \times 10^3$ |
| ethylene glycol | 8.6 | $(1.5 \pm 0.3) \times 10^8$ | $(3 \pm 1) \times 10^7$ | $(2.5 \pm 1) \times 10^3$ |
| <i>cis</i> -1,2-cyclohexanediol | 8.7 | $(1.5 \pm 0.3) \times 10^8$ | $(8 \pm 1) \times 10^7$ | $(3 \pm 1) \times 10^3$ |
| <i>trans</i> -1,2-cyclohexanediol | 8.7 | $(3.7 \pm 0.3) \times 10^8$ | $(7.5 \pm 1) \times 10^7$ | $(3 \pm 1) \times 10^3$ |

the pulse. The species observed nearly 56 μs after the pulse could be the mixture of $\text{Ag}^{\text{II}}(\text{OH})_2(\text{gly})_2$ and $\text{Ag}^{\text{II}}(\text{OH})(\text{gly})_2$ as nearly $1/6$ of the decrease in conductance is regained in this time period (Figure 4). It is evident from the above results that the presence of ethylene glycol causes an additional release of OH^- , but the data cannot be quantized accurately because of the practical limitations in adjusting the pH and concentrations of the reactants.

cis- and *trans*-1,2-Cyclohexanediols. The spectral transformations and kinetics with these substrates followed the same pattern as observed with glycol and ethanolamine. Therefore, the results will not be discussed in detail.

A survey of Table I shows that the rate of complexation of Ag(II) in the initial step is slightly higher for *trans*-1,2-cyclohexanediol than for *cis*-1,2-cyclohexanediol. However, the oxidation rates are quite similar with the two in agreement with the previous findings of Greenspan and Woodburn² for $\text{Ag}^+ - \text{S}_2\text{O}_8^{2-}$. The small difference in the complexation rates in the initial step appears to be due to the difference in the strength of the intramolecular hydrogen bonding of these two substrates. According to Kuhn's data¹⁷ *cis*-1,2-cyclohexanediol will be more strongly bonded through hydrogen bonding between hydroxyl groups than the *trans*-1,2-cyclohexanediol. The similarity in the oxidation rates of the two rules out the controversial participation of Ag(III) in these oxidations. If Ag(III) species had been involved in the oxidation step, then, as with other two-electron oxidants,^{18,19} the rate of oxidation should have been comparatively much higher with the *cis* form than with the *trans* because of cyclic complex formation in the first step.

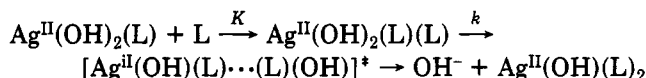
In steady-state radiolysis experiments with N_2O -saturated solutions of $\text{Ag}^+ - \text{cis}$ -1,2-cyclohexanediol and *trans*-1,2-cyclohexanediol, a continuous growth in the spectrum at 230 and ~ 280 nm (a shoulder) was observed with increasing irradiation. Most likely this product is hexanediol as the other possible product 2-hydroxycyclohexanone was found not to absorb in this region. In fact, the product formed cannot be determined exactly because of the nonavailability of an authentic sample and literature data on the expected product.

C-C Bond Scission of 2,2-Dimethylpropane-1,3-diol by Ag(II). Unlike propane-1,3-diol, 2,2-dimethylpropane-1,3-diol was found to undergo oxidation through C-C bond scission by Ag(II). Its cleavage results in the formation of formaldehyde with $G = 4.0$.²⁰ In contrast with OH radicals, formaldehyde formation with only $G = 0.5$ was observed.

In parallel to the previous studies, complexation of the substrates through hydroxyl groups by Ag(II) would precede the oxidation. Oxidation which would be taking place by an intramolecular electron transfer from substrate to Ag(II) would result in the formation of the alkoxy radicals. The alkoxy radicals thus produced would undergo β scission to give cleavage product. The observed discrep-

ancy in the behavior of propane-1,3-diol and 2,2-dimethylpropane-1,3-diol can be explained by the following reasoning. The substitution of hydrogens at carbon 2 in propane-1,3-diol by two methyl groups would cause an increasing electrophilic attack at OH group by Ag(II) because of their +I effect and thereby weaken the C-C bond strength at the β position. The alkoxy radicals thus produced from 2,2-dimethylpropane-1,3-diol due to weakening of the C-C bond strength at the β position would undergo β scission to result in the cleavage product.

General Discussion. On the basis of the above-stated results, the following scheme seems to be operating for complexation at pH 8.5. The initial step leads to the formation of the five-coordination species of the general structure $\text{Ag}^{\text{II}}(\text{OH})_2(\text{L}) \cdot 2\text{H}_2\text{O}$. In the subsequent step this precursor takes up another ligand presumably through associative (A) and dissociative ion exchange (I_D) mechanisms simultaneously. The A mechanism would lead to the formation of the six-coordinated species $\text{Ag}^{\text{II}}(\text{OH})_2(\text{L})_2 \cdot 2\text{H}_2\text{O}$ while the I_D mechanism would yield $\text{Ag}^{\text{II}}(\text{OH})(\text{L})_2 \cdot 2\text{H}_2\text{O}$ through the following course of reactions:



The suggested mechanism explains the release of OH^- on the observed time scale. The possibility of the formation of the five- and six-coordinated complexes of Ag(II) with the mixed ligands has been invoked earlier by Murtha and Walton.²¹ The preceding proposed scheme is an attempt to elucidate the practical findings; still, an elaborate study with other systems is required for its further verification.

A perusal of Table I shows that the complexation rates of Ag(II) with the studied substrates at pH 8.6 are higher by 1 order of magnitude than that observed at lower pH.⁶ Similar results were previously obtained with glycine.¹² From the above-stated mechanism, these observations can be explained qualitatively in the following manner. Since OH^- is being released during the complexation process, therefore, because of electrostatic charge at the central metal atom, complexation rates would be higher with the species $\text{Ag}^{\text{II}}(\text{OH})_2$, which is predominant at basic pH, in comparison to Ag^{2+} at acidic pH. As expected, complexation rates of Ag(II) are higher by nearly a factor of 3 with ethanolamine in comparison to glycol, since with ethanolamine complexation through the basic amino group can take place more efficiently.

Conclusions

The present study reveals the involvement of Ag(II) in the oxidation of ethanolamine and diols. The mechanism was found to involve an initial complexation of the substrates with Ag(II), followed by oxidation. Since complexation and oxidation take place in less time than that required for Ag(III) formation, it is concluded that Ag(III) is not involved in these oxidations. A similarity in the oxidation rates of *cis*- and *trans*-1,2-cyclohexanediols also strengthens the participation of Ag(II). Moreover, it rules out the requirement of cyclic complexation between Ag(II) and these substrates in the initial step. For the accom-

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(20) Steady-state radiolysis experiments were carried out with N_2O -saturated solution of silver perchlorate (1.2×10^{-3} M) and 2,2-dimethylpropane-1,3-diol (9.6×10^{-4} M) at pH 5.1.

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plishment of oxidation by Ag(II), its complexation with the substrates in the first step appears to be the prerequisite. At pH 8.5 complexation of the substrate by Ag(II) could be kinetically distinguished to take place in two steps. With the help of optical and pulse conductivity data, it could be demonstrated that the previous step results in the formation of the precursor five-coordinated species which in the following step takes up another ligand through associative and dissociative ion-exchange mechanisms. Electrostatic charge at the central metal atom of the Ag(II) species seems to affect the complexation rates. Oxidation then takes place by intramolecular electron

transfer from substrate to Ag(II) within the complex to result in the formation of the alkoxy radicals. The alkoxy radicals thus formed might or might not undergo β scission depending upon the C-C bond strength at that position. It is worth pointing out that most of our results are consistent with the earlier reports on the oxidation of these substrates by the $\text{Ag}^+ - \text{S}_2\text{O}_8^{2-}$ system and thus confirms that those previous oxidations indeed involved Ag^{II} .

Acknowledgment. I am indebted to Dr. P. Neta for his valuable suggestions and to Dr. E. Janata for his help in measurement of the pulse conductivity data.

Kinetics of the Hydrolysis of Hydroxyl Groups on Zeolite Surfaces Using the Pressure-Jump Relaxation Method

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Single relaxations were observed in basic aqueous suspensions of zeolites X and Y by using the pressure-jump relaxation method with electric conductivity detection. The reciprocal relaxation times obtained for both zeolite X and Y suspensions show the difference which is due to the composition of a crystalline aluminosilicate framework at the zeolite surface. The single relaxations in both systems were attributed to hydrolysis on the zeolite surfaces. The forward and backward rate constants of the surface hydrolysis were determined to be $k_f = 2.0 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_b' = 2.0 \times 10^{-2} \text{ s}^{-1}$ for zeolite X, and $k_f = 8.1 \times 10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_b' = 7.3 \times 10^{-1} \text{ s}^{-1}$ for zeolite Y, respectively, at 25 °C.

Introduction

Crystalline aluminosilicate frameworks of zeolites¹ which are terminated by surface hydroxy groups²⁻⁴ play an important role in the determination of acidic properties of zeolites.⁵ In order to understand dynamic properties of acid sites on zeolite surfaces, the pressure-jump relaxation method has been recently applied to acetate ion adsorption-desorption on an amorphous silica-alumina surface⁶ and to the hydrolysis of hydroxyl groups on a zeolite 4A surface.⁷ In a basic aqueous suspension of zeolite 4A, ion exchange of methylammonium ion for Na^+ , reported previously,⁸ and the hydrolysis of surface hydroxyl groups on the aluminosilicate framework occur independently. Therefore, the kinetic behavior of surface hydroxyls of zeolites X and Y, which differs greatly from that of γ -alumina or titanium dioxide,^{9,10} must be clarified before

TABLE I: Kinetic and Static Data in the Zeolite X-OH⁻ System at 25 °C

| τ^{-1}, s^{-1} | $10^4[\text{OH}^-], \text{mol dm}^{-3}$ | $10^3[\text{SOH}], \text{mol dm}^{-3}$ | $10^3[\text{SO}^-], \text{mol dm}^{-3}$ |
|----------------------------|---|--|---|
| 0.65 ± 0.07 | 0.41 | 3.21 | 3.46 |
| 0.55 ± 0.04 | 1.05 | 2.77 | 3.90 |
| 0.44 ± 0.02 | 2.09 | 1.88 | 4.79 |
| 0.42 ± 0.01 | 5.89 | 1.27 | 5.40 |
| 0.41 ± 0.01 | 10.7 | 0.74 | 5.93 |
| 0.39 ± 0.01 | 16.6 | 0.33 | 6.34 |

the mechanism of ionic adsorption and exchange can be well understood.

In this paper, we present the results of pressure-jump relaxation experiments on the kinetics of surface hydrolysis on zeolite X and Y surfaces.

Experimental Section

Zeolites X ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2$) and Y ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.8\text{SiO}_2$) were supplied from the Toyo Soda Co. and were used without further purification. Microscopic examination confirms that the mean diameters of the monodispersed zeolite particles are nearly 3 μm for the zeolite X and 1 μm for the zeolite Y. Aqueous suspensions of the zeolites were equilibrated for 24 h after addition of NaOH or HNO_3 . The measurements were done in a nitrogen atmosphere at a particle concentration of $C_p = 30 \text{ g dm}^{-3}$ and at 25 °C.

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