Optical Bleaching of Trapped Electrons in γ-Irradiated Alkaline Ice. Location of Energy Levels

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Abstract: The optical bleaching of radiation-produced trapped electrons in glassy alkaline ice (10 *M* NaOH) has been studied by epr. The optical bleaching rate shows no temperature dependence between 4 and 77°K; this indicates that the optical transition occurs directly to a continuum state and that no bound excited state exists for electrons trapped in this matrix. Between 90 and 140°K the optical bleaching rate decreases with temperature and is characterized by a negative activation energy of 0.05 eV. This indicates the existence of shallow traps. A similar temperature dependence is found for electrons produced by photoionization of ferrocyanide ion in alkaline ice. The shallow traps appear to provide a common path for combination of the optically detrapped electrons with their counterpart holes. Only 70% of the optically detrapped electrons ultimately react with the matrix hole, O^-, to cause loss of the O^- epr signal; this per cent is independent of temperature and of radiation dose. The other electrons may react to form dielectrons and hole–electron charge pairs.

Electrons produced by γ irradiation are trapped in glassy alkaline ice (10 *M* NaOH) at 77°K and can be observed by their epr or optical spectrum.[1] The mere observation of these trapped electrons indicates that their ground state is stable. Information on the location of the first excited state has been deduced from the temperature dependence of the photocurrent associated with optical detrapping of these electrons.[2,3] Here we have studied the temperature dependence of the photobleaching process of these trapped electrons to gain additional and confirmatory information about the location of the first excited state. The results support the photoconductivity work and show that no bound excited state for the trapped electron exists and that the optical transition occurs directly to the continuum.

In γ-irradiated alkaline ice at 77°K equal yields of trapped electrons, e_t^- and O^-, which is formally a hole, are formed. One might expect the optical and thermal decay reactions of e_t^- and O^- to be simple combination. Thermal decay studies which only monitored e_t^- are interpreted in this way.[4] In the present study the reactions of optically detrapped electrons have been investigated by monitoring both e_t^- and O^- by epr. Only about 70% of the optically detrapped electrons ultimately react with O^- and this per cent is independent of temperature and of radiation dose.

The overall temperature dependence of the photobleaching process also reveals the presence of shallow traps of about 1.2-kcal/mol depth. Shallow traps are likewise shown to exist for trapped electrons produced by photoionization of ferrocyanide ion in alkaline ice. The results suggest that the shallow trap may provide a common path for the combination of electrons with their counterpart holes even when the nature of the hole may be different, as it is for radiation-produced and photoionization-produced electrons.

Experimental Section

A 10 *M* solution of reagent grade NaOH was prepared and used to fill 3-mm i.d. spectrosil quartz tubes to a level of 1.2 cm. Subsequent plunging of the tubes into liquid nitrogen produced clear glasses. Trapped electrons, e_t^-, were produced in this glassy matrix by irradiation at 77°K in a U. S. Nuclear ^{60}Co γ irradiator at a dose rate of 0.4 Mrad/hr. To produce e_t^- by uv photoionization of $Fe(CN)_6^{4-}$, some of the 10 *M* NaOH was made 10^{-2} *M* in potassium ferrocyanide. Glasses were prepared from this solution and were exposed for 10 min to 254-nm light in a Rayonett uv irradiator. A solution filter containing 1.0 *M* $NiSO_4$ and 0.16 *M* $CoSO_4$ was used to prevent photobleaching of e_t^- by the associated visible light during the uv irradiation.

The e_t^- concentration was measured with a Varian 4502 epr spectrometer, using low microwave power to avoid saturation. Samples were bleached with broad-band visible light through slits in the side of the microwave cavity by using a 500-W slide projector equipped with a Corning No. 3961 filter to remove ir radiation. The glass lens of the slide projector removed light below 300 nm. Initially a monochromator was used with the slide projector to provide a 30-nm wide band of light centered at the e_t^- maximum of 588 nm. However, no difference in the temperature dependence of the bleaching rate was noted when comparing experiments with and without the monochromator, so just the slide projector and filter were used thereafter. Since it is possible to selectively bleach on the low-energy side of the absorption band and shift the peak maximum toward the high-energy side by retrapping,[5] the use of broad band light may avoid some potential complications. The samples studied contained sufficient e_t^- to initially absorb 99% or more of the incident light, so there was a large gradient of light intensity across the sample.

Temperatures of 4 and 77°K were obtained by using liquid nitrogen and liquid helium in appropriate quartz dewars with unsilvered tail sections which inserted into the 11-mm access hole in the microwave cavity. The helium dewar had a liquid nitrogen shield at the top but the tail section had none. Although this produced a greater heat leak, it gave a 5-mm i.d. sample volume and was as easy to tune as a standard liquid nitrogen epr dewar. Liquid helium bubbling did not cause any noise problems. Temperatures between 90 and 150°K were obtained by using a Varian variable-temperature flow dewar in which the temperature is maintained by cold flowing nitrogen. In these latter experiments a copper–constantan thermocouple was placed inside the quartz sample tubes just above the NaOH glass sample and the temperature was continuously measured with a Digitec digital thermocouple thermometer.

The dependence of the photobleaching rate of e_t^- on light intensity was measured by reducing the projector light intensity with a piece of copper mesh whose "optical density" had been measured with a spectrophotometer. The absolute light intensity at the sample position was measured with a YSI-Kettering radiometer.

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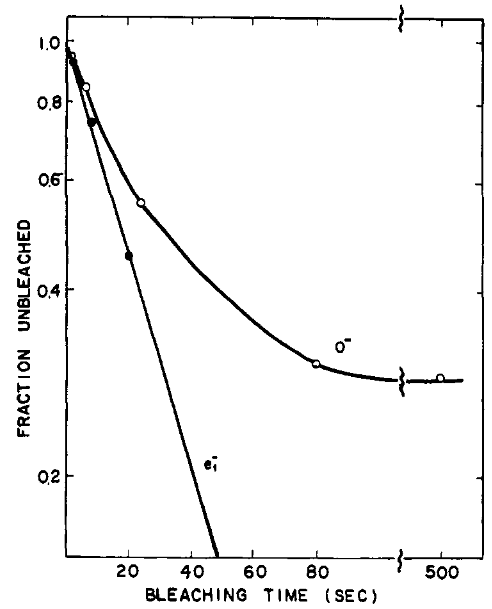

Figure 1. Photobleaching behavior of e_t^- and O^- at 4°K in 10 M NaOH γ irradiated to 1 Mrad at 77°K.

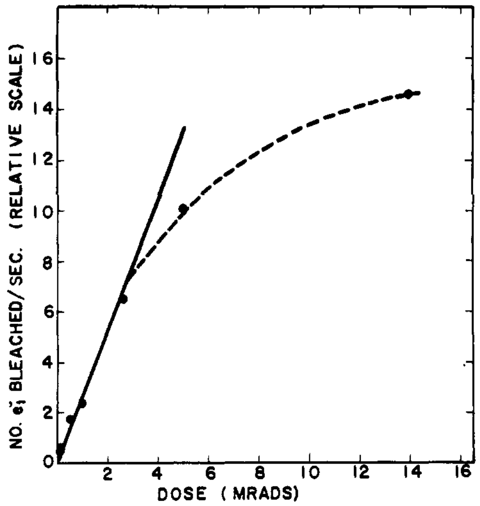

Figure 2. Dose dependence for number of e_t^- lost in first 5 sec of photobleaching with same light intensity. Since the samples absorb all incident quanta, the ordinate also represents the relative quantum efficiency for photobleaching.

Results

1. Photobleaching Phenomenology. The net photobleaching rates of the paramagnetic species, e_t^- and O^-, produced in the radiolysis of frozen 10 M NaOH were studied *vs.* radiation dose and temperature. The e_t^- has a broad optical absorption band with a peak at 588 nm and a full width at half maximum from 450 to 720 nm. The O^- absorption is not well characterized; it presumably has a weak absorption in the 220–250-nm range. Thus the visible light used for photobleaching in this work was all absorbed by the e_t^- band.

As a sample is photobleached both e_t^- and O^- concentrations decrease with time as shown in Figure 1. The behavior shown in Figure 1 is typical for radiation doses up to about 3 Mrad for which the initial e_t^- and O^- yields are equal;[6] results at higher doses are discussed below. It is apparent that some e_t^- is detrapped and undergoes some loss reaction as a consequence of light absorption in its absorption band. The decrease in O^- must be associated with the detrapping of e_t^- and its subsequent reactions. No new paramagnetic species are observed after photobleaching.

Note that the e_t^- concentration can be bleached to zero while the O^- decreases to a plateau at long bleaching times. Since the initial e_t^- and O^- yields were equal, this suggests that some detrapped e_t^-'s undergo another reaction than with O^- and/or some O^- is "unreactive" toward detrapped electrons. These two possibilities were distinguished by the following experiment. A 10 M NaOH glass containing 10^{-2} M ferrocyanide was γ irradiated to 0.1 Mrad. The e_t^-'s were completely photobleached and the remaining O^- concentration was measured by epr. Then the sample was uv irradiated for 10 min to produce new e_t^- by photoionization of ferrocyanide. About half of the remaining O^-'s were lost during the uv photolysis. This loss must have been due to reaction with photoionization-produced electrons since uv photolysis of O^- in 10 M NaOH without ferrocyanide did not change the O^- concentration. After uv photolysis the relative concentrations of e_t^- and O^- were comparable. Visible photobleaching of the new e_t^-'s further decreased the O^- concentration by about 50%. Thus the O^-'s remaining after complete photobleaching of e_t^- in a γ-irradiated system are not "unreactive" toward detrapped e_t^-.

The effect of light intensity on the initial bleaching rate of e_t^- was measured at 77°K on samples irradiated to 1 Mrad. Reduction of the light intensity by sevenfold with a calibrated wire mesh caused a sevenfold reduction in the initial bleaching rate $(-d[e_t^-]/dt)$ of e_t^-. Even though >98% of the light is absorbed in the sample, this result shows that the photobleaching of e_t^- is a one-photon process.

2. Radiation Dose Dependence of Photobleaching. Figure 2 shows the dose dependence for the number of e_t^-'s lost during the first 5 sec of photobleaching at a fixed light intensity. Even at 0.08 Mrad the samples are sufficiently colored to absorb essentially all of the incident light, so the ordinate in Figure 2 is also a measure of the quantum efficiency for photobleaching e_t^-. Since the penetration of light falls off with increasing e_t^- concentration, the experiments approximate "complete bleaching" of successive thin layers. Thus the quantum efficiency for "complete bleaching" increases linearly with dose up to about 3 Mrad, and at higher doses the curve begins to bend over and approach a maximum.

The quantum efficiency for photobleaching e_t^- in a 0.08-Mrad sample has been determined in other work[7] to fall from 0.15 initially to less than 0.01 as the fraction of e_t^- bleached increases. The average value for complete bleaching at this dose is about 0.04. The present work shows that between 0.08 and 14 Mrad there is a 30-fold increase in the quantum efficiency for "complete bleaching," so the quantum efficiency approaches 1 at the higher dose.

The existence of photoconductivity in γ-irradiated alkaline ice[2] demonstrates that e_t^- is promoted to a mobile state by photobleaching. For e_t^- to be lost or

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Table I. Loss of O$^-$ during Complete Photobleaching of e_t^-

	A. Dose Dependence at 77°K					
Dose, Mrad	0.17	0.6	1.0	5.0	14.0	
Prebleaching: (O$^-$)/(e_t^-)	1.0	1.0	1.0	1.75	8.3	
After bleaching [amount of O$^-$ bleached/ amount of e_t^- bleached]	0.73	0.73	0.67	0.62	0.6 ± 0.2	
	B. Temperature Dependence at 1 Mrad					
Temp, °K	4	77	90	113	134	151
After bleaching [amount of O$^-$ bleached/ amount of e_t^- bleached]	0.71	0.67	0.66	0.61	0.59	0.65

bleached the mobile electron must not be retrapped to form e_t^-. Thus the net bleaching rate as given in Figure 2 will depend on how the mobile electron loss rate depends on dose. To evaluate this, let us consider how the yields of e_t^- and O$^-$ vary with dose.[6]

The initial yields of e_t^- and O$^-$ are equal. O$^-$ increases linearly to about 5 Mrad and slightly less than linearly to above 20 Mrad. e_t^- increases linearly to about 3 Mrad, reaches a broad maximum between 5 and 8 Mrad, and decreases to about 60% of the maximum by 14 Mrad. Figure 2 shows that the mobile electron loss rate changes with dose, as does the O$^-$ yield, and not as the e_t^- yield. So the net photobleaching rate for e_t^- depends largely on the O$^-$ concentration.

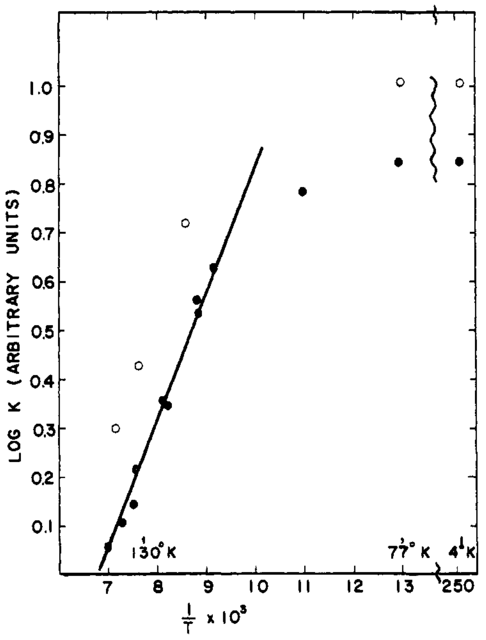

Figure 3. Log of the rate constant (k) for electron photobleaching in 10 M NaOH *vs.* T^{-1}: ●, e_t^- produced by γ irradiation to 1 Mrad; ○, e_t^- produced by photoionization of ferrocyanide ion. The initial e_t^- concentration is about 14 times greater in the γ-irradiated samples.

The *net* photobleaching process for e_t^- is not a simple, elementary reaction. Consequently, the kinetic analysis of e_t^- photobleaching can be confusing. However, all kinetic observations indicate that the net bleaching rate of e_t^- has approximately a first-order dependence on [O$^-$] and does not depend on [e_t^-]. At doses up to about 3 Mrad, in which range [e_t^-] = [O$^-$], log [e_t^-] *vs.* bleaching time gives a linear plot as in Figure 1. It would seem that first-order kinetics with respect to [e_t^-] are being observed. But such kinetics are only apparent and occur because [e_t^-] ≈ [O$^-$] during initial photobleaching. At doses above 5 Mrad, the concentration of e_t^- *vs.* bleaching time deviates from apparent first-order kinetics and approaches apparent zero-order kinetics. At 14 Mrad a plot of [e_t^-] *vs.* time is linear. This indicates zero-order kinetics with respect to [e_t^-] for e_t^- photobleaching. Again if we examine the O$^-$ concentration the situation simplifies. At 14 Mrad [O$^-$] decreases by only 10% when [e_t^-] decreases by 90%. So [e_t^-] decreases linearly wih time at high doses since [O$^-$] is nearly constant.

As shown in Figure 1, photobleaching of e_t^- also "bleaches" O$^-$. The fraction of O$^-$ left after e_t^- is completely bleached is about 0.3 at 0.17–1.5 Mrad, but the O$^-$ fraction increases to 0.6 at 5 Mrad and to 0.9 at 14 Mrad. At 1 Mrad, a plot of log [bleachable O$^-$] *vs.* time gives an apparent first-order rate constant which is the same as the apparent first-order rate constant obtained from a plot of log [e_t^-] *vs.* time.

Table I shows the effect of radiation dose on the fraction of bleached e_t^- that quantitatively corresponds to O$^-$ loss. These data were calculated on the basis that each O$^-$ is lost ("bleached") by one bleached e_t^-. The effect of dose on this fraction is small. There does seem to be a small decrease in this faction as the dose increases. However, at 14 Mrad the data are more uncertain owing to the small absolute change in [O$^-$] upon bleaching and to interference from a signal in the irradiated quartz sample tube. It is clear that the change in the fraction of bleached e_t^- lost to O$^-$ does not reflect the change in the [O$^-$]/[e_t] ratio with dose.

3. Temperature Dependence of Photobleaching. Figure 3 shows the results of a careful study of the temperature dependence of the electron photobleaching rate constant at 1 Mrad dose. The rate constants were determined from the initial slope of semilogarithmic plots like Figure 1. An Arrhenius temperature dependence is found between 140 and 108°K; however, the apparent activation energy of 1.2 kcal/mol is negative instead of positive. At lower temperatures the photobleaching rate shows a smaller temperature dependence, and between 4 and 77°K the photobleaching rate is independent of temperature.

Temperature studies were also undertaken on photobleaching of e_t^- in 10 M NaOH produced by photoionization of ferrocyanide ion. The initial trapped-electron yield in these photoionized samples corresponds to that produced by an ≈0.07-Mrad γ-ray dose. Although the concentration difference makes the bleaching rate constant somewhat greater in the photoionized samples, the temperature dependence is identical within experimental error with that for γ-irradiated samples.

Less comprehensive temperature-dependence results for doses from 0.2 to 14 Mrad are given in Figure 4. The observed Arrhenius temperature dependence between 100 to 140°K corresponds to a negative activation energy of 1.2 kcal/mol. There seems to be little if any effect of radiation dose on the observed activation energy.

Table I shows that the ratio of bleached O^- to bleached e_t^- varies little with temperature between 4 and 150°K. The partitioning of mobile electrons between reaction with O^- and other species is thus as unaffected by temperature as it is by dose.

Discussion

1. Nature of the Optical Transition of e_t^-. The temperature dependence of the photobleaching rate constant can show whether or not the excited state of the trapped electron lies below the bottom of the conduction band of the solids. For example, the photobleaching rate constant for a trapped electron (F center) in KCl shows a positive temperature dependence that corresponds to an Arrhenius activation energy of 1.3 kcal/mol.[8] This indicates that the exicted state of e_t^- in KCl is bound by 1.3 kcal/mol with respect to the conduction band.

For e_t^- in alkaline ice, Figure 3 shows that no temperature dependence for photobleaching exists between 4 and 77°K. Furthermore, the initial photobleaching quantum efficiency is probably close to one for the primary optical excitation. We conclude that the optical transition for light absorption by e_t^- occurs from a stable ground state directly to a continuum state in the conduction band or to a state which autoionizes[9] to the conduction band. Photoconductivity experiments on e_t^- in alkaline ice in our laboratory[2,3] give independent support to the energy-level structure deduced from the photobleaching data.

At temperatures between 100 and 140°K a temperature dependence for e_t^- photobleaching is observed, but it is *negative* and corresponds to an Arrhenius activation energy of -1.2 kcal/mol. This negative activation energy cannot relate to the primary photobleaching process itself. It is explained by the existence of shallow traps near the conduction band and re-formation of e_t^- by retrapping mobile electrons from the conduction band. The consequence of these shallow traps will be discussed in the next section. Their existence does not affect the energy level structure deduced above for e_t^-.

A variety of simplified theoretical calculations of the energy levels of trapped electrons in water and in ice have been reported.[10-16] The calculations differ principally in the type of model potential they invoke for the electron trap. Models which include long-range polarization potentials (dielectric continuum models) invariably give excited states that are strongly bound by 1-3 eV.[10] The relevant quantitative theoretical results have been discussed in connection with the photoconductivity evidence for direct optical excitation to the conduction band of e_t^- in alkaline ice.[3] When short-range interactions are included in the potential the excited state becomes less strongly bound.[15] If only short-range interactions are used in the potential, recent calculations show that the excited state is bound by only 0.1[16]-0.05[11] eV. Thus, short-range interactions certainly seem to make the dominant contribution to the binding of e_t^- in alkaline ice.

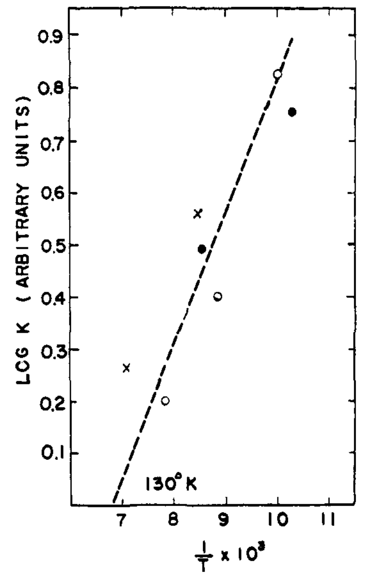

Figure 4. Log of the rate constant (k) for electron photobleaching in 10 M NaOH γ irradiated to different doses *vs.* T^{-1}: ●, 14 Mrad; ×, 5 Mrad; ○, 1.17 Mrad. The dotted line represents the slope observed at 1 Mrad from Figure 3. The relative rate constants are not comparable for different doses.

The data presented in this paper imply that the first excited state of e_t^- is not bound at all. The simplest case of a short-range potential consistent with this experimental result is a box whose potential depth is adjusted so that it has one bound state (ground state) and whose radius is adjusted so that the depth of this bound state below the continuum corresponds to the observed optical transition energy of 2.1 eV. A spherical box with radius of 5.3 Å satisfies these conditions.[17] Inclusion of specific molecular interactions, like charge-dipole interactions, as the short-range interactions would probably decrease this radius.

2. Reactions of Mobile Optically Detrapped Electrons. Observation of photoconductivity[2] shows that photobleaching of e_t^- produces mobile electrons, e_m^-. The reactions known for e_m^- in alkaline ice are (a) reaction with a trap to give e_t^-, (b) reaction with O^- resulting in loss of O^-, and (c) reaction with e_t^- to produce trapped dielectrons.[1] Figure 1 and Table I suggest that e_m^- reaction with O^- predominates in the photobleaching experiments. However, Figures 3 and 4 show that the e_t^- net loss by photobleaching has a negative temperature dependence. This implies that

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(8) Calculated from H. Pick, *Ann. Phys.*, **31**, 365 (1938); also see Figure 9.2 in J. J. Markham, "F-Centers in Alkali Halides," Academic Press, New York, N. Y., 1966.

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reaction 1 occurs, in which thermal detrapping from the

$$e_m^- + \text{shallow trap} \rightleftharpoons e_{st}^- \qquad (1)$$

shallow trap occurs at temperatures above 90°K. At 4 and 77°K reaction 1 occurs only in the forward direction and e_{st}^- apparently does not contribute to the epr spectrum of e_t^-. The lack of epr is rationalized below. Thus there is no temperature dependence for e_t^- photobleaching at 4 and 77°K. Above 77°K e_{st}^- is thermally detrapped and at least some of the e_m^- produced will be retrapped to form e_t^-. This back-reaction explains the negative temperature dependence. At higher temperatures more retrapping to form e_t^- occurs and decreases the net rate of e_t^- loss.

The fit to an Arrhenius plot in Figures 3 and 4 suggests that the average shallow trap depth is 1.2 kcal/mol (0.05 eV). The shallow-trap model implies that the photocurrent should show a positive temperature dependence corresponding to 0.05 eV. This has indeed been observed.[3] The photocurrent data also show that the density of shallow traps is radiation dose dependent and therefore suggest that the shallow trap is associated with O^-. If so, one might expect similar shallow traps to be associated with other holes in the alkaline ice matrix. Figure 3 shows the same negative temperature dependence for photobleaching of e_t^- from photoionization of ferrocyanide ion as for radiation-produced e_t^-. So, similar shallow traps appear to be associated with ferricyanide ion holes and O^- holes in the alkaline ice matrix. The epr spectrum of e_{st}^- could well be broadened beyond detection by spin-spin interaction with the holes.

Table I shows that the fraction of e_t^- that corresponds to O^- loss on prolonged optical bleaching is nearly independent of temperature and radiation dose. At 150°K dielectrons are not thermally stable.[18] Thus competition between e_t^- and O^- for e_m^- does not determine the fractions in Table I. Likewise the thermal instability of e_{st}^- precludes competition between O^- and shallow traps as the rationalization for Table I. The results seem to be tentatively explained by invoking two reactions of either e_m^- or e_{st}^- with O^- which have temperature independent rates. One reaction must lead to loss of both O^- and the electron species and the other reaction must lead to loss of only the electron species. The latter reaction may be regarded as analogous to the reaction of photobleached electrons with $TMPD^+$ in 3-methylpentane at 77°K which leads to loss of the electron optical spectrum but does not change the $TMPD^+$ optical spectrum.[19] The product of such a reaction is unknown in detail, but one possible model is a hole-electron charge pair.

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Metal-Ion Catalysis of Ethyl Oxalate Hydrolysis

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Abstract: The hydrolysis of ethyl oxalate, $^-O_2CCO_2Et(EtOx^-)$, is catalyzed by a variety of metal ions; the rate is given by the expression: rate = $k_3[EtOx^-][M^{2+}][OH^-]$. The values of k_3 (M^{-2} sec^{-1}) at 25° decrease with M^{2+} in the order Cu^{2+} (1.63×10^7) > Pb^{2+} (3.72×10^6) > Zn^{2+} (1.14×10^5) > Ni^{2+} (6.81×10^4) > Co^{2+} (4.15×10^4) > Mg^{2+} (1.02×10^3). The data have been interpreted in terms of a mechanism [$M^{2+} + EtOx^- \rightleftharpoons MEtOx^+$ (K_f); $MEtOx^+ + OH^- \rightarrow M(C_2O_4) + EtOH$ (k)], in which the ester, which is coordinated to the metal ion in a prior rapid equilibrium, is attacked by OH^-. The experimental k_3 is then kK_f. Using estimated values of K_f, it is found that k for different metal ions follows the same trend as given above. The rate of OH^- attack on the ester is 2×10^5 larger when the ester is coordinated to Cu^{2+} than when free in solution. Activation parameters for the reaction indicate that an increase in ΔS^* is primarily responsible for the catalytic effect of the metal ions.

In recent years metal-ion catalysis of ester hydrolysis[2-4] has been of increasing interest. Our own investigations[5] have concentrated on the kinetics and mechanisms of amino acid ester hydrolysis. In the present paper we report the results of studies on the metal-ion catalysis of the hydrolysis of ethyl oxalate, $^-O_2CCO_2Et(EtOx^-)$, to oxalate, $C_2O_4^{2-}(Ox^{2-})$, according to the equation

$$M^{2+} + EtOx^- + H_2O \longrightarrow M(Ox) + H^+ + EtOH \qquad (1)$$

A less detailed study of this reaction as catalyzed by Cu(II) and Ni(II) was reported previously.[6]

Experimental Section

Materials. Potassium ethyl oxalate, $KO_2CCO_2Et(KEtOx)$, was prepared by half hydrolyzing diethyl oxalate.[7] The analytical

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