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Oxidation of Ascorbic Acid by Aquopentabromoiridate(IV): An Assessment of the Effect of Aquation on Rates of Oxidation by Bromo- and Chloroiridium(IV) Complexes

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The preparation and spectral and electrochemical characterization of the aquopentabromoiridate(IV) anion are described as well as the results of a kinetic study of the oxidation of ascorbic acid (H_2A) by aquopentabromoiridate(IV) at 20.0 °C and $\mu = 1.0$ M ($LiClO_4-HClO_4$). This reaction is first order with respect to ascorbic acid concentration and first order with respect to Ir(IV) concentration. The acidity dependence is compatible with a rate law of the form $^{-1}/2 d[Ir(IV)]/dt = (k_a + k_b[H^+]^{-1})[H_2A][Ir(IV)]$, where k_a pertains to the reaction of undissociated ascorbic acid and k_b to reaction of the ascorbate monoanion. The effect of changing ionic strength provides additional evidence for a mechanism consistent with the proposed mechanism. Results from this investigation are compared to previously published results obtained with hexabromo-, hexachloro-, aquopentachloro-, and diaquotetrachloroiridium(IV) reactions with ascorbic acid to assess the effect of aquation on the Ir(IV) standard reduction potentials and the values of k_a and k_b . It is shown that replacing a halide ion with a water molecule increases the standard reduction potential of the Ir(IV) complex and also increases the rate of reaction via each pathway in a manner that yields linear free energy relationships for the bromo- and chloroiridium(IV) complexes, respectively.

Introduction

Oxidation of ascorbic acid by haloiridium(IV) species has been the subject of several previous studies.¹⁻⁵ In the most comprehensive of these studies, Pelizzetti, Mentasti, and Pramauro⁶ found the reactions to be first order with respect to oxidizing agent and first order with respect to ascorbic acid concentration. The acidity dependence was found to be compatible with a rate law of the form $^{-1}/2 d[Ir(IV)]/dt = (k_a + k_b[H^+]^{-1})[ascorbic\ acid][Ir(IV)]$, where k_a pertains to the reaction of undissociated ascorbic acid and k_b to the reaction of the ascorbate monoanion. The relative contributions of the dual pathways of these reactions were determined from the acidity dependence studies and were related to the standard reduction potentials and intrinsic parameters of the haloiridium(IV) oxidizing agents. The haloiridium(IV) complexes used by Pelizzetti et al. were hexabromo-, hexachloro-, aquopentachloro-, and diaquotetrachloroiridium(IV).

In this investigation, the kinetics of the oxidation of ascorbic acid by aquopentabromoiridate(IV) have been studied to further assess the effect of aquation on the Ir(IV) standard reduction potentials and the values of k_a and k_b . The existence of the aquopentabromoiridate(IV) and has been previously reported,⁶ but this paper presents the first report of a kinetic study of an electron-transfer reaction involving the aquopentabromoiridate(IV) anion.

Experimental Section

Reagents. During a previous study,⁵ it was noted that dark purple aqueous solutions of K_2IrBr_6 turned dark blue due to aquation of $IrBr_6^{2-}$ when kept at room temperature for extended periods of time and that the rate of aquation appeared to be light sensitive. It was therefore decided to attempt to prepare $IrBr_5H_2O^-$ from $IrBr_6^{2-}$ under conditions that would optimize the aquation process. K_2IrBr_6 was prepared by the method of Drury and DeKorte⁵ and was shown to be of high purity spectrochemically. However, attempts to use thermal and photolytic means of aquating $IrBr_6^{2-}$ were shown to yield a mixture of products. Subsequently, a 0.00010 M solution of K_2IrBr_6 in 1.0 M $HClO_4$ was prepared and electrolytically reduced in an ice bath at -1.3 V for 1.5 h. The dark purple $IrBr_6^{2-}$ solution turned light yellow on reduction to $IrBr_6^{3-}$. The $IrBr_6^{3-}$ solution was placed in a constant-temperature bath at 15 °C for 10 h, and the color changed to a darker yellow with the change from $IrBr_6^{3-}$ to $IrBr_5H_2O^{2-}$. The $IrBr_5H_2O^{2-}$ was oxidized electrolytically in an ice bath at +1.2 V for 1.5 h with a corresponding color change from yellow to dark blue. Potentiometric titration with $Fe(CN)_6^{4-}$ at 20 °C and $\mu = 1.0$ M $HClO_4$ was used to show there was only

one electroactive Ir(IV) species in solution and that the conversion of $IrBr_6^{2-}$ to $IrBr_5H_2O^-$ was quantitative. The spectral data of aqueous solutions of the resulting $IrBr_5H_2O^-$ agreed well with literature values:⁶ $\epsilon_{obsd} = 3.41 \times 10^3$ M⁻¹ cm⁻¹ at $\lambda_{max} = 587$ nm vs. $\epsilon = 3.32 \times 10^3$ M⁻¹ cm⁻¹; $\epsilon_{obsd} = 2.13 \times 10^3$ M⁻¹ cm⁻¹ at $\lambda_{max} = 675$ nm vs. $\epsilon = 2.00 \times 10^3$ M⁻¹ cm⁻¹.

L-Ascorbic acid (Eastman) was used as supplied. Double-vacuum-distilled, lead-free 70% $HClO_4$ (G. Frederick Smith) was used as the source of $HClO_4$. Anhydrous $LiClO_4$ (Baker) was used to maintain ionic strength. Triple-distilled water was used in the preparation of all solutions, the last two distillations being from alkaline permanganate solution.

Kinetic Measurements. The rates of the ascorbic acid-aquopentabromoiridate(IV) reactions were determined with a Dionex D110 stopped-flow spectrophotometer interfaced to a PDP 8/e laboratory computer. Freshly prepared solutions of ascorbic acid and $IrBr_5H_2O^-$ were used, and the concentrations of these solutions were calculated from the mass of ascorbic acid and K_2IrBr_6 used. The desired acidity and ionic strength were obtained by diluting 1.00 M $HClO_4$ solutions of the reactants with 1.00 M $LiClO_4$ or in the case of the ionic strength dependence with 1.00 M $LiClO_4$ and triply distilled water.

The reactions were followed for at least 3 half-lives by monitoring the disappearance of $IrBr_5H_2O^-$ at 587 nm. Absorbance vs. time data were collected and ensemble-averaged for three kinetic runs. The data for each set of runs were subject to on-line linear regression analyses of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ vs. time to obtain values of the pseudo-first-order rate constant, k_{obsd} , described by eq 1. Values of A_∞ , the final absor-

$$^{-1}/2 d[Ir(IV)]/dt = k_{obsd}[Ir(IV)] \quad (1)$$

bance, were obtained by computer averaging of 10 points in the range where there was no longer any appreciable change in absorbance whereas the value of A_0 , the initial absorbance reading, was selected after examining the absorbance vs. time curve for each set of runs.

Results

$Ir^{IV}Br_5H_2O^-/Ir^{III}Br_5H_2O^{2-}$ Reduction Potential. The value of the thermodynamic reduction potential, E° , for the $Ir^{IV}Br_5H_2O^-/Ir^{III}Br_5H_2O^{2-}$ half-reaction was determined from potentiometric titrations of $IrBr_5H_2O^-$ with $Fe(CN)_6^{4-}$ with a Sargent Welch autotitrator. A platinum wire was used as the working electrode, and a Photovolt calomel electrode containing saturated NaCl was used as a reference electrode; NaCl was used in place of KCl to prevent precipitating $KClO_4$. The potentiometric titrations showed only one electroactive Ir(IV) species to be present in solution and yielded an E° value of 0.970 ± 0.006 V vs. NHE when adjusted to conditions corresponding to unit activities. The following method was used to obtain the E value pertaining to unit activities. Starting with the general Nernst equation expression for the $Ir^{IV}Br_5H_2O^-/Ir^{III}Br_5H_2O^{2-}$ reduction half-reaction

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\gamma_{red}[red]}{\gamma_{ox}[ox]} \quad (2)$$

in which γ is used to represent activity coefficients, it was noted

- (1) Pshenitsyn, N. K.; Prokeffeva, I. V. *Chem. Abstr.* 1956, 50, 9215b.
- (2) Novoselov, R. I.; Muzykantova, Z. A. *Chem. Abstr.* 1971, 74, 25115n.
- (3) Mushran, S. P.; Agrawal, M. C.; Gupta, K. C. *Indian J. Chem.* 1972, 10, 642.
- (4) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* 1978, 17, 1181.
- (5) Drury, W. D.; DeKorte, J. M. *Inorg. Chem.* 1983, 22, 121.
- (6) Melvin, W. S.; Haim, A. *Inorg. Chem.* 1977, 8, 2016.

Table I. Acidity Dependence of the Second-Order Rate Constants for the Oxidation of Ascorbic Acid by $\text{IrBr}_5\text{H}_2\text{O}^-$ at 20.0 °C and $\mu = 1.0 \text{ M}$ ($\text{LiClO}_4\text{-HClO}_4$)

$[\text{H}^+]$, M	1.00	0.70	0.50	0.30	0.10
k_0 , $\text{M}^{-1} \text{s}^{-1}$	22.5 ± 0.1	28.1 ± 0.6	34.7 ± 0.5	55.9 ± 0.6	138 ± 1

Table II. Ionic Strength Dependence of Second-Order Rate Constants for the Oxidation of Ascorbic Acid by $\text{IrBr}_5\text{H}_2\text{O}^-$ at 20.0 °C and $[\text{H}^+] = 0.10 \text{ M}^a$

μ , M ($\text{LiClO}_4\text{-HClO}_4$)	0.10	0.20	0.30	0.40	0.50
k_0 , $\text{M}^{-1} \text{s}^{-1}$	109 ± 1	140 ± 2	114 ± 2	135 ± 6	139 ± 3

^a $[\text{H}_2\text{A}] = 1.39 \times 10^{-3} \text{ M}$ and $[\text{IrBr}_5\text{H}_2\text{O}^-] = 1.12 \times 10^{-4} \text{ M}$.

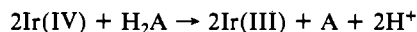
that the electrode potential E would equal E° when the ratio $[\text{red}]/[\text{ox}]$ equaled the ratio $\gamma_{\text{ox}}/\gamma_{\text{red}}$. Davies' equation⁷

$$\log \gamma = Z^2 \left(\frac{-0.512\mu^{1/2}}{1 + \mu^{1/2}} + 0.15\mu \right) \quad (3)$$

was then used to calculate $\gamma_{\text{IrBr}_5\text{H}_2\text{O}^-} = 0.783$ and $\gamma_{\text{IrBr}_4\text{H}_2\text{O}^{2-}} = 0.377$ at $\mu = 1.0$. Thus, $\gamma_{\text{ox}}/\gamma_{\text{red}} = 0.783/0.377 = 2.08$, and the point in the titration at which $[\text{red}]/[\text{ox}] = 2.08$ is 0.675 times the distance to the equivalence point. The average value of E at that point, $0.970 \pm 0.006 \text{ V}$ vs. NHE, was taken to be the value of E° . This value is in good agreement with a value of $\sim 0.96 \text{ V}$ vs. NHE that was obtained using cyclic voltammetry and 0.1 M HClO_4 media.⁸

Potentiometric titration data were used in a similar manner to obtain values of 0.844 ± 0.006 and $\sim 1.09 \text{ V}$ vs. NHE for the $\text{Ir}^{\text{IV}}\text{Br}_6^{2-}/\text{Ir}^{\text{III}}\text{Br}_6^{3-}$ and $\text{Ir}^{\text{IV}}\text{Br}_4(\text{H}_2\text{O})_2/\text{Ir}^{\text{III}}\text{Br}_4(\text{H}_2\text{O})_2$ reduction couples, respectively. The value of 0.844 V for $\text{Ir}^{\text{IV}}\text{Br}_6^{2-}/\text{Ir}^{\text{III}}\text{Br}_6^{3-}$ may be compared with a previously published value of 0.882 V⁴ and a value of $\sim 0.84 \text{ V}$ vs. NHE that was obtained by using cyclic voltammetry and 0.1 M HClO_4 media.⁸

Ascorbic Acid- $\text{IrBr}_5\text{H}_2\text{O}^-$ Reaction Stoichiometry. The stoichiometry of ascorbic acid-haloiridium(IV) reactions has previously been studied with use of a spectrophotometric titration technique.^{4,5} Increasing amounts of ascorbic acid were added to flasks containing equal concentrations of IrCl_6^{2-} or IrBr_6^{2-} . In each case, the following stoichiometric equation was obtained



where H_2A and A are used to represent ascorbic acid and dehydroascorbic acid, respectively. Hence, it was assumed that the stoichiometry of the ascorbic acid-aquopentabromoiridate(IV) reaction would be the same.

Kinetic Rate Law. At least a 10-fold equiv excess of ascorbic acid was present in each kinetic run. Under these conditions, excellent first-order plots were obtained. Thus, the reactions were shown to be first order with respect to $\text{IrBr}_5\text{H}_2\text{O}^-$. A linear variation of k_{obsd} with $[\text{ascorbic acid}]$ was obtained (Figure 1), showing that the reaction is also first order with respect to ascorbic acid.

Second-order rate constants (k_0) were obtained by dividing each pseudo-first-order rate constant by the appropriate ascorbic acid concentration. Second-order rate constants so obtained were found to increase with decreasing hydrogen ion concentration, and a plot of k_0 vs. $[\text{H}^+]^{-1}$ yielded a straight line with a nonzero intercept (Figure 2). Thus, the following form of the empirical rate law that has been proposed by Pellizzetti et al. for oxidation of ascorbic acid by other haloiridium(IV) species was confirmed:

$$-\frac{1}{2}d[\text{Ir(IV)}]/dt = k_0[\text{Ir(IV)}][\text{H}_2\text{A}] = (k_a + k_b[\text{H}^+]^{-1})[\text{Ir(IV)}][\text{H}_2\text{A}] \quad (4)$$

Values of k_0 obtained at 20.0 °C and $\mu = 1.0 \text{ M}$ ($\text{LiClO}_4\text{-HClO}_4$) are listed in Table I. A linear regression analysis of these data yields $k_a = (1.11 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ and $k_b = (1.27 \pm 0.01) \times 10^4 \text{ s}^{-1}$.

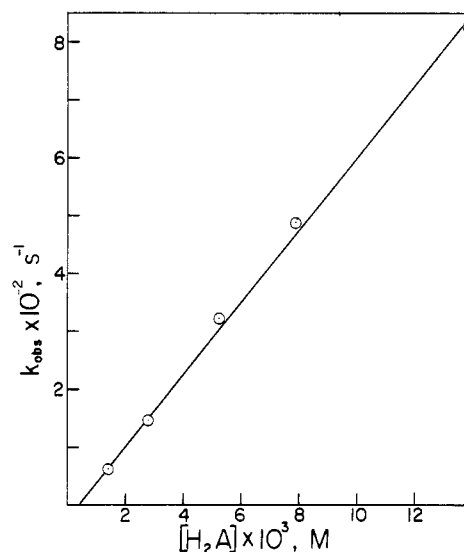


Figure 1. Ascorbic acid concentration dependence of the first-order rate constant for the disappearance of $\text{IrBr}_5\text{H}_2\text{O}^-$ ($1.12 \times 10^{-4} \text{ M}$) at 20.0 °C, $[\text{H}^+] = 1.0 \text{ M}$, and $\mu = 1.0 \text{ M}$ (HClO_4). A least-squares analysis yields the solid line and a value of 1.13 ± 0.04 for the order with respect to ascorbic acid.

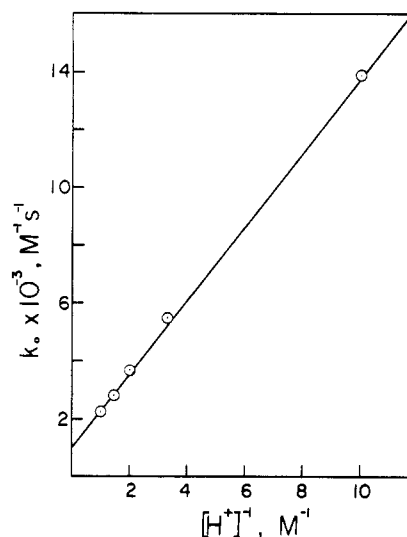


Figure 2. Acidity dependence of the second-order rate constants for the reaction of $\text{IrBr}_5\text{H}_2\text{O}^-$ with ascorbic acid at 20.0 °C and $\mu = 1.0 \text{ M}$ ($\text{LiClO}_4\text{-HClO}_4$). A least-squares analysis of all the data yields the solid line with a k_a intercept value of $(1.1 \pm 0.05) \times 10^4 \text{ M}^{-1} \text{s}^{-1}$ and a k_b slope value of $(1.27 \pm 0.01) \times 10^4 \text{ s}^{-1}$.

Effect of Reduced Form. Pellizzetti et al.⁴ examined the influence of IrCl_6^{3-} and IrBr_6^{3-} at concentrations up to 10 times that of IrCl_6^{2-} and IrBr_6^{2-} in oxidations of ascorbic acid and observed no effect on the calculated rate constants. Similar results have also been obtained for reactions of other oxidizing agents with ascorbic acid. Hence, such effects were not examined in this investigation.

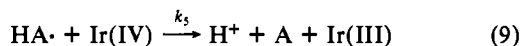
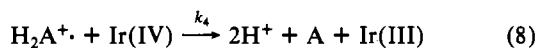
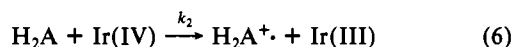
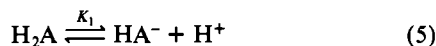
(7) Ramette, R. "Chemical Equilibrium and Analysis"; Addison-Wesley: Reading, MA, 1981; p 94.

(8) Nemeth, M. T.; Margerum, D. W., private communication.

Effect of Ionic Strength. Kinetic runs were carried out at 20.0 °C, $[\text{HClO}_4] = 0.10 \text{ M}$, and $[\text{LiClO}_4] = 0.00\text{--}0.40 \text{ M}$ to ascertain the effect of changing ionic strength on the second-order rate constant k_0 . Values of second-order rate constants obtained with this portion of the study of the ascorbic acid– $\text{IrBr}_5\text{H}_2\text{O}^-$ reaction are listed in Table II and are observed to increase with increasing ionic strength. This is to be expected on the basis of a contribution from the reaction of the ascorbate monoanion with the aquopentabromoiridate(IV) anion, as is suggested by the acidity dependence portion of this investigation.

Discussion

Reaction Mechanism. The presence of free radicals in the oxidation of ascorbic acid has previously been confirmed by ESR measurements and kinetic considerations.⁹ This evidence combined with the acidity and ionic strength dependencies and the lack of influence of the reduced forms of the iridium(IV) species is compatible with the reaction mechanism given by eq 5–9. With



the assumption of steady-state conditions for H_2A^+ and $\text{HA}\cdot$ and with ascorbic acid primarily in the form of H_2A , eq 5–9 yield the rate law (10) and comparison with eq 4 shows $k_a = k_2$ and $k_b = k_3K_1$. That is, data obtained in this investigation support the rate law and mechanism offered by Pelizzetti et al.⁴

$$-1/2 d[\text{Ir(IV)}]/dt = (k_2 + k_3K_1[\text{H}^+]^{-1})[\text{Ir(IV)}][\text{H}_2\text{A}] \quad (10)$$

Ionic Strength Dependence. The second-order rate constant obtained in this study (k_0) is related to the rate constant for the parallel pathways (k_2 and k_3), the ascorbic acid dissociation constant (K_1), and the molar hydrogen ion concentration by eq 11 and is observed to increase with increasing ionic strength (Table

$$k_0 = k_2 + k_3K_1[\text{H}^+]^{-1} \quad (11)$$

II). Assuming the rate constant for the reaction of undissociated ascorbic acid (k_2) is independent of ionic strength effects, owing to its lack of charge, permits changes in k_0 to be attributed to variations in k_3 and K_1 with ionic strength. The contribution due to change in k_3 can then be assessed with use of the intercept value of the acidity dependence study for k_2 and published data for the ionic strength dependence of the ascorbic acid dissociation constant.^{4,10}

The data are scattered, but the best straight line through a plot of $\log k_3$ vs. $\mu^{1/2}/(1 + \mu^{1/2})$ has a slope of ~ 1.2 (Figure 3). This value is approximately that predicted for reaction of HA^- with $\text{IrBr}_5\text{H}_2\text{O}^-$ and is further evidence for the two-path mechanistic interpretation of the data.

Marcus Theory Considerations. Rate constants for displacement of ligands from IrCl_6^{2-} are considerably less than the rate constants obtained in the present study.^{6,11} Assuming the rate constant for displacement of a ligand from $\text{IrBr}_5\text{H}_2\text{O}^-$ is comparable to those for IrCl_6^{2-} and IrBr_6^{2-} , it is likely that the ascorbic acid–aquopentabromoiridate(IV) reaction proceeds via an outer-sphere electron-transfer process. The Marcus theory¹² is quite useful for

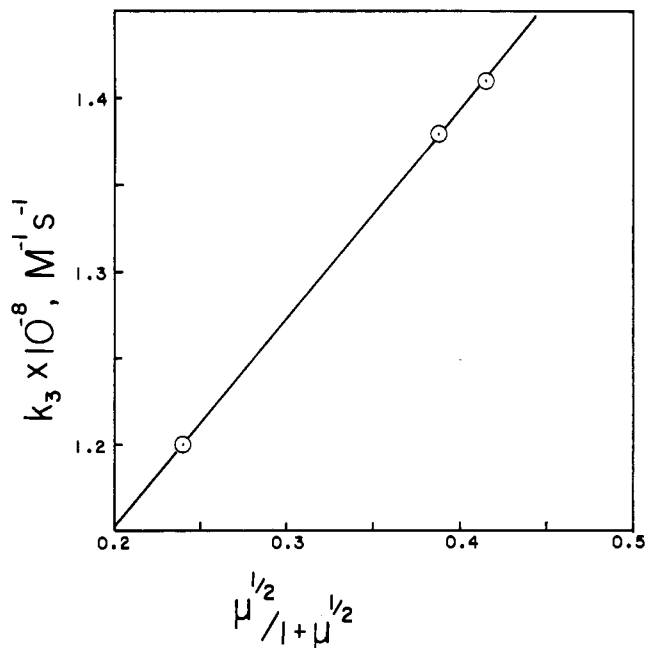


Figure 3. Ionic strength dependence of the acid-dependent pathway rate constant for the $\text{IrBr}_5\text{H}_2\text{O}^-$ –ascorbic acid reaction at 20.0 °C and $[\text{HClO}_4] = 0.10 \text{ M}$. See text for discussion.

predicting and interpreting rates of outer-sphere electron-transfer reactions in terms of pertinent reactivity parameters. According to this theory

$$k_{12} = Z \exp(-\Delta G^*_{12}/RT) \quad (12)$$

and

$$\Delta G^*_{12} = \omega_{12} + \lambda(1 + \Delta G^{\circ}_{12'}/\lambda)^2/4 \quad (13)$$

with k_{12} being the cross-reaction rate constant, Z being the bimolecular collision frequency for neutral reactants in the prevailing medium (taken to be $10^{11} \text{ M}^{-1} \text{ s}^{-1}$), ΔG^*_{12} being the free energy of activation for the cross reaction, ω_{12} being the Coulombic work required to bring the reactants together at the distance of separation in the activated complex, and λ , the intrinsic reorganization parameter, being as defined in

$$\lambda = 2(\Delta G^*_{11} - \omega_{11} + \Delta G^*_{22} - \omega_{22}) \quad (14)$$

where ΔG^*_{11} and ΔG^*_{22} are the free energies of activation for the self-exchange electron-transfer reactions of the reactants and ω_{11} and ω_{22} are the Coulombic work terms for the same reactions. The term $\Delta G^{\circ}_{12'}$ is further defined as

$$\Delta G^{\circ}_{12'} = \Delta G^{\circ}_{12} + \omega_{21} - \omega_{12}$$

where G°_{12} is the free energy change for the cross reaction under standard conditions and ω_{21} is the Coulombic work term for bringing products of the cross reaction together at the distance of separation in the activated complex.

The Coulombic work terms ω_{11} , ω_{22} , and ω_{21} can be calculated from eq 15, where Z_1 and Z_2 are the charges of the pertinent

$$\omega = (Z_1 Z_2 / Dr) \exp[-(8\pi e^2 N^2 \mu / 10^3 DRT)^{1/2} Dr^*] \quad (15)$$

reactants, D is the static dielectric constant of the solvent, r is the distance of separation between the reactants, r^* is the activated complex distance of separation, and the exponential coefficient is the Debye–Hückel term in which all symbols have their usual meaning.¹³ The terms ω_{12} and ω_{21} are quite small, owing to the size of the reactants and the ionic strength used in this study. Hence, the applicable form of eq 13 is

$$\Delta G^*_{12} = \lambda(1 + \Delta G^{\circ}_{12}/\lambda)^2/4 \quad (16)$$

(12) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891 and references therein.

(13) Reynolds, W. L.; Lumry, R. W. "Mechanisms of Electron Transfer"; Ronald Press, Co.: New York, 1966; p 123.

(9) (a) Yamazaki, I.; Mason, H. S.; Piette, L. H. *J. Biol. Chem.* **1960**, *235*, 2444. (b) Piette, L. H.; Yamazaki, I.; Mason, H. S. "Free Radicals in Biological Systems"; Bloise, M. S., Brown, H. W., Lemmon, R. M., Lindblom, R. O., Weissbluth, M., Eds.; Academic Press: New York, 1961; p 165. (c) Yamazaki, I.; Piette, L. H. *Biochim. Biophys. Acta* **1962**, *50*, 62. (d) Lagercrantz, C. *Acta Chem. Scand.* **1964**, *18*, 562. (e) Kirino, Y.; Kwan, T. *Chem. Pharm. Bull.* **1971**, *19*, 718. (f) Kirino, Y.; Kwan, T. *Chem. Pharm. Bull.* **1971**, *19*, 831.
 (10) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898.
 (11) Poulsen, I. A.; Garner, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 2032.

Equation 16 can be used to estimate values of ΔG°_{12} and E°_{12} for cross reactions involved in kinetic studies, provided values of λ can be ascertained. An estimate of λ for the reaction of undissociated ascorbic acid with IrBr_6^{2-} can be gleaned from data for the oxidation of 1,2-benzenediols by IrBr_6^{2-} . A reasonable value appears to be $\lambda = 19 \pm 2 \text{ kcal mol}^{-1}$.⁴ Assuming this is also a reasonable value of λ for reaction of undissociated ascorbic acid with $\text{IrBr}_5\text{H}_2\text{O}^-$ and using $k_2 = 1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ with $E^\circ(\text{IrBr}_5\text{H}_2\text{O}^-/\text{IrBr}_5\text{H}_2\text{O}^{2-}) = 0.970 \text{ V}$ yield the following $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A})$ values: $\lambda = 21 \text{ kcal mol}^{-1}$, $E^\circ = 1.28 \text{ V}$; $\lambda = 19 \text{ kcal mol}^{-1}$, $E^\circ = 1.30 \text{ V}$; $\lambda = 17 \text{ kcal mol}^{-1}$, $E^\circ = 1.33 \text{ V}$. Hence, a value of $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A}) = 1.30 \pm 0.03 \text{ V}$ is obtained from the kinetic data of this investigation. This value is in excellent agreement with a value based on $E^\circ(\text{A}^-/\text{A}^{2-})$ measured by pulse radiolysis¹⁴ and agrees well with $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A})$ values obtained from kinetic studies of IrBr_6^{2-} and IrCl_6^{2-} oxidations of ascorbic acid in $\text{LiClO}_4\text{-HClO}_4$ media.⁵

The value of the reduction potential for the $\text{HA}\cdot/\text{HA}^-$ couple is more difficult to estimate, owing to the greater uncertainty in λ values. Pelizzetti et al. have suggested λ values up to $4.5 \text{ kcal mol}^{-1}$ lower than those obtained with benzenediols should be considered.⁴ Using HA^- and $\text{IrBr}_5\text{H}_2\text{O}^-$ kinetic data from this investigation with λ values of Pelizzetti for the reaction of HA^- with IrBr_6^{2-} yields the following $E^\circ(\text{HA}\cdot/\text{HA}^-)$ values: $\lambda = 21 \text{ kcal mol}^{-1}$, $E^\circ = 0.84 \text{ V}$; $\lambda = 19 \text{ kcal mol}^{-1}$, $E^\circ = 0.89 \text{ V}$; $\lambda = 16.5 \text{ kcal mol}^{-1}$, $E^\circ = 0.95 \text{ V}$. The value of $0.89 \pm 0.06 \text{ V}$ that is obtained for $E^\circ(\text{HA}\cdot/\text{HA}^-)$ is in good agreement with the corresponding value of $0.93 \pm 0.06 \text{ V}$ obtained with IrCl_6^{2-} and IrBr_6^{2-} oxidations of the ascorbate ion.^{4,5} However, Creutz has noted that the λ values suggested by Pelizzetti et al. lead to an $E^\circ(\text{HA}\cdot/\text{HA}^-)$ value that is at least 150 mV more positive than that derived from thermodynamic data.¹⁵ This strongly suggests the λ values of Pelizzetti et al. are inappropriate but does not negate the observation that using equivalent λ values with IrBr_6^{2-} and $\text{IrBr}_5\text{H}_2\text{O}^-$ leads to virtually equivalent $E^\circ(\text{HA}\cdot/\text{HA}^-)$ values.^{4,5}

The $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A})$ and $E^\circ(\text{HA}\cdot/\text{HA}^-)$ agreement that is obtained by using equivalent λ values with IrBr_6^{2-} and $\text{IrBr}_5\text{H}_2\text{O}^-$ reactions with ascorbic acid can be interpreted to mean that the reactions proceed via the same mechanism and that the IrBr_6^{2-} and $\text{IrBr}_5\text{H}_2\text{O}^-$ self-exchange reactions proceed at very nearly the same rates. Having determined this, it is instructive to ascertain whether IrX_6^{2-} and $\text{IrX}_{6-n}(\text{H}_2\text{O})_n^{(2-n)-}$ reactions with ascorbic acid yield linear free energy relationships.

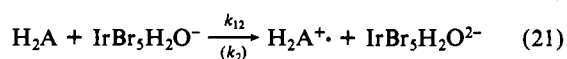
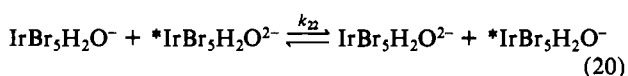
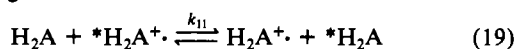
According to Marcus theory, the rate constant for an outer-sphere cross-exchange reaction (k_{12}) is directly related to the self-exchange rate constants for the reactants (k_{11} and k_{22}) and the equilibrium constant for the cross reaction (K_{12}) by eq 17 and eq 18 where Z is the bimolecular collision frequency for neutral

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (17)$$

$$\log f = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)] \quad (18)$$

reactants in the prevailing medium and is taken to be $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Equation 17 can be used to predict that $\ln(k_{12}/f^{1/2})$ should be linearly related to $\ln K_{12}$ for cross reactions in which the self-exchange rate constants for a series of redox couples are the same and that the slope of such a plot should be 0.50.

For H_2A reacting with $\text{IrBr}_5\text{H}_2\text{O}^-$, appropriate self- and cross-exchange reactions are



Since neither k_{11} nor k_{22} is known, an iterative process was used

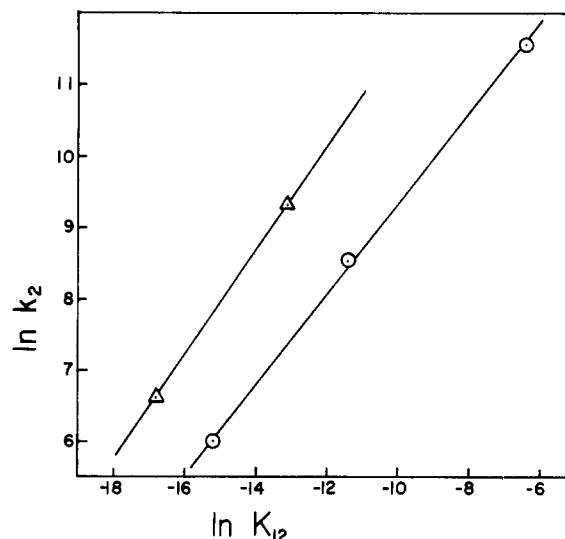


Figure 4. Relationship between the natural logarithms of the rate constants (k_2) for the reactions of undissociated ascorbic acid with (Δ) bromoiridium(IV) species and (\circ) chloroiridium(IV) species and the natural logarithms of the equilibrium constants for those reactions. The slope of the line for the bromoiridium species is 0.73 whereas that for the chloroiridium(IV) species is 0.63. See text for discussion.

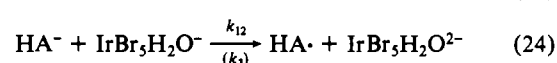
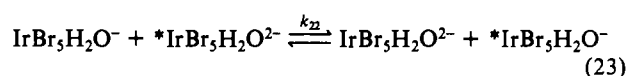
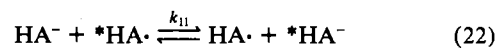
Table III. Comparison of Kinetic Data for the Oxidation of Undissociated Ascorbic Acid (k_2 , $\text{M}^{-1} \text{ s}^{-1}$) and the Ascorbate Monoanion (k_3 , s^{-1}) by Haloiridium(IV) Species at 20.0°C and $\mu = 1.0 \text{ M}$

oxidant	E° ^a	k_2	k_3
IrBr_6^{2-}	0.844 ^b	$(7.4 \pm 3.7) \times 10^2$ ^d	$(4.6 \pm 0.1) \times 10^7$ ^d
$\text{IrBr}_5\text{H}_2\text{O}^-$	0.970 ^b	$(11.1 \pm 0.4) \times 10^3$ ^b	$(13.7 \pm 0.1) \times 10^7$ ^b
IrCl_6^{2-}	0.957 ^c	ca. 4×10^2 ^c	2.8×10^7 ^c
$\text{IrCl}_5\text{H}_2\text{O}^-$	1.088 ^c	ca. 5×10^3 ^c	2.7×10^8 ^c
$\text{IrCl}_4(\text{H}_2\text{O})_2$	1.203 ^c	1.2×10^5 ^c	3.3×10^9 ^c

^a Standard reduction potential of oxidant in V. ^b This investigation. ^c Reference 4; $\mu = 1.0 \text{ M}$ ($\text{NaClO}_4\text{-HClO}_4$). ^d Reference 5; $\mu = 1.0 \text{ M}$ ($\text{LiClO}_4\text{-HClO}_4$).

to attempt to calculate the value of f . Initially f was set equal to 1, and a value for the product $k_{11}k_{22}$ was computed using eq 17. This estimate of $k_{11}k_{22}$ was used in eq 18 to calculate a new value of f . The new f value was introduced back into eq 17 to calculate a second value for $k_{11}k_{22}$, and the iterative process was continued to try to obtain constant values for f and $k_{11}k_{22}$. The same procedure was used to attempt to calculate values of f and $k_{11}k_{22}$ for reactions of H_2A with IrBr_6^{2-} , IrCl_6^{2-} , $\text{IrCl}_5\text{H}_2\text{O}^-$, and $\text{IrCl}_4(\text{H}_2\text{O})_2$. However, none of these attempts gave constant f and $k_{11}k_{22}$ values, so it was decided to resort to plotting $\ln k_{12}$ ($\ln k_2$) vs. $\ln K_{12}$ (Figure 4). The slope of the linear plot for oxidation of ascorbic acid by the bromoiridium(IV) species is 0.73 whereas that for the chloroiridium(IV) species is 0.63. These high slope values undoubtedly reflect the lack of f values and the uncertainty of the k_2 values that are obtained as intercept values of plots of second-order rate constants vs. $[\text{H}^+]^{-1}$ (Table III).¹⁶

For HA^- reacting with $\text{IrBr}_5\text{H}_2\text{O}^-$, appropriate self- and cross-exchange reactions are



(14) Pelizzetti, E.; Meisel, D.; Mulac, W. A.; Neta, P. *J. Am. Chem. Soc.* **1979**, *101*, 6954.

(15) Creutz, C. *Inorg. Chem.* **1981**, *20*, 4449.

(16) There is an additional uncertainty associated with the k_2 values for the chloroiridium(IV) species that is due to a Na^+ vs. Li^+ specific cation medium effect. There is also an effect on k_3 that is less significant. See ref 5.

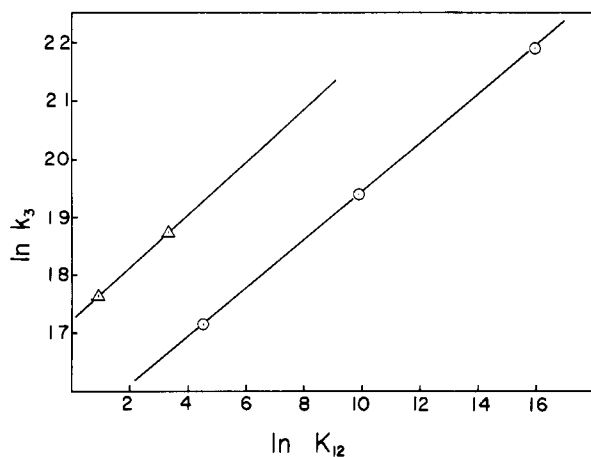


Figure 5. Relationship between the natural logarithms of the rate constants (k_3) for the reactions of the ascorbate monoanion with (Δ) bromoiridium(IV) species and (O) chloroiridium(IV) species and the natural logarithms of the equilibrium constants for those reactions. The slope of the line for the bromoiridium(IV) species is 0.47 whereas that for the chloroiridium(IV) species is 0.42.

and neither k_{11} nor k_{22} is known. The same iterative procedure was used and was found to yield constant values of f and $k_{11}k_{22}$ for reactions of HA^- with $IrBr_5H_2O^-$, $IrBr_6^{2-}$, and $IrCl_6^{2-}$ but not with $IrCl_5H_2O^-$ or $IrCl_4(H_2O)_2$.¹⁷ Thus, it was also decided to resort to plotting $\ln k_{12}$ ($\ln k_3$) vs. $\ln K_{12}$ for this pathway of the reaction (Figure 5). The slope of the linear plot for the reactions of the ascorbate monoanion with the bromoiridium(IV) species is 0.47 whereas that for the chloroiridium(IV) species is 0.42. These values are closer to 0.50, owing to the lesser importance of f when E° for the cross reactions is more nearly 0.0 V¹⁸ and to the greater certainty with which values of k_3 are known compared to values of k_2 (Table III).¹⁶

Aquation Effects. Replacing a halide ion with a water molecule increases the standard reduction potential of an Ir(IV) complex and increases the rate of reaction with ascorbic acid via both pathways (Table III). These data can be interpreted in terms of the relative electron density on the Ir(IV) center of the complex. The greater the degree of aquation, the lower the electron density on the Ir(IV) center and the higher the standard reduction potential for the Ir(IV) complex. This in turn causes a greater potential energy driving force for reactions and, according to Marcus theory for outer-sphere processes, results in faster elec-

tron-transfer reactions. This interpretation of the effect of aquation is supported by an examination of the relative standard reduction potentials and rates of reaction for the bromo complexes vs. the corresponding chloro complexes. The Ir(IV) complexes with bromide ions as ligands have standard reduction potentials that are ~ 0.11 V less than the corresponding complexes with chloride ions as ligands. Since Br^- is more polarizable than Cl^- , there is a greater electron density about the Ir(IV) center of the bromo complexes, leading to lower reduction potentials and slower rates of reaction than would be expected on the basis of a comparison of λ values.¹⁹ That is, the effect of changing from Br^- ligands to Cl^- ligands is the same as changing from Br^- to Cl^- to H_2O as a ligand, as both types of substitution lower the electron density on the Ir(IV) center.

Conclusions

The results of the first investigation of an electron-transfer reaction involving $IrBr_5H_2O^-$, the results of a kinetic study of the reaction of $IrBr_5H_2O^-$ with ascorbic acid, have been presented. It has been shown that using the Marcus theory and the same intrinsic reorganization parameters, λ values, as were used for the reaction of $IrBr_6^{2-}$ with ascorbic acid gives $E^\circ(H_2A^+/H_2A)$ and $E^\circ(HA^-/HA^-)$ values that are in excellent agreement with those obtained by Drury and DeKorte.⁵ Thus, it appears that both $IrBr_5H_2O^-$ and $IrBr_6^{2-}$ react with ascorbic acid via outer-sphere processes and that the self-exchange reactions for $IrBr_5H_2O^-$ and $IrBr_6^{2-}$ proceed at the same or very nearly the same rate.

The results from this investigation have been compared to previously published results obtained with hexabromo-, hexachloro-, aquopentachloro-, and diaquotetrachloroiridium(IV) reactions with ascorbic acid to assess the effect of aquation. It has been shown that replacing a halide ion with a water molecule increases the rate of reaction with ascorbic acid in a manner that yields linear free energy relationships for the bromo- and chloroiridium(IV) complexes, respectively. The relative magnitude of the reduction potential for each iridium(IV) complex can be interpreted in terms of the relative electron density on the iridium(IV) center; the lower the electron density, the higher the standard reduction potential and the faster the reaction with ascorbic acid. Thus, the greater the degree of aquation, the faster the reaction with ascorbic acid with either type of haloiridium(IV) complex.

Acknowledgment. This investigation was partially supported by a grant from the Northern Arizona University Organized Research Committee.

Registry No. $IrBr_5H_2O^-$, 62708-01-4; $IrBr_6^{2-}$, 16919-98-5; H_2A , 50-81-7.

(17) The f values that were obtained for the reactions of HA^- with $IrBr_5H_2O^-$, $IrBr_6^{2-}$, and $IrCl_6^{2-}$ were as follows: $IrBr_5H_2O^-$, $f = 1.32$ with $E^\circ_{12} = +0.08$ V; $IrBr_6^{2-}$, $f = 1.07$ with $E^\circ_{12} = -0.05$ V; $IrCl_6^{2-}$, $f = 1.32$ with $E^\circ_{12} = +0.07$ V. They were deemed to be inappropriate. See ref 18.

(18) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, MA, 1974; p 281.

(19) λ values for ascorbic acid–bromoiridium(IV) species reactions are 5 kcal mol^{-1} lower than λ values for ascorbic acid–chloroiridium(IV) species reactions; see ref 4. Thus, the observation that corresponding bromo- and chloroiridium(IV) species have reasonably comparable rates of reaction with ascorbic acid is due to the lower reduction potentials for the bromoiridium(IV) complexes.