

Specific-Cation Medium Effects in the Oxidation of Ascorbic Acid by Hexachloroiridate(IV) and Hexabromoiridate(IV)

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The kinetics of the oxidation of ascorbic acid (H_2A) by hexachloroiridate(IV) and hexabromoiridate(IV) have been investigated at 20.0 °C and $\mu = 1.0$ M ($LiClO_4-HClO_4$). These reactions are first order with respect to ascorbic acid concentration and first order with respect to iridium(IV) concentration. The acidity dependence is compatible with a rate law of the form $^{-1}/2d[Ir(IV)]/dt = (k_a + k_b[H^+]^{-1})[H_2A][Ir(IV)]$, where k_a pertains to the reaction of undissociated ascorbic acid and k_b to the reaction of the ascorbate monoanion. The effect of changing ionic strength provides additional evidence for a mechanism consistent with the proposed rate law. Results from this investigation are compared to previously published results obtained with $NaClO_4-HClO_4$ media. Excellent second-order rate constant agreement is obtained when the concentrations of $LiClO_4$ or $NaClO_4$ are ≤ 0.30 M. Higher concentrations of supporting electrolyte yield lower second-order rate constants when $LiClO_4-HClO_4$ media are used. The Li^+ vs. Na^+ specific-cation medium effect behavior affects the values of k_a and k_b , the appropriateness of reactivity parameter values used with Marcus theory interpretations of k_a and k_b , and the percentage reaction thought to occur via each pathway. The difference in the specific-cation behavior is correlated with changes in mean ionic activity coefficients for $HClO_4$, $LiClO_4$, and $NaClO_4$ as a function of concentration, and the superiority of Li^+ over Na^+ as a substitute for H^+ in aqueous perchlorate media is thereby reaffirmed. A new estimate of the reduction potential for the H_2A^+/H_2A couple is given.

Introduction

Oxidation of ascorbic acid by haloiridium(IV) species has been the subject of at least four previous studies.¹ In the most comprehensive study, Pelizzetti, Mentasti, and Pramauro^{1d} found these 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 $^{-1}/2d[Ir(IV)]/dt = (k_a + k_b[H^+]^{-1})[ascorbic\ acid][Ir(IV)]$, 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 data obtained with $[H^+] = 0.30-1.00$ M ($HClO_4$) and $\mu = 1.0$ M ($NaClO_4-HClO_4$) and were related to the reduction potentials and intrinsic parameters of the haloiridium(IV) oxidizing agents.² The relative contribution of the pathway involving undissociated ascorbic acid is small under conditions most favorable for such a pathway, though this is the highly predominant form of the acid: $\leq 4\%$ for $IrBr_6^{2-}$, ca. 13% for $IrCl_6^{2-}$, ca. 17% for $Ir(H_2O)Cl_5^-$, and 35% for $Ir(H_2O)_2Cl_4$ at 20 °C, $[H^+] = 1.0$ M, and $\mu = 1.0$ M ($NaClO_4-HClO_4$).

The apparently small contribution of the $[H^+]$ -independent pathway of these reactions raises a question as to the extent to which the value of k_a is influenced by a Na^+ vs. H^+ medium effect and how the values of k_a and k_b might change with use of $LiClO_4$ as a supporting electrolyte. The superiority of Li^+ over Na^+ as an ionic substitute for H^+ in aqueous perchlorate solutions has previously been demonstrated with use of electrochemical means,³ and the change from $NaClO_4-HClO_4$ media to $LiClO_4-HClO_4$ media has been reported to have a significant effect upon the $[H^+]$ dependence of the rates of several oxidation-reduction reactions involving Cr(II) and Co(III).⁴ In addition, data reported for the oxidation of

ascorbic acid by $Mo(CN)_8^{3-}$ with $\mu = 1.0$ M ($NaClO_4-HClO_4$) and $\mu = 1.0$ M ($LiClO_4-HClO_4$) media indicate the importance of the $[H^+]$ -independent term is greatly enhanced when $LiClO_4$ is used as the supporting electrolyte whereas Pelizzetti et al. claimed no significant differences were observed when $LiClO_4$ was substituted for $NaClO_4$.^{1d} Thus this investigation was conducted to fully examine the effect of Li^+ vs. Na^+ upon the rate of oxidation of ascorbic acid by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ to more clearly determine the validity and relative contributions of the dual pathways proposed by Pelizzetti et al. and the impact of Li^+ vs. Na^+ specific-cation medium effects upon reactivity parameters that are calculated for each pathway.

Experimental Section

$Na_2IrCl_6 \cdot 6H_2O$ (Aldrich) was dissolved in water, treated with $Cl_2(g)$, lyophilized, and stored in a desiccator. K_2IrBr_6 samples obtained from Platinum Chemicals were shown to be impure. Subsequently, K_2IrBr_6 was prepared from $Na_2IrCl_6 \cdot 6H_2O$, with use of a modification of the procedure reported by Melvin and Haim.⁵ $Na_2IrCl_6 \cdot 6H_2O$ (1.6 g) was treated with 10 mL of bromine and 30 mL of 40% hydrobromic acid, and the mixture was allowed to reflux for 14 h. The hydrobromic acid was partially neutralized by adding 50% potassium hydroxide until reaching $pH \approx 3$, and then 10 mL of a saturated potassium acetate solution was added. The solid obtained was separated by decantation and washed three times with 40-mL portions of carbon tetrachloride and then three times with 40-mL portions of absolute ethanol. The resulting solid was treated with 6 mL of bromine and 10 mL of 40% hydrobromic acid, and this mixture was also allowed to reflux for 15 h. Dark purple crystals were obtained with use of the decantation and washing procedure described above but were shown to be impure by spectrophotometric means. A solution of these crystals was lyophilized, and the purity substantially improved. However, a second 14-h refluxing with 6 mL of bromine and 10 mL of 40% hydrobromic acid followed by decanting, washing with carbon tetrachloride and then ethanol, and drying by suction filtration was required to obtain distinct, fine dark purple crystals. The spectral data of aqueous solutions of the resulting Ir(IV) species agreed with literature values: $\epsilon_{obsd} = 4075$ $M^{-1} cm^{-1}$ at $\lambda_{max} = 490$ nm vs. $\epsilon = 4075$ $M^{-1} cm^{-1}$ for $IrCl_6^{2-}$ and $\epsilon_{obsd} = 3960$ $M^{-1} cm^{-1}$ at $\lambda_{max} = 584$ nm vs. $\epsilon = 3800$ $M^{-1} cm^{-1}$ and $\epsilon = 3870$ $M^{-1} cm^{-1}$ for $IrBr_6^{2-}$.⁵⁻⁷

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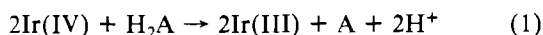
Table I. Acidity Dependence of Second-Order Rate Constants ($M^{-1} s^{-1}$) at 20.0 °C and $\mu = 1.0 M$ ($LiClO_4-HClO_4$)

	[H ⁺], M						
	1.0	0.90	0.70	0.50	0.30	0.20	0.10
$10^{-3}k_0(IrCl_6^{2-})$	2.82 ± 0.04	3.31 ± 0.05	4.0 ± 0.1	5.0 ± 0.1	7.6 ± 0.1		20.2 ± 0.3
$10^{-3}k_0(IrBr_6^{2-})$	5.17 ± 0.04		6.9 ± 0.3	9.7 ± 0.1	14.7 ± 0.3	21.1 ± 0.8	43.7 ± 0.8

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) and $LiClO_4$ prepared by Li_2CO_3 neutralization of $HClO_4$ and recrystallization 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.

Results

Reaction Stoichiometry. The stoichiometry of the ascorbic acid- $IrCl_6^{2-}$ reaction was verified with use of a spectrophotometric titration technique. Increasing amounts of ascorbic acid were added to flasks containing equal concentrations of $IrCl_6^{2-}$, and the absorbance of each resultant solution was measured at 490 nm; $[IrCl_6^{2-}]:[ascorbic\ acid]$ ratios ranging from 0.63:1.00 to 5.88:1.00 were used. A similar procedure was used with the ascorbic acid- $IrBr_6^{2-}$ reaction. In each case, the following stoichiometric equation was obtained:



where H_2A and A are used to represent ascorbic and dehydroascorbic acid, respectively.

Kinetic Measurements. The rates of the oxidation-reduction reactions were measured with a Dionex D110 stopped-flow spectrophotometer interfaced to a PDP 8/e laboratory computer. Freshly prepared solutions of ascorbic acid, hexachloroiridate(IV), and hexabromoiridate(IV) were used, and the concentrations of these solutions were calculated from the mass of substance used. The desired acidity and ionic strength were obtained by adding appropriate amounts of 70% $HClO_4$ and $LiClO_4$ (or $LiClO_4 \cdot 3H_2O$) to the ascorbic acid and $Ir(IV)$ solutions.

The reactions were followed for at least 3 half-lives by monitoring the disappearance of the oxidizing agents; $\lambda = 490$ nm was used with $IrCl_6^{2-}$ and $\lambda = 584$ nm with $IrBr_6^{2-}$. Absorbance vs. time data were collected and ensemble for three kinetic runs. The data for each ensemble set of runs were subject to off-line linear regression analyses of $\ln(A_t - A_\infty)$ vs. t to obtain values of the pseudo-first-order rate constant, k_{obsd} .

Kinetic Rate Law. At least a 10-fold equivalent 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 the $Ir(IV)$ species. A linear variation of k_{obsd} with $[ascorbic\ acid]$ was obtained in both cases (Figure 1), showing that the reactions are 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 plots of k_0 vs. $[H^+]^{-1}$ yielded straight lines with nonzero intercepts. Thus, the following form of the empirical rate law proposed by Pelizzetti et al. was confirmed:

$$-\frac{1}{2}d[Ir(IV)]/dt = k_0[Ir(IV)][H_2A] = (k_a + k_b[H^+]^{-1})[Ir(IV)][H_2A] \quad (2)$$

Values of k_0 obtained at 20.0 °C and $\mu = 1.0 M$ ($LiClO_4-HClO_4$) are listed in Table I. Linear regression analyses of these data yield values of $k_a = (1.1 \pm 0.1) \times 10^3 M^{-1} s^{-1}$ and $k_b = (1.91 \pm 0.02) \times 10^3 s^{-1}$ for $IrCl_6^{2-}$ and $k_a = (7.4 \pm 3.7) \times 10^2 M^{-1} s^{-1}$ and $k_b = (4.25 \pm 0.08) \times 10^3 s^{-1}$ for $IrBr_6^{2-}$. These values are compared to 20.0 °C and $\mu = 1.0 M$ ($Na-$

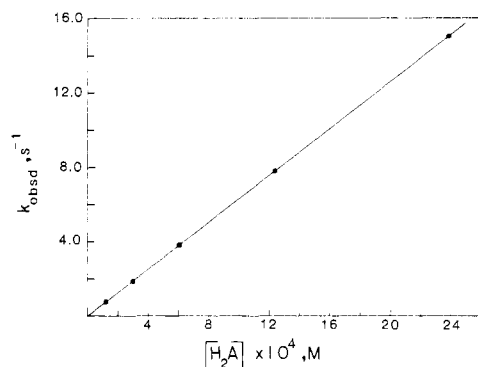


Figure 1. Ascorbic acid concentration dependence of the first-order rate constant for the disappearance of $IrCl_6^{2-}$ ($(1.0-1.3) \times 10^{-5} M$) at 20.0 °C, $[H^+] = 1.0 M$, and $\mu = 1.0 M$ ($HClO_4$). A least-squares analysis yields the solid line and a value of 1.03 ± 0.01 for the order with respect to ascorbic acid.

Table II. Specific-Cation Medium Dependence of Acid-Independent and Acid-Dependent Ascorbic Acid-Hexahaloiridium(IV) Reaction Rate Constants k_a and k_b at 20.0 °C and $\mu = 1.0 M$

oxidant	medium	$k_a, M^{-1} s^{-1}$	k_b, s^{-1}
$IrCl_6^{2-}$	$LiClO_4-HClO_4$	$(1.1 \pm 0.1) \times 10^3$	$(1.91 \pm 0.02) \times 10^3$
	$NaClO_4-HClO_4$	ca. 4×10^2 ^a	2.6×10^3 ^a
$IrBr_6^{2-}$	$LiClO_4-HClO_4$	$(7.4 \pm 3.7) \times 10^2$	$(4.25 \pm 0.08) \times 10^3$
	$NaClO_4-HClO_4$	$\leq 2 \times 10^2$ ^a	5.5×10^3 ^a

^a Reference 8.

ClO_4-HClO_4) values in Table II.^{1d,8}

Effect of Reduced Forms. Pelizzetti et al. examined the influence of $IrCl_6^{3-}$ and $IrBr_6^{3-}$ at concentrations up to 10 times that of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ and observed no effect upon the calculated rate constants. Similar results have also been obtained for other oxidizing agent reactions with ascorbic acid.^{1d,9} Hence, such effects were not examined in this investigation.

Effect of Ionic Strength. Stanbury et al.¹⁰ observed specific-cation medium effects when investigating the ionic strength dependence of the $I^- + IrBr_6^{2-}$ reaction in $NaClO_4-HClO_4$ and $LiClO_4-HClO_4$ media, and similar effects were observed with the acidity dependence portion of this investigation. Thus kinetic runs were carried out at 20.0 °C, $[HClO_4] = 0.10 M$, and $[LiClO_4] = 0.00-0.20 M$ to ascertain whether the ionic strength dependencies of ascorbic acid reactions with haloiridium(IV) species are also subject to specific-cation medium effects and whether these effects have any bearing on the support for the dual-pathway mechanism that is compatible with the acid dependence data.

- (8) Rate constants k_a quoted from the work of Pelizzetti et al. correspond to 20 °C k_2 values given in Table IV of ref 1d. Rate constants quoted as k_b values were obtained by multiplying 20 °C k_3 values from Table IV of ref 1d by 9.3×10^{-5} , the value given for the dissociation constant of ascorbic acid at 20 °C and $\mu = 1.0 M$ ($NaClO_4$) in ref 9a. (Least-squares analyses of the average acid-dependent second-order rate constant values given in Table II of ref 1d for $IrCl_6^{2-}$ yield $k_a = (5.25 \pm 1.06) \times 10^2 M^{-1} s^{-1}$ and $k_b = (2.50 \pm 0.04) \times 10^3 s^{-1}$ while those for $IrBr_6^{2-}$ yield $k_a = (2.7 \pm 1.4) \times 10^2 M^{-1} s^{-1}$ and $k_b = (5.34 \pm 0.06) \times 10^3 s^{-1}$.)
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Table III. Ionic Strength Dependence of Second-Order Rate Constants ($M^{-1} s^{-1}$) at 20.0 °C and $[H^+] = 0.10 M$

	$\mu, M (LiClO_4-HClO_4)$				
	0.10	0.15	0.20	0.25	0.30
$10^{-3}k_0 (IrCl_6^{2-})$	8.1 ± 0.3		11.2 ± 0.2		13.08 ± 0.03
$10^{-4}k_0 (IrBr_6^{2-})$	1.96 ± 0.03	2.42 ± 0.04	2.51 ± 0.03	2.70 ± 0.06	

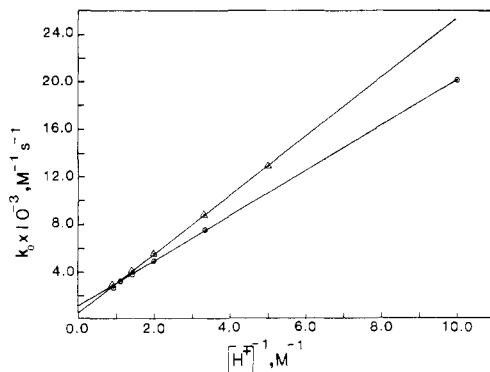
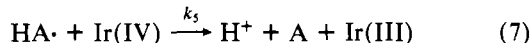
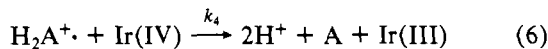
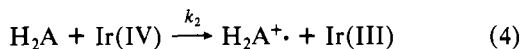
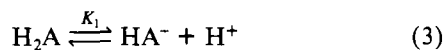


Figure 2. Acidity dependencies of the second-order rate constants for the reaction of $IrCl_6^{2-}$ with ascorbic acid in (Δ) $NaClO_4-HClO_4$ and (\circ) $LiClO_4-HClO_4$ media at 20.0 °C and $\mu = 1.0 M$. The solid lines were obtained from least-squares analyses. Average k_0 vs. $[H^+]$ values from ref 1d were used for $NaClO_4-HClO_4$ data while all k_0 vs. $[H^+]$ data were used for the $LiClO_4-HClO_4$ plot. Data for $IrBr_6^{2-}$ -ascorbic acid reactions yield analogous acid dependence plots. k_a and k_b intercept and slope values are given in Table II.

Values of second-order rate constants obtained for this portion of the investigation are listed in Table III and are observed to increase with increasing ionic strength, as would be expected for reaction of the ascorbate monoanion with IrX_6^{2-} species.

Discussion

Reaction Mechanism. The presence of free radicals in the oxidation of ascorbic acid has previously been confirmed by ESR measurements and kinetic considerations.¹¹ 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 3-7. With the assumption of steady-state con-



ditions for $H_2A^{\cdot+}$ and HA^{\cdot} and with ascorbic acid primarily in the form of H_2A , eq 3-7 yield rate law 8 and comparison

$$-\frac{1}{2}d[Ir(IV)]/dt = (k_2 + k_3K_1[H^+]^{-1})[Ir(IV)][H_2A] \quad (8)$$

with eq 2 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.

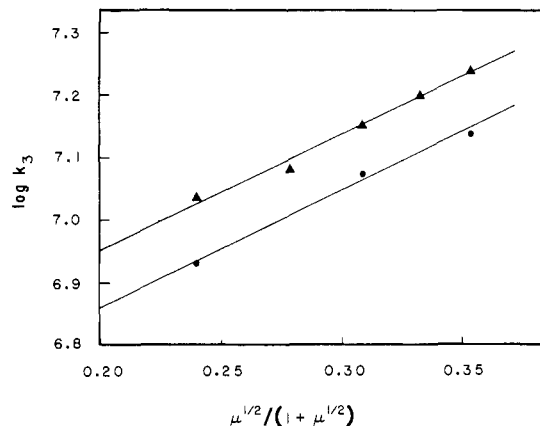


Figure 3. Ionic strength dependence of the acid-dependent pathway rate constant for ascorbic acid- $IrCl_6^{2-}$ reactions at 20.0 °C and $[HClO_4] = 0.10 M$: (\bullet) $LiClO_4-HClO_4$ media data; (\blacktriangle) $NaClO_4-HClO_4$ media data. See text for discussion.

Medium Effects upon Acid Dependence. Plots of second-order rate constants for reactions of ascorbic acid with halo-iridium(IV) species vs. $[H^+]^{-1}$ yield straight lines in both $NaClO_4-HClO_4$ and $LiClO_4-HClO_4$ media. However, values of the intercepts and slopes of these lines differ considerably (Figure 2), and the presumed relative contribution of each pathway is therefore a function of the perchlorate medium employed. With $IrCl_6^{2-}$, the percentage reaction occurring via reaction of undissociated ascorbic acid at 20.0 °C, $[H^+] = 1.0$ and $\mu = 1.0 M$, is calculated to be 13% by using data obtained in $NaClO_4-HClO_4$ media whereas data obtained with $LiClO_4-HClO_4$ media yield 36% for the same conditions. Similarly, the data at these conditions for $IrBr_6^{2-}$ yield $\leq 4\%$ reaction via undissociated ascorbic acid with $NaClO_4-HClO_4$ media studies and 14% with $LiClO_4-HClO_4$.

Medium Effects upon Ionic Strength Dependence. The second-order rate constant obtained in this study (k_0) is related to the rate constants for the parallel pathways (k_2 and k_3), the ascorbic acid dissociation constant (K_1), and the molar hydrogen ion concentration by eq 9 and is observed to increase

$$k_0 = k_2 + k_3K_1[H^+]^{-1} \quad (9)$$

with increasing ionic strength (Table 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.^{1d,9a}

Plot of $\log k_3$ vs. $\mu^{1/2}/(1 + \mu^{1/2})$ yield straight lines with the ascorbic acid- $IrCl_6^{2-}$ data (Figure 3). The slope of the straight line obtained for $LiClO_4-HClO_4$ media is 1.9 ± 0.1 , and the intercept corresponding to $\log k$ at infinite dilution is 6.49 ± 0.03 . The slope value is qualitatively as predicted for the reaction of HA^- with $IrCl_6^{2-}$ and is further evidence of the two-path mechanistic interpretation of the data. By way of contrast, data reported by Pelizzetti et al. for $NaClO_4-HClO_4$ media yield a slope of 1.85 ± 0.13 and a $\log k$ intercept value of 6.58 ± 0.04 . That is, almost parallel $\log k_3$ vs. $\mu^{1/2}/(1 + \mu^{1/2})$ lines are obtained with $NaClO_4-HClO_4$ and $LiCl-$

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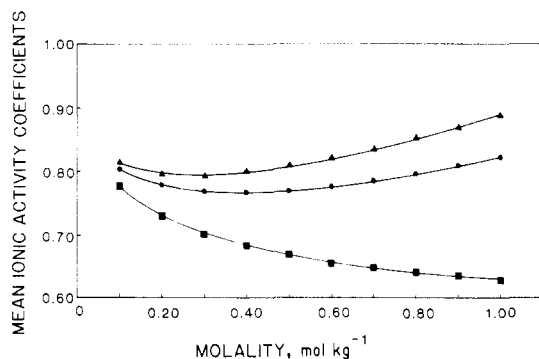


Figure 4. Experimentally determined aqueous solution mean ionic activity coefficients for (▲) LiClO₄, (●) HClO₄, and (■) NaClO₄ as a function of the molality of the perchlorate electrolyte at 25 °C. Values were taken from ref 15.

O₄-HClO₄ media data collected at 20.0 °C, and log *k*₃ values are approximately 0.1 lower with LiClO₄-HClO₄ media. This appears to be due to the difference in *k*₀ values obtained at μ = 0.1 M (HClO₄) and the difference in *k*₂ values obtained from intercepts of acid dependence studies in these two investigations.¹² Consequently, there is no obvious reason to postulate specific-cation medium effects upon the ionic strength dependence of ascorbic acid-IrCl₆²⁻ reaction rate constants.

Plots of log *k*₃ vs. μ^{1/2}/(1 + μ^{1/2}) fail to yield straight lines with ascorbic acid-IrBr₆²⁻ reaction data. The degree of curvature is more pronounced with NaClO₄-HClO₄ data than with LiClO₄-HClO₄ data, but marked deviation from ideal straight line behavior is observed with results from both media.

Activity Coefficient Correlations. The ability of Li⁺ or Na⁺ to mimic H⁺ in its electrostatic interactions with anionic reactants such as HA⁻ and IrCl₆²⁻ or IrBr₆²⁻ should be reflected in the values of activity coefficients for these cations and therefore in values of mean ionic activity coefficients for aqueous solutions of lithium perchlorate, sodium perchlorate, and perchloric acid. The limiting form of the Debye-Hückel expression implies these electrolytes have equal mean ionic activity coefficients at any given ionic strength while the extended Debye-Hückel expression for binary electrolytes

$$\log \gamma_{\pm} = A z_+ z_- \mu^{1/2} / (1 + a B \mu^{1/2}) \quad (10)$$

introduces a parameter that precludes equal values. The adjustable parameter *a* in eq 10 takes the distance of closest approach of ions into account and therefore corresponds to a rough measure of the effective sizes of the hydrated ions involved. This parameter has been estimated to be equal to 9 Å for H⁺, 6 Å for Li⁺, 4 Å for Na⁺, and 3 Å for ClO₄⁻, with mean ion *a* values yielding the best agreement with experimentally measured activity coefficients for binary electrolytes.^{13,14} Hence, theoretical activity coefficient considerations suggest the superiority of Li⁺ over Na⁺ as a substitute for H⁺ in aqueous perchlorate media, and this implication is further supported by experimentally obtained activity coefficient values (Figure 4).

Medium effects upon ionic strength dependence were shown to be negligible for oxidation of the ascorbate monoanion by hexachloroiridate(IV). This is best understood by noting that

the ionic strength studies of this investigation were conducted with constant perchloric acid concentration (0.10 M) and limited amounts of added lithium perchlorate (0.05–0.20 M) while Pelizzetti et al. made use of similar conditions in sodium perchlorate-perchloric acid media. Single-ion activity coefficients for ions of differing *a* values are predicted to be nearly equal at low ionic strengths,¹³ and experimentally determined mean ionic activity coefficients for lithium perchlorate and sodium perchlorate are similar under such conditions (Figure 4). Hence, the effect of substituting lithium perchlorate for sodium perchlorate should be negligible at low ionic strengths.

Second-order rate constants obtained with [HClO₄] = 1.00–0.70 M and [LiClO₄] = 0.00–0.30 M are in excellent agreement with sodium perchlorate-perchloric acid media values obtained by Pelizzetti et al. However, second-order rate constants determined at lower perchloric acid concentrations and higher concentrations of supporting electrolyte are appreciably lower for lithium perchlorate-perchloric acid media (Figure 2). The negligible effect of substituting lithium perchlorate or sodium perchlorate for perchloric acid at low concentrations of supporting electrolyte (≤0.30 M) can be attributed to similar mean ionic activity coefficients at those concentrations (Figure 4). The divergence of the second-order rate constants at higher concentrations of supporting electrolyte (>0.30 M) can be correlated with diverging mean ionic activity coefficients. Mean ionic activity coefficients for lithium perchlorate and perchloric acid pass through minima in the concentration range 0.20–0.50 M while that of sodium perchlorate decreases throughout 0.10–1.00 M (Figure 4). Thus lithium perchlorate should be vastly superior to sodium perchlorate as a substitute for perchloric acid whenever >0.30 M concentrations of supporting electrolyte are required. This investigation offers excellent agreement with published rate constants when medium effects are minimal and also presents activity coefficient considerations to suggest that more accurate values of the rate constants for the reaction of ascorbic acid and ascorbate monoanion with hexachloroiridate(IV) or hexabromoiridate(IV) are provided by studies conducted in lithium perchlorate-perchloric acid media.¹⁶

Marcus Theory Considerations. Rate constants for displacement of ligands from IrCl₆²⁻ and IrBr₆²⁻ are considerably less^{5,6a} than rate constants obtained in the present study; thus it is likely that the ascorbic acid-hexahaloiridium(IV) reactions proceed via outer-sphere electron-transfer processes. The Marcus theory¹⁷ is quite useful for predicting and interpreting rates of outer-sphere electron-transfer reactions in terms of pertinent reactivity parameters. According to this theory

$$k_{12} = Z \exp(-\Delta G^*_{12}/RT) \quad (11)$$

and

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

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 10¹¹ M⁻¹ s⁻¹), Δ*G*^{*}₁₂ being the free energy of activation for the cross reaction, ω₁₂ 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 eq 13,

$$\lambda = 2(\Delta G^*_{11} - \omega_{11} + \Delta G^*_{22} - \omega_{22}) \quad (13)$$

where Δ*G*^{*}₁₁ and Δ*G*^{*}₂₂ are the free energies of activation for the self-exchange electron-transfer reactions of the reactants

(12) $\log(k_0 - k_2) = \log[(9.2 \times 10^3) - (4 \times 10^3)] = 3.94$ with NaClO₄-HClO₄ data from Pelizzetti et al. while $\log(k_0 - k_2) = \log[(8.1 \times 10^3) - (1.1 \times 10^3)] = 3.85$ for this investigation.

(13) Butler, J. N. "Ionic Equilibrium"; Addison-Wesley: Reading, MA, 1964; pp 431–439.

(14) An *a* value of 3 Å is assumed when log *k* is plotted vs. μ^{1/2}/(1 + μ^{1/2}) for mixed-electrolyte media. Since data are also obtained beyond the concentration range for which Debye-Hückel expressions are applicable, only qualitative charge product agreement is to be expected.

(15) Robinson, R. A.; Stokes, R. A. "Electrolyte Solutions"; Academic Press: New York, 1955; pp 476, 477.

(16) The suppressed second-order rate constants obtained in LiClO₄-HClO₄ media affect both the slope and the intercept of a plot of *k*₀ vs. [H⁺]⁻¹ and therefore influence rate constants *k*_a and *k*_b pertaining to the reaction of ascorbic acid and ascorbate monoanion, though the former has no net charge. See Figure 2 and Table II.

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

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 ΔG°_{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} , ω_{12} , and ω_{21} can be calculated by using eq 14, where Z_1 and Z_2 are the charges

$$\omega = (Z_1 Z_2 / Dr) \exp[-(8\pi e^2 N^2 \mu / 10^3 DRT)^{1/2} Dr^*] \quad (14)$$

of the pertinent 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.¹⁸ 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.¹⁹ Hence, the applicable form of eq 12 is

$$\Delta G^\circ_{12} = \lambda(1 + \Delta G^\circ_{12}/\lambda)^2/4 \quad (15)$$

Equation 15 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 IrCl_6^{2-} (eq 4) can be gleaned from data for the oxidation of 1,2-benzenediols by IrCl_6^{2-} . Pelizzetti et al. found a λ value of 26 kcal mol⁻¹ to be compatible with kinetic data for these systems and subsequently used $\lambda = 26$ kcal mol⁻¹ with $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A}) = 1.35$ V and $\lambda = 24$ kcal mol⁻¹ with $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A}) = 1.40$ V to try to account for the rate constant pertaining to the reaction of H_2A with IrCl_6^{2-} .^{1d} The calculated rate constants (1.5×10^2 and 8.2×10 M⁻¹ s⁻¹) are lower than the experimental value (ca. 4×10^2 M⁻¹ s⁻¹) and much lower than the corresponding acid dependence intercept value obtained in this investigation (1.1×10^3 M⁻¹ s⁻¹). The λ values used by Pelizzetti et al. appear to be compatible with the IrCl_6^{2-} - IrCl_6^{3-} self-exchange rate constant and rate constants for self-exchange between other radicals and parent molecules.^{1d} However, the values of 1.35 and 1.40 V used for $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A})$ are based upon kinetic data for the oxidation of undissociated ascorbic acid by $\text{Fe}^{\text{III}}\text{L}_3$, where L represents 1,10-phenanthroline and six substituted 1,10-phenanthrolines.^{1d} The acid dependence portion of studies of these reactions was also conducted in NaClO_4 - HClO_4 media and is most likely the source of rate constants in error due to Li^+ vs. Na^+ specific-cation medium effects of the type reported in this paper. A more reliable estimate of the $\text{H}_2\text{A}^+/\text{H}_2\text{A}$ reduction potential is provided by using $k_2 = 1.1 \times 10^3$ M⁻¹ s⁻¹ (as obtained in this study), $E^\circ(\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}) = 0.957$ V, and several λ values

of appropriate magnitude with eq 11 and 15:^{1d} $\lambda = 26$ kcal mol⁻¹, $E^\circ = 1.28$ V; $\lambda = 24$, $E^\circ = 1.31$; $\lambda = 22$, $E^\circ = 1.34$. It can be seen that a value of 1.31 ± 0.03 V is suggested, and this is compatible with a value of 1.31 ± 0.02 V determined from H_2A - IrBr_6^{2-} kinetic data obtained in LiClO_4 - HClO_4 media. Using $k_2 = 7 \times 10^2$ M⁻¹ s⁻¹, $E^\circ(\text{IrBr}_6^{2-}/\text{IrBr}_6^{3-}) = 0.887$ V, and several λ values of appropriate magnitude^{1d} yields the following $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A})$ values: $\lambda = 21$ kcal mol⁻¹, $E^\circ = 1.29$ V; $\lambda = 19$, $E^\circ = 1.31$; $\lambda = 17$, $E^\circ = 1.33$. Hence, a value of $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A}) = 1.31 \pm 0.03$ V is obtained from the kinetic data of this investigation, and this is 0.05–0.10 V less than that estimated by Pelizzetti et al. and is in excellent agreement with $E^\circ(\text{H}_2\text{A}^+/\text{H}_2\text{A}) = 1.32 \pm 0.01$ V as obtained with $\mu = 1.0$ M (LiClO_4 - HClO_4) data for the reaction of ascorbic acid and $\text{Mo}(\text{CN})_8^{3-}$: $k_2 = 23$ M⁻¹ s⁻¹, $\lambda = 21$ and 19 kcal mol⁻¹.^{1d}

The value of the reduction potential for the HA^-/HA^- couple is more difficult to estimate, owing to greater uncertainty in λ values; Pelizzetti et al. have suggested λ values up to 4.5 kcal mol⁻¹ lower than those obtained with benzenediols should be considered.^{1d} Using HA^- - IrCl_6^{2-} kinetic data from this investigation yields the following $E^\circ(\text{HA}^-/\text{HA}^-)$ values: $\lambda = 26$ kcal mol⁻¹, $E^\circ = 0.81$ V; $\lambda = 24$, $E^\circ = 0.86$; $\lambda = 21.5$, $E^\circ = 0.92$. Using HA^- - IrBr_6^{2-} kinetic data from this investigation yields the following: $\lambda = 21$ kcal mol⁻¹, $E^\circ = 0.89$ V; $\lambda = 19$, $E^\circ = 0.93$; $\lambda = 16.5$, $E^\circ = 0.99$. These values may be compared to 0.88 ± 0.07 , 0.92 ± 0.06 , and 0.98 ± 0.05 kcal mol⁻¹, reported for corresponding λ values for 18 systems by Pelizzetti et al.^{1d} The agreement between the two investigations is better for this couple, since the slopes of the acid dependence plots are less subject to specific-cation medium effects than the intercepts (Table II). It would seem that λ values for HA^- - IrX_6^{2-} reactions should be at least 2 kcal mol⁻¹ less than those for benzenediol- IrX_6^{2-} reactions on the basis of the discussion by Pelizzetti et al. Thus a value of 0.93 ± 0.06 V for $E^\circ(\text{HA}^-/\text{HA}^-)$ is compatible with the results of both investigations.

Conclusions

The results of this investigation emphasize the importance of avoiding major medium changes while maintaining constant ionic strength. Mean ionic activity coefficients clearly suggest the superiority of Li^+ over Na^+ or any other cation as a substitute for H^+ in aqueous perchlorate media. Failure to use lithium perchlorate as a supporting electrolyte with acidity dependence kinetic studies involving perchloric acid yields results that are subject to specific-cation medium effects. It has been previously shown that such medium effects can mask the true acidity dependence of a reaction rate and therefore mask the actual mechanism by which reaction occurs.⁴ In this case, specific-cation medium effects were shown to substantially influence the percentage reaction thought to occur via each of two pathways and the estimate of the reduction potential for the $\text{H}_2\text{A}^+/\text{H}_2\text{A}$ couple.

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Registry No. H_2A , 50-81-7; IrCl_6^{2-} , 16918-91-5; IrBr_6^{2-} , 16919-98-5.

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

(19) The specific nature of the ionic medium surrounding the reactants plays a subtle but important role in affecting the rate of reaction as evidenced by activity coefficient correlations given in this paper. This implies a change in the cross-reaction work terms accompanies a change in supporting electrolyte, but the macroscopic quantity form of eq 14 does not lend itself to evaluating such a change. Nevertheless, in either $\mu = 1.0$ M media, the work terms for the cross reaction are likely to be small in comparison to the standard free energy change.