$$H_2O_2^+ \overset{K_a}{\rightleftharpoons} H^+ + HO_2\cdot; \quad Cl_2^- \overset{K_d}{\rightleftharpoons} Cl^- + Cl\cdot \tag{2}$$

$$HO_2\cdot + Cl\cdot \overset{k_3}{\rightarrow} O_2 + H^+ + Cl^- \tag{3}$$

Before proceeding further, a few comments on this mechanism are in order. Step 1 represents a simple electron transfer, as does its reverse, step 2. The reactions described by the constants K_a and K_d may only represent stationary states, rather than true equilibria, due to the rapidity with which radicals are normally consumed. Steps 2 and 3 can be represented by two sets of four reactions each; step 2, for example, would include the reaction $HO_2 + Cl_2^- \rightarrow HO_2^- + Cl_2$. The sequence shown is consistent with the observed rate law; inclusion of all reactions does not lead to consistency. Finally, we do not include chain-propagating steps between reactants and intermediates; for instance, $Cl_2^- + H_2O_2 \rightarrow 2Cl^- + H_2O_2^+$. If Cl_2 reacts relatively slowly with H_2O_2, then it is plausible that Cl_2^- will also be relatively slowly reduced. Thus, chain reactions are not observed because the radical-radical terminating steps are too fast at these concentrations. This reasoning depends upon the actual values of the steady-state concentrations, some of which may increase drastically in the presence of a catalyst.

The observed rate law is obtained by applying the steady-state assumption to $[H_2O_2^+]_t = [H_2O_2^+] + [HO_2]$ and $[Cl_2^-]_t = [Cl_2^-] + [Cl]$. Therefore

$$\frac{1}{k_{app}} = \frac{k_2[H^+][Cl^-]}{k_3k_1K_aK_d} + \frac{1}{k_1}$$

which is formally identical with the result obtained from the HOOCl mechanism. If, now, we assume that step 3 is diffusion controlled,[9] then $k_3 \approx 10^9\ M^{-1}\ sec^{-1}$. The product K_aK_d is approximately 10^{-5};[10] therefore, from the graphical analysis, $k_1 = k_a$ and $k_2 \approx 1.6 \times 10^{-5}k_3 \approx 2 \times 10^4\ M^{-1}\ sec^{-1}$.

Catalyzed Reaction. It has been shown that the manganese(III)-manganese(II) couple catalyzes the reaction between chlorine and hydrogen peroxide.[4] We believe, however, that the mechanism proposed is unacceptable and is based on inadequate data. The chief reasons for our objections to the proposed establishment of a rate law and mechanism are the following. Except for one experiment at [HCl] = 1.0 *M*, the study was restricted to [HCl] = 2.0 *M*, which is not adequate to establish the acidity dependence.[11] Moreover, as the inset in Figure 1 shows, failure of the simple rate law begins to show itself in this region, as Makower and Bray first pointed out (*vide* Figure 2 of ref 2a.) Previous work[12] has shown that at [HCl] = 2.0 *M* the predominant manganese(III) species is $MnCl^{2+}$. It is therefore hardly surprising that no evidence was found for a stoichiometrically important peroxomanganese(III) species. We know of no independent evidence to support the existence of manganese(II)-peroxo complexes in acidic, aqueous solution. Kinetic and thermodynamic considerations indicate that Cl· is a stoichiometrically insignificant species in this system.[8]

In view of the lack of adequate data for the catalytic reaction we do not propose a detailed mechanistic analysis. Nevertheless, it is known that manganese(III) reacts rapidly with hydrogen peroxide, generating $H_2O_2^+$ in a reversible rate-determining step.[7] If we neglect reverse steps of this and the uncatalyzed reaction on the grounds that the forward steps are much faster in the catalytic system, then the minimum number of steps for a radical mechanism consistent with catalysis by the manganese(III)-manganese(II) couple would be

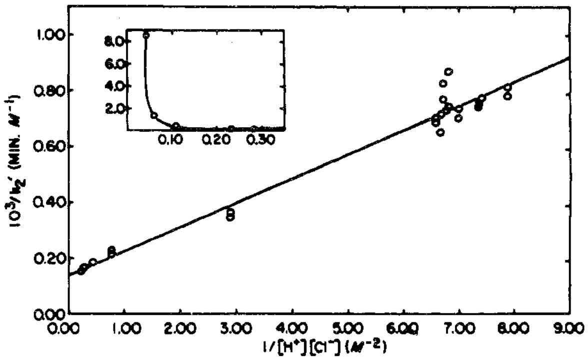

Figure 1. Makower and Bray's $1/k_2'$ ($=1/k_{app}[H^+][Cl^-]$) as a function of $1/[H^+][Cl^-]$. The line drawn through the data is computed by least-squares analysis: slope = $(0.868 \pm 0.031) \times 10^{-2}$ *M* min; intercept = $0.139 \pm 0.017\ M^{-1}$ min. The inset shows selected experimental points at [HCl] $\geq$ 1.88 *M*; least-squares line is continued with a hand-drawn curve to connect the last few points.

$$H_2O_2 + Cl_2 \rightarrow H_2O_2^+ + Cl_2^-$$
$$HO_2 + Cl \rightarrow H^+ + Cl^- + O_2$$
$$Mn(III) + H_2O_2 \rightarrow Mn^{2+} + H_2O_2^+$$
$$Mn(III) + H_2O_2^+ \rightarrow Mn^{2+} + 2H^+ + O_2$$
$$Mn^{2+} + Cl_2^- \rightarrow Mn(III) + 2Cl^-$$
$$Cl_2 + H_2O_2^+ \rightarrow Cl_2^- + 2H^+ + O_2$$
$$H_2O_2 + Cl_2^- \rightarrow H_2O_2 + 2Cl^-$$

The reported attrition of the catalyst would be accounted for by the fourth reaction. As previously mentioned, many of the reactions shown are actually composite. A detailed analysis of this complicated system must await a more complete experimental study.

Registry No. H_2O_2, 7722-84-1; Cl_2, 7782-50-5; Mn, 7439-96-5.

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Thermochemical Parameters of Aqueous Halogen Radicals

Sir:

The halogen radical species X·(aq) and X_2^-(aq) have often been mentioned as possible intermediates in halogen redox mechanisms.[1-5] Knowledge of the $\Delta H°$ and $\Delta S°$ values for

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reactions 1 and 2 is desirable in the interpretation of these mechanisms and is useful in general in studies which involve halogen radicals in aqueous solution. To this end, we have attempted to estimate the thermochemical parameters ΔH_f° and S° for $X_2^-(aq)$ and $X\cdot(aq)$ for chlorine, bromine, and iodine.

Estimates have been made[6,7] of the ΔG° of reactions such as (1) and (2). Recently, equilibrium constants (from radiolysis studies) have been reported for reaction 3, in the cases where X is bromine[8] and iodine.[9] The ΔH° of reaction 3 has been determined for iodine.[10]

$$X_2(aq) + {}^1/_2H_2(g) = X\cdot(aq) + X^-(aq) + H^+(aq) \qquad (1)$$

$$X_2(aq) + {}^1/_2H_2(g) = X_2^-(aq) + H^+(aq) \qquad (2)$$

$$X\cdot(aq) + X^-(aq) \overset{K}{\rightleftarrows} X_2^-(aq) \qquad (3)$$

In the present work, NBS values[11] were used for the thermodynamic parameters of standard-state and aqueous halogen molecules, halide and trihalide ions, noble gases, and gaseous halogen atoms. The recent values proposed by Cobble, *et al.*,[12] were used for $I^-(aq)$; $\Delta H_f^\circ = -13.55$ kcal mol^{-1} and $\bar{S}^\circ = 25.4$ cal mol^{-1} deg^{-1}. Pauling and van der Waals radii were employed for halide ions and halogen atoms, respectively. Tabulated values[13] were used for the internuclear distances in trihalide ions. The values due to Person[14] were taken as the internuclear distances in the X_2^- species. The "half-lengths" of the trihalide ions and dihalide radicals were evaluated as half the total internuclear lengths of the species, plus the Pauling radius of the corresponding halide ion. Molal volumes of the noble gases were taken from the tabulations of Hildebrand, *et al.*[15]

The entropies of the aqueous halogen atoms were estimated using eq 4,[16] where M is the atomic weight of the halogen,

$$\bar{S}^\circ = {}^3/_2R \ln M + S_{\text{int}} + 10 - 0.22V_m \qquad (4)$$

S_{int} is a term due to the electronic degeneracy of the $^2P_{3/2}$ halogen atom, and V_m is the molal volume of the corresponding noble gas. The ΔH_f° values for the aqueous halogen atoms were estimated by assuming that the enthalpy of solution of a given gaseous halogen atom is equal to that of the corresponding noble gas.[7,10] The thermochemical parameters for the aqueous halogen atoms are summarized in Table I.

Table I. Estimated Thermochemical Parameters of Aqueous Halogen Atoms

Species	V_m, cm^3/mol^a	ΔH_f°, kcal mol^{-1}	$\bar{S}^\circ$, cal mol^{-1} deg^{-1}
$Cl\cdot(aq)$	28.6	+26.2	16.5
$Br\cdot(aq)$	34.7	+23.0	17.6
$I\cdot(aq)$	43.0	+21.3	17.2

^{a} Reference 15.

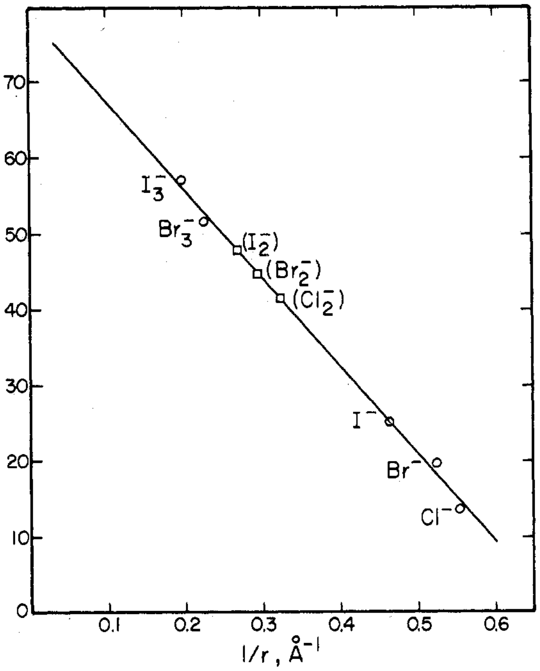

Figure 1. Entropy (25°) *vs.* reciprocal radius or half-length for aqueous halide and trihalide ions. The squares represent the intersection of the least-squares line with the half-lengths of the dihalide radicals.

The equilibrium constant of reaction 3 is 4.6×10^6 M^{-1} for bromine[8] and 8.4×10^4 M^{-1} for iodine;[9] thus, the ΔG° of reaction 3 is -9.08 kcal mol^{-1} for bromine and -6.71 kcal mol^{-1} for iodine. The ΔH° of eq 3 is -5.6 kcal mol^{-1} for iodine,[10] leading to a ΔS° value for the iodine reaction of +3.7 eu. Therefore, the ΔH_f° and S° values for $I_2^-(aq)$ can be calculated from NBS parameters and the values for $I\cdot(aq)$ in Table I.

In order to calculate ΔH_f° for $Br_2^-(aq)$ from the ΔG° of eq 3, it is necessary to estimate the standard entropy of $Br_2^-(aq)$. This is accomplished by plotting the known entropies of the aqueous halide and trihalide ions *vs.* the inverse of their radii or half-lengths, r. The plot which is obtained is shown in Figure 1. An estimate of the entropy of the radical ion may be obtained using this plot and the reciprocal half-length of X_2^-. This was done for Cl_2^-, Br_2^-, and I_2^-.

The thermochemical parameters of the X_2^- species are summarized in Table II. The estimated value of the entropy of $I_2^-(aq)$ compares well with the value calculated from the experimental ΔG° and ΔH° values for reaction 3, demonstrating the validity of the method of estimation. The last set of values for $I_2^-(aq)$ are used in subsequent calculations because there is one fewer estimate for this case. No equilibrium constant for reaction 3 has been reported in the case of chlorine, and therefore no estimate was made of the ΔH_f° value for $Cl_2^-(aq)$.

It is noted from Table II that there is a substantial difference in ΔH_f° between $Br_2^-(aq)$ and $I_2^-(aq)$. If the relationships among the ΔH_f° values of X_2, X_2^-, $X\cdot$, and X^- are studied using an appropriate Born-Haber cycle, it is evident that this difference is primarily due to the greater electron

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Table III. Thermodynamics of One-Electron Reductions of Halogens in Aqueous Solution

Reaction, halogen	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	$\Delta G_{298}°$, kcal mol^{-1}
1, Br·	−5.4	−9.5	−2.6
1, I·	+2.4	−5.8	+4.1
2, Br_2^-	−12.3	−2	−11.7
2, I_2^-	−3.2	−2	−2.6

affinity of bromine. The unfavorable $\Delta H°$ of solution of I_2(c) also contributes to this difference.

The thermochemical parameters for reactions 1 and 2 are given in Table III, for bromine and iodine. The $E°$ values for these reactions are entered in the reduction potential diagrams in eq 5 for bromine and eq 6 for iodine. These

$$\begin{tikzcd}
Br_2(aq) \arrow[r, dash, "0.51\ V"] \arrow[rr, dash, bend left, "1.087\ V"] \arrow[rd, dash, "0.11\ V"'] & Br_2^-(aq) \arrow[r, dash, "1.67\ V"] & Br^-(aq) \\
& Br\cdot(aq) \arrow[ru, dash, "2.06\ V"'] &
\end{tikzcd} \qquad (5)$$

$$\begin{tikzcd}
I_2(aq) \arrow[r, dash, "0.11\ V"] \arrow[rr, dash, bend left, "0.6197\ V"] \arrow[rd, dash, "-0.18\ V"'] & I_2^-(aq) \arrow[r, dash, "1.13\ V"] & I^-(aq) \\
& I\cdot(aq) \arrow[ru, dash, "1.42\ V"'] &
\end{tikzcd} \qquad (6)$$

potentials, along with the known $E°$ values for the two-electron reduction of X_2,[17,18] allow the unknown reduction potentials to be calculated. Agreement with previous estimates is satisfactory.[6,7,19]

Table II. Estimated Thermochemical Parameters of Aqueous Dihalide Radicals

Species	$\Delta H_f°$, kcal mol^{-1}	$S°$, cal mol^{-1} deg^{-1}
Cl_2^-(aq)		41.4
Br_2^-(aq)[a]	−12.9	44.7
I_2^-(aq)[b]	+2.6	47.8
I_2^-(aq)[c]	+2.2	46.3

[a] Reference 8 and present work (Table I and Figure 1). [b] Reference 9 and present work (Table I and Figure 1). [c] References 9 and 10 and present work (Table I).

Registry No. Cl, 22537-15-1; Br, 10097-32-2; I, 14362-44-8; Cl_2^-, 12595-89-0; Br_2^-, 12595-70-9; I_2^-, 12190-71-5.

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(19) Note Added in Proof. A recent measurement by J. Lilie [*J. Phys. Chem.*, 76, 1487 (1972)] is purported to give $E_{1/2}$ values for the reduction of I_2^- and Br_2^-. These voltages differ greatly (by −1.7 and −2.0 V) from our $E°$ calculations. However, Lilie's values cannot be close to the correct $E°$ values because if they were then X^- and X_2 would react spontaneously to give X_2^-.