The foregoing results clearly show that the paramagnetism exhibited by this complex is not a result of a high-spin–low-spin equilibrium but rather of a thermal decomposition, measurable at ambient temperature, to a cobalt(II) species. However, since the ligand field produced by the urea molecules must closely approach the crossover condition it is conceivable that a first step in the decomposition is a promotion of the metal from the singlet to the quintet state.

We have not been able to elucidate fully the nature of the mauve paramagnetic decomposition product. It is either insoluble in or decomposed by all common solvents. The elemental analyses differ little from those of the original compound. *Anal.* Found: C, 9.9; H, 3.4; N, 23.0; Cl, 15.6; Co, 7.9. The ir spectrum (Nujol mull) is also very similar to that of the starting material, differing only in that there are minor shifts of the major bands in the C=O stretch, NH_2 deformation region. However, that the decomposition product is a high-spin six-coordinate Co(II) species is evidenced by the magnetic properties in conjunction with the electronic spectrum of the solid. This consists of a well-defined maximum at 18,800 cm^{-1} (shoulder at 20,000 cm^{-1}) and a weaker maximum at 8700 cm^{-1}. These bands may be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ in O_h symmetry, the former being split by spin-orbit coupling.[4] A weak shoulder at ~13,500 cm^{-1} may be due to the two-electron $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition. The volatile decomposition product was shown by ir spectroscopy to be CO_2. No HNCO or NH_3, thermal dissociation products of uncomplexed urea at temperatures above the melting point,[5] were detected.

Registry No. Hexaureacobalt(III) perchlorate, 27894-63-9.

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 871.

(5) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1966, p 419.

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The Hydrogen Peroxide–Chlorine Reaction and Its Catalysis by Manganese(III)-Manganese(II)[1]

Sir:

Investigations of the kinetics of the reaction

$$H_2O_2 + Cl_2 \rightleftharpoons 2H^+ + 2Cl^- + O_2$$

by Makower and Bray[2] in the 1930's culminated in a definitive study of this system by Connick, published in 1947.[3] The rate law for the reaction was shown to consist of several terms which could be ascribed to interactions between H_2O_2 and OCl^-, HOCl, and Cl_2. At $[H^+][Cl^-] \geq 0.1\ M^2$, the reacting species are H_2O_2 and Cl_2. Catalysis of this reaction by the manganese(III)-manganese(II) couple has also been reported in hydrochloric acid solutions in this concentration range.[4]

The purpose of this letter is to suggest a mechanism for the uncatalyzed reaction which is consistent with the best available evidence concerning the nature of the reaction intermediates. The mechanism proposed also explains the main features of the Mn(III)-Mn(II) catalysis. A critique of the experimental evidence collected for the catalyzed reaction indicates, however, that a detailed analysis of the rate law is at present not justified for this system.

Uncatalyzed Reaction. At relatively low concentrations of hydrochloric acid ($10^{-4}\ M^2 \gtrsim [H^+][Cl^-] \gtrsim 10^{-7}\ M^2$) it seems clear that HOCl and OCl^- are the molecular species responsible for reaction with H_2O_2. (The actual value of the rate constant for reaction with OCl^- reported by Connick[3] may be incorrect as it is very difficult to vary the $[H^+]$ over a sufficiently wide range.) However, at sufficiently high acidity, the approximation $[Cl_2]_t = [Cl_2]$ ($[H_2O_2]_t = [H_2O_2]$ throughout) is valid (subscript "t" refers to total stoichiometric concentration) and the rate law is

$$-\frac{d[Cl_2]}{dt} = -\frac{d[H_2O_2]}{dt} = k_{app}[Cl_2][H_2O_2]$$

This result is consistent with the following mechanism, in which the intermediate HOOCl is assumed to be in a steady state.

$$H_2O_2 + Cl_2 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} HOOCl + H^+ + Cl^-$$

$$HOOCl \xrightarrow{k_c} O_2 + H^+ + Cl^-$$

The variation of k_{app} with $[H^+][Cl^-]$ is best demonstrated through the expression

$$\frac{1}{k_{app}} = \frac{k_b[H^+][Cl^-]}{k_c k_a} + \frac{1}{k_a}$$

Our treatment of Makower and Bray's data is shown in Figure 1. From the least-squares line drawn through the points, we obtain $k_a = (1.92 \pm 0.07) \times 10^2\ M^{-1}\ sec^{-1}$, $k_b/k_c = 1.60 \pm 0.15\ M^{-2}$ and $k_{app} = 25.9\ M^{-1}\ sec^{-1}$ at $[HCl] = 2.0\ M$, in excellent agreement with Connick's analysis of the same data.[3]

Numerous studies by conventional and radiolytic techniques have failed to provide further evidence for the existence of HOOCl. Indeed, it seems unlikely that it could be formed in a single step should it be shown to exist. The reverse reaction, formally third-order, also represents a composite process. On the other hand, ample evidence has accumulated for the existence of hydroperoxy and chlorine radicals. The predominant forms of these radicals in these solutions are $H_2O_2^+$ and Cl_2^-, respectively.[5,6] The $H_2O_2^+$ radical has been postulated as an intermediate in the oxidation of H_2O_2 by manganese(III);[7] Cl_2^- is even more well known, as it and other X_2^- species (X = halogen) have been invoked to explain a number of reaction mechanisms, including manganese(III) catalysis of the oxidation of oxalate by permanganate in HCl solutions.[8] A free radical mechanism, in its simplest form, is

$$H_2O_2 + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O_2^+ + Cl_2^- \tag{1}$$

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(1) The authors gratefully acknowledge partial support from a Research Corp. grant (G. D.) and from National Science Foundation Grant GP-4277 (K. K.).

(2) (a) B. Makower and W. C. Bray, *J. Amer. Chem. Soc.*, **55**, 4765 (1933); (b) B. Makower, *ibid.*, **56**, 1315 (1934).

(3) R. E. Connick, *J. Amer. Chem. Soc.*, **69**, 1509 (1947).

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(5) B. H. J. Bielski and J. M. Gebicki, *Advan. Radiat. Chem.*, **2**, 177 (1970).

(6) M. E. Langmuir and E. Hayon, *J. Phys. Chem.*, **71**, 3808 (1967).

(7) G. Davies, L. J. Kirschenbaum, and K. Kustin, *Inorg. Chem.*, **7**, 146 (1968).

(8) H. Taube, *J. Amer. Chem. Soc.*, **69**, 1418 (1947); **70**, 3928 (1948).

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

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

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

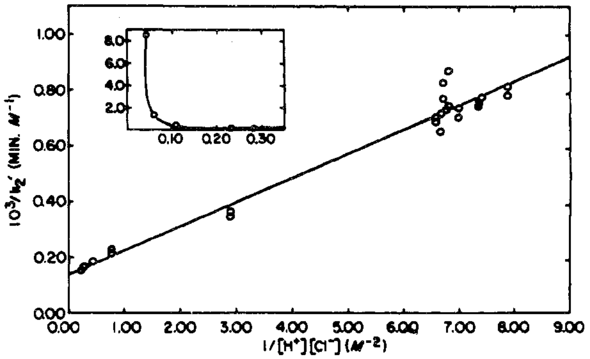

Figure 1. Makower and Bray's $1/k_2'$ ($=1/k_{app}[H^+][Cl^-]$) as a function of $1/[H^+][Cl^-]$. The line drawn through the data is computed by least-squares analysis: slope = $(0.868 \pm 0.031) \times 10^{-2}$ *M* min; intercept = $0.139 \pm 0.017\ M^{-1}$ min. The inset shows selected experimental points at [HCl] ≥ 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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(9) L. M. Dorfman and M. S. Matheson, *Progr. React. Kinet.*, **3**, 237 (1965).

(10) We have taken $K_a \approx 10^{-1}\ M$ (ref 5); $K_d \sim 10^{-4}\ M$: I. A. Taub, unpublished data.

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