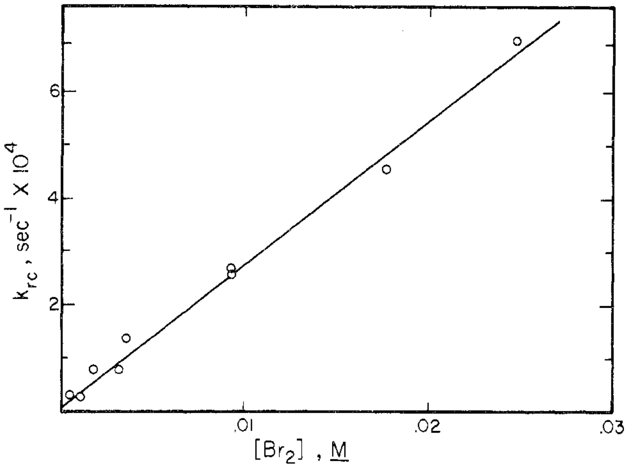

Figure 1. Dependence of k_{rc} upon the concentration of molecular bromine. The slope, k_a, is $(2.6 \pm 0.1) \times 10^{-2}\ M^{-1}\ sec^{-1}$. The intercept is $(2 \pm 1) \times 10^{-5}\ sec^{-1}$.

The previous study which most closely parallels the present work is the aforementioned aquation of $[Cr(H_2O)_5I]^{2+}$ in the presence of iodine.[8] Espenson observed inhibition by iodide ion of the acceleration (due to iodine) of the aquation reaction. The iodide inhibition requires a mechanism such as that shown in eq 1 and 2. This type of inhibition is not observed for bromide ion in the present study. It is therefore proposed that the acceleration of the ring closure of $[Co^{III}(EDTA)Br]^{2-}$ is due to electrophilic attack of bromine upon the coordinated bromide ion, as shown in eq 4 and 5. The Br_3^- ion does not take part in direct

$$[Co^{III}(EDTA)Br]^{2-} + Br_2 \xrightarrow{k_a} [Co^{III}EDTA]^- + Br_3^- \qquad (4)$$

$$Br_3^- \underset{}{\overset{\text{very rapid}}{\rightleftarrows}} Br_2 + Br^- \qquad (5)$$

electrophilic attack on $[Co^{III}(EDTA)Br]^{2-}$ as it is a poor electrophile for Br^- (*i.e.*, Br_4^{2-} is not a stable species).

The rate constant for the ring closure of $[Co^{III}(EDTA)OH_2]^-$ is 1.8×10^{-3} sec^{-1} at 25.0°.[11] This is faster than the fastest k_{rc} value in Table I, 7.7×10^{-4} sec^{-1}. Therefore it is not possible on the basis of the present data to rule out the aquated intermediate prior to the ring-closure step. In any case electrophilic attack by Br_2 accelerates the loss of coordinated Br^- from the cobalt(III) complex.

Registry No. $Co(EDTA)Br^{2-}$, 28135-63-6; Br_2, 7726-95-6.

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[11] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

Correspondence

Magnetic Properties of Hexaureacobalt(III) Perchlorate

Sir:

The preparation and properties of the title compound have recently been described by Bennett.[1] Of particular interest is the observation of a residual paramagnetism at 20°, corresponding to an effective magnetic moment of 0.95 BM considerably in excess of that expected for temperature-independent paramagnetism for low-spin Co(III) compounds.[2] It was suggested that since oxygen-coordinated urea occupies a lower spectrochemical position than water, the anomalously high paramagnetism might be due to a sufficiently close approach to the spin crossover for the high-spin state to be measurably populated at this temperature. Although spin isomerism is known for Co(II) complexes in both five- and six-coordinate geometries[3] there are as yet no known instances of the phenomenon in Co(III) compounds. We were therefore stimulated to investigate this compound further by magnetic susceptibility measurements by the Gouy method over a wide temperature range.

The complex was prepared as described by Bennett and characterized by elemental analyses. *Anal.* Calcd for $C_6H_{24}N_{12}O_{18}Cl_3Co$: C, 10.0; H, 3.2; N, 23.4; Cl, 14.8; Co, 8.2. Found: C, 9.9; H, 3.3; N, 23.0; Cl, 15.4; Co, 8.0. Ir and uv-visible spectra agreed with those previously reported.[1] All measurements were made in an atmosphere of oxygen-free nitrogen.

Samples from three separate preparations showed essentially the same behavior though differing initial room-temperature moments, within the range 1.2-1.8 BM, were found for them. The susceptibilities are independent of the applied field strength. All samples showed an increasing paramagnetism as a function of time. The rate of change, negligible below 293°K, increased with increase in temperature. At 373°K the moment changed from the initial value to a final value of *ca.* 5.0 BM (calculated on the molecular weight of the parent compound) within 20 hr; no further change occurred on maintaining this temperature for a further 48 hr. The increase in paramagnetism was accompanied by a small loss in weight (*ca.* 3.0% in all) of the sample. The rates of change of susceptibility and of weight paralleled each other closely and no further change in weight was observed after the magnetic properties became constant. Freshly prepared samples, and samples incompletely decomposed by maintaining them at *ca.* 353°K for a few hours, obeyed the Curie-Weiss law over the temperature range 90-273°K with a Weiss constant (negative temperature intercept) of 17-25°. Samples which had been completely aged by maintaining them at 373°K for more than 48 hr also showed Curie-Weiss behavior, this time over the complete temperature range studied, 90-373°K.

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[1] L. E. Bennett, *Inorg. Chem.*, 9, 1941 (1970).

[2] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 37 (1964).

[3] See E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, 22, 457 (1968); W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc. A*, 388 (1971); W. V. Dahlhoff and S. M. Nelson, *ibid.*, 2184 (1971).

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

$$H_2O_2 + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O_2^+ + Cl_2^- \qquad (1)$$

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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.).

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