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Catalytic Hydrolysis of Hydroxopentafluoroarsenate(V) Ion in the Presence of Iron(III) Complexes

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The release of fluoride in aqueous solutions of $[AsF_5(OH)]^-$ may be followed continuously by measuring the decrease in absorption of the 610-mμ band of an added indicator, the iron(III) complex of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Ferron). The measured rate constants for the hydrolysis are linearly dependent upon the concentration of indicator, indicating catalysis by it, and extrapolation to zero indicator concentration is necessary to obtain the rate constant for the uncatalyzed reaction. The hydrolysis is also catalyzed by iron(III) complexes with sulfosalicylate and with thiocyanate.

In a search of experimental methods suitable for continuously following the rate of fluoride release into aqueous solution, it was decided to examine the use of an internal indicator, since indicator methods have proved useful in the colorimetric analysis of trace amounts of fluoride.[1] The reaction examined was the hydrolysis of the hydroxypentafluoroarsenate(V) complex, $[AsF_5(OH)]^-$. This has been previously studied (although no *rate* data were collected) by Dess and Parry[2] and by Kolditz,[3] and the over-all hydrolysis reaction is

$$[AsF_5(OH)]^- + 3H_2O \rightleftharpoons H_2AsO_4^- + 5F^- + 5H^+$$

under conditions of low pH. The reaction is reversible, however, as the ion $[AsF_5(OH)]^-$ is formed in concentrated hydrofluoric acid solutions. The indicators used were the iron(III) complexes with Ferron (7-iodo-8-hydroxyquinoline-5-sulfonate), sulfosalicylate, and thiocyanate. Ferron was used for most of this work because of the greater regularity of the rate data obtained when it was used. These indicator complexes are colored initially and are decolorized by conversion to iron(III) fluoride complexes as fluoride is released by the hydrolysis of the arsenic complex.

Experimental Section

Materials.—The complex $K[AsF_5(OH)]$ was prepared and purified using previously published procedures.[2,3] *Anal.* Calcd for $K[AsF_5(OH)]$: As, 33.14. Found: As, 33.15. The complex was subjected to complete hydrolysis at pH 9.0 prior to use of the titrimetric procedure for arsenic.[2]

The indicator solution was prepared using the procedure of Urech[4] as a guide, but with an acetate–acetic acid buffer as the solvent. First 750 mg of Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) was dissolved in a buffer solution of the appropriate pH and made up to a volume of 500 ml. Gentle heating was occasionally necessary to effect complete solution. The iron(III) complex solution was then prepared by mixing 450 ml of this Ferron solution with 50 ml of a solution of 0.1 *M* $FeCl_3$, also in the appropriate acetate buffer but containing enough HCl to ensure that the iron(III) was completely dissolved. This was then diluted to a final volume of 1 l. using the appropriate acetate buffer solution. The absorbance of this solution must be checked daily as the indicator solution deteriorates on aging. The indicator used is essentially the 1:1 iron(III)–Ferron complex.

Method.—To begin a kinetic run, a given aliquot of the stock indicator solution described above is diluted to 100 ml with acetate buffer, and its absorbance is measured at 610 mμ with a spectrophotometer. A weighed amount of the solid complex (about 0.1 mmole for an indicator concentration of 2.5×10^{-4} *M* and about 0.2 mmole for indicator concentrations greater than this) is added to the solution and dissolved with shaking. All solutions are kept in a thermostat at 25° prior to and after mixing. The absorbance of the solution is determined at intervals up to the point where the reaction is about 50% complete, and then a final reading was obtained after 2 days. When following the hydrolysis of a fluoride at low pH, all solutions should be kept in polyethylene bottles (or the equivalent), and the spectrophotometer cells should be rinsed carefully after each use to preclude any possibility of fluoride attack on the glass.

Since the absorbance of these solutions does not follow Beer's law with respect to fluoride, it is necessary to prepare calibration curves using sodium fluoride to introduce known amounts of fluoride. This was done by taking aliquots of the stock indicator solution to which were added known amounts of 0.1 *M* sodium fluoride solution in acetate buffer, and the whole was then made up to a volume of 100 ml using the acetate buffer. The absorbance was determined after thorough mixing. By using various amounts of sodium fluoride, a plot of the absorbances *vs.* $[F^-]$ could be constructed. Calibration curves were constructed for all indicator complex concentrations at which rate data were collected.

The amount of complex used in the runs was such that, if all of the fluoride were released, it would be insufficient to decolorize the indicator solution completely.

Results and Discussion

The rate of release of fluoride was obtained by measurement of the absorbance at 610 mμ at various times and then reading the fluoride concentration from a standard graph of absorbance *vs.* $[F^-]$. A graph of this type is shown in Figure 1.

The hydrolytic reaction rate does have a pH dependence, and for this reason all studies were carried out in buffered solutions. The buffer capacity was sufficient to hold the pH of the solution effectively constant throughout the runs. Under these conditions, the rate data fit a first-order rate law which has the form

$$\frac{-d\{[AsF_5(OH)]^-\}}{dt} = k_{obsd}\{[AsF_5(OH)]^-\}$$

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[1] G. Charlot, "Colorimetric Determination of Elements," Elsevier Publishing Co., Amsterdam, 1964, pp 239–243.

[2] H. M. Dess and R. W. Parry, *J. Am. Chem. Soc.*, **79**, 1589 (1957).

[3] L. Kolditz and W. Röhnsch, *Z. Anorg. Allgem. Chem.*, **293**, 168 (1957).

[4] P. Urech, *Helv. Chim. Acta*, **25**, 1115 (1942).

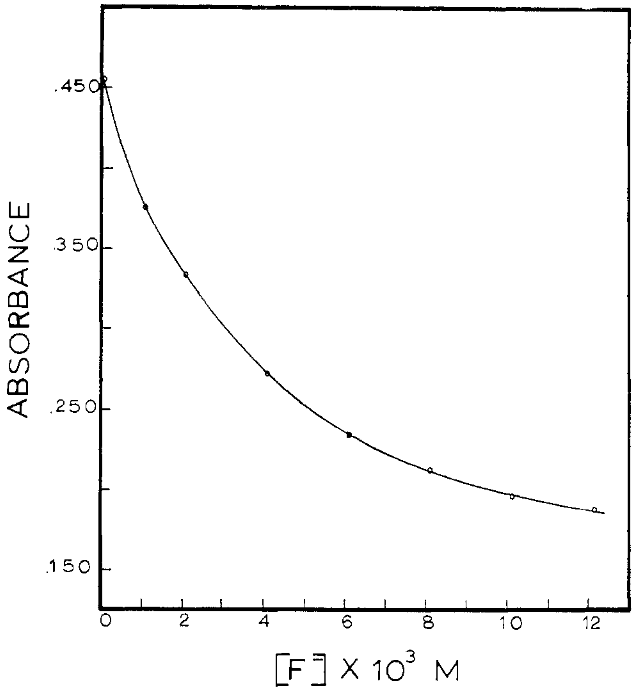

Figure 1.—A typical calibration curve. The solutions contain 15 ml of stock indicator solution and various amounts of standard sodium fluoride solution as described in the text. All solutions were then diluted to 100 ml with acetate buffer (pH 3.50). Final indicator concentration is 7.5×10^{-4} *M*.

The data were treated using a graphical method,[5] which gave a value of k_{obsd}. Data for a typical run are given in Table I. Rate constants for several values of pH are shown in Table II. The first-order dependence on the concentration of the arsenic complex is demonstrated by the data summarized in Table III.

TABLE I

DATA FOR A TYPICAL KINETIC RUN[a]

Time, min	Absorbance (610 mμ)	$10^3[F^-]$, *M*
0.00	0.453	0.00
1.35	0.422	0.36
3.70	0.399	0.63
6.43	0.374	1.04
9.50	0.357	1.40
13.61	0.336	1.90
20.20	0.316	2.44
25.82	0.294	3.10
34.98	0.280	3.62
42.26	0.263	4.40
52.89	0.255	4.80
63.43	0.245	5.20
∞	0.193	10.40

[a] The solution contains 15 ml of stock indicator solution diluted to 100 ml with acetate buffer (pH 3.50) and 0.2 mmole of $K[AsF_5(OH)]$. Final indicator concentration is 7.5×10^{-4} *M*.

TABLE II

FIRST-ORDER RATE CONSTANTS AT VARYING INDICATOR CONCENTRATIONS

10^4[Ind], *M*	pH 3.50	pH 3.75	pH 4.00
	10^4k_{obsd}, sec^{-1}		
2.5	1.30	1.27	1.39
5.0	1.67	1.48	1.70
7.5	2.13	1.75	2.00
10.0	2.58	2.01	2.37
12.5	2.93	2.29	2.65

TABLE III

EFFECT OF ARSENIC COMPLEX CONCENTRATION ON OBSERVED FIRST-ORDER RATE CONSTANT[a]

Initial $K[AsF_5(OH)]$ concn $\times 10^3$, *M*	10^4k_{obsd} sec^{-1}, for each of four runs
1.08	2.37, 2.25, 2.33, 2.37 (av 2.33)
2.15	2.22, 2.25, 2.23, 2.38 (av 2.30)
3.22	2.30, 2.30, 2.30, 2.18 (av 2.27)

[a] [Ind] = 12.5×10^{-4} *M;* indicator present is the 1:1 iron(III)–Ferron complex. pH 3.75; $T = 25°$.

When the k_{obsd} values, determined for a variety of indicator concentrations, are plotted against the gross indicator concentration of the iron(III) complex, a straight line is obtained, as is shown in Figure 2 for data at pH 3.5. From this, it is apparent that $k_{\text{obsd}} = k_{\text{uncat}} + k_{\text{cat}}[\text{Ind}]$, where k_{uncat} is the value of k_{obsd} when no indicator is present, k_{cat} is the value of the constant for the catalyzed reaction, and [Ind] is the gross concentration of the indicator complex. From an equation of this sort, one would expect that the rate constant would decrease as time passed and should soon reach a value characteristic of the uncatalyzed reaction. Data relevent to this point are the values of k_{obsd} after various numbers of half-lives are elapsed. For a run with an initial solution 1.08×10^{-3} *M* in $K[AsF_5(OH)]$, 12.5×10^{-4} *M* in Fe(III)–Ferron, and at pH 3.75, the following results were obtained

No. of half-lives elapsed	0.54	0.79	1.54	1.92
10^4k_{obsd}, sec^{-1}	2.42	2.27	2.22	2.20

Although a slow decrease is observed, this decrease is much less than anticipated. This is because the reaction is catalyzed (although to a slighter extent) by the complexes formed as the indicator is decolorized. A more exact expression for k_{obsd} would incorporate this as

$$k_{\text{obsd}} = k_{\text{uncat}} + \sum_j k_j[\text{Fe}^{\text{III}}\text{L}_x]_j$$

where the summation is over the *j* sorts of complexes of iron(III) which are present. Thus, while there are differences in the effectiveness of the various iron(III) species, this does not interfere with the extrapolation procedure used to obtain k_{uncat} from k_{obsd}.

For the data in Figure 2, $k_{\text{uncat}} = 8.9 \times 10^{-5}$ sec^{-1} and $k_{\text{cat}} = 1.64 \times 10^{-1}$ M^{-1} sec^{-1}. The values of these constants for several values of pH are shown in Table IV.

TABLE IV

UNCATALYZED AND CATALYTIC RATE CONSTANTS AT VARYING pH

pH	10^5k_{uncat}, sec^{-1}	$10k_{\text{cat}}$, M^{-1} sec^{-1}
3.50	8.9	1.64
3.75	9.4	1.08
4.00	10.5	1.35

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[5] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 12.

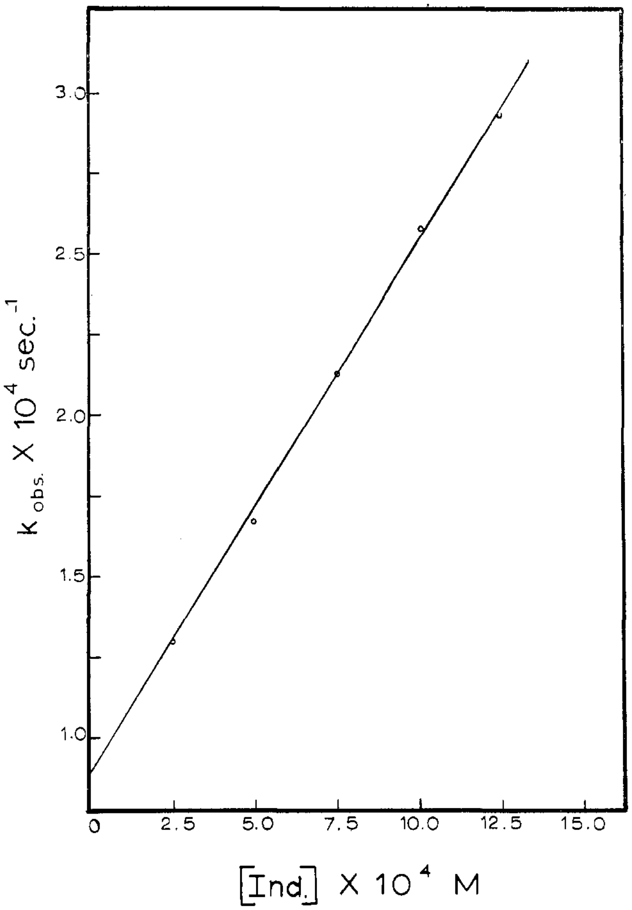

Figure 2.—A plot of k_{obsd} *vs.* the indicator complex concentration. The indicator complex is the 1:1 complex of 7-iodo-8-hydroxyquinoline-5-sulfonate and iron(III). The initial concentrations of $[AsF_6(OH)]^-$ were 1.08×10^{-3} *M* for an indicator concentration of 2.5×10^{-4} *M* and 2.15×10^{-3} *M* for all other indicator concentrations.

These results show that the iron(III) complex has a very profound catalytic effect on the hydrolysis of the As–F bond. In a solution in which the mole ratio of iron(III) complex to $[AsF_5(OH)]^-$ is 0.125, the catalytic reaction accounts for about 30% of the total reaction (at pH 3.50). This is especially striking when it is noted that the reaction is not subject to proton–acid catalysis in the pH range examined and that only a very small fraction of the indicator is involved in a catalytic intermediate at any one time. As can be seen, k_{uncat} decreases steadily as the pH drops. The variation in k_{cat}, shown in Table IV, is irregular and may be tentatively attributed to a variation in the hydrolytic reactions of the iron(III) over this pH range.

Studies with the iron(III) complexes of sulfosalicylic acid and thiocyanate showed a similar but much more pronounced catalysis of the hydrolysis of the $[AsF_5(OH)]^-$ ion. In both cases the kinetic behavior is more complex than that found for the Ferron system. Some measurements of the half-life of the arsenic complex in these systems are compared in Table V.

TABLE V

HALF-LIVES FOR THE HYDROLYSIS OF $[AsF_5(OH)]^-$ IN THE PRESENCE OF VARIOUS IRON(III) COMPLEXES

Iron(III)–Thiocyanate Indicator

$10^3[Fe^{3+}]$, *M*	$[Fe^{3+}]/[SCN^-]$	pH	$t_{1/2}$, sec
3.8	1:1	2.75	110
2.9	1:1	2.75	115
4.0	1:4	2.75	203
4.0	1:6	2.75	229

Iron(III)–Sulfosalicylate Indicator

$10^4[Fe^{3+}]$, *M*	$[Fe^{3+}]/[sulfosalicylate]$	pH	$t_{1/2}$, sec
4.0	1:2	3.40	4846
8.0	1:2	3.40	5172

Iron(III)–Ferron Indicator

$10^4[Fe^{3+}]$, *M*	$[Fe^{3+}]/[Ferron]$	pH	$t_{1/2}$, sec
2.5	1:1	3.50	5331
7.5	1:1	3.50	3254
12.5	1:1	3.50	2365
2.5	1:1	4.00	4986
7.5	1:1	4.00	3465
12.5	1:1	4.00	2615

The practical usefulness of the Fe(III)–SCN⁻ indicator system is limited by the fact that its catalytic efficiency is so great that the uncatalyzed rate (which is the desired datum) is only a small proportion of the total rate. This system also cannot be varied over a wide range of concentrations and still yield extinction coefficient ranges suitable for kinetic studies. While the iron(III)–sulfosalicylate indicator was free from these restrictions, it was found that it did undergo a slow reaction with arsenic acid, one of the products of the reaction, and this tended to introduce undesirable variations in the data. None of the products of the hydrolysis reaction was found to affect the iron(III)–Ferron indicator in this manner.

It is very probable that the phenomenon found here is one of reasonable generality and is analogous to the catalysis of the hydrolysis of Co–Cl bonds by Hg^{2+} and similar species.[6] There is reason to believe that the general principles governing the occurrence of the catalysis are determined by the relative donor properties of the halide and the acceptor specificity of the metal ions as outlined by Ahrland, Chatt, and Davies.[7] Thus it would be expected that other acceptors which can form stable complexes with fluoride will also be capable of furnishing catalytic routes for the hydrolysis of fluorides.

A reasonable mechanism for such a process is one in which the fluoride of the As–F bond becomes temporarily (and perhaps weakly) coordinated to the iron(III), using one of the coordination positions of the iron(III) normally filled by a water molecule. This process weakens the As–F bond and facilitates its rupture. This is supported by the observation that an *excess* of thiocyanate reduces the rate of hydrolysis in an iron(III)–thiocyanate system.

This reaction is reminiscent of the metal chelate catalyzed reactions reported for some compounds

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(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 153.

(7) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

containing P–F linkages,[8] such as diisopropyl phosphorofluoridate. For such reactions, Gustafson and Martell proposed a mechanism in which the metal chelate forms bonds to an oxygen on the phosphorus and to the fluoride, using coordination sites which are otherwise occupied by water or a hydroxide ion. This facilitates the attack of water or hydroxide and thus catalyzes the hydrolysis. Because most of these studies were done at pH 6.9 or above the partly hydrolyzed chelates (such as Cu(OH)L) played an important role as catalysts. An analogous mechanism seems very attractive in the present case.

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[8] (a) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens' and R. Proper, *J. Am. Chem. Soc.*, **77**, 922 (1955); (b) R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiainen, S. C. Chaberek, Jr., and A. E. Martell, *ibid.*, **79**, 3030 (1957); (c) F. M. Fowkes, G. S. Ronay, and L. B. Ryland, *J. Phys. Chem.*, **62**, 867 (1958); (d) R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, **84**, 2309 (1962). The similarity is enhanced by the presence of basic complexes in the iron(III)–Ferron system: C. F. Richard, R. L. Gustafson, and A. E. Martell, *ibid.*, **81**, 1033 (1959).

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The Oxidation of Iron(II) by Chlorine

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The kinetics of the oxidation of iron(II) by aqueous chlorine has been investigated spectrophotometrically at an ionic strength of 1.00. In solutions with $[H^+] = 0.05–1.00\ F$, $[Cl^-] = 0.10–1.00\ F$, $[Fe^{2+}] = 10^{-5}–10^{-4}\ F$, $Cl_2 = 10^{-5}–10^{-4}\ F$, and $[Fe^{3+}]_0 = 0–10^{-4}\ F$, the rate law is $d[Fe^{3+}]/dt = 2k_1[Fe^{2+}][Cl_3^-] + 2k_3[Fe^{2+}][Cl_2]$; $k_1 = 910\ M^{-1}\ sec^{-1}$, $k_3 = 163\ M^{-1}\ sec^{-1}$, and $\bar{k} = (k_1K_{Cl_3}[Cl^-] + k_3)/(1 + K_{Cl_3}[Cl^-]) = 10^{10.5} \exp(-11{,}200/RT)$, all at 30.0°. There is no apparent ferric inhibition of the reaction. Small amounts of copper(II) catalyze the reaction; the data do not distinguish between a copper(I) or a copper(III) intermediate for the catalyzed reaction. In solutions with $[H^+] = [Cl^-] = 1.00\ F$, $[Fe^{3+}]_0 = 0.00–4.40 \times 10^{-5}\ F$, and $[Cu^{2+}]_0 = 10^{-6}–10^{-4}\ F$, the data are consistent with the rate law $d[Fe^{3+}]/dt = 2k_1[Fe^{2+}][Cl_3^-] + 2k_3[Fe^{2+}][Cl_2] + 2k_{11}[Fe^{2+}][Cu^{2+}]$; $k_{11} = 145\ M^{-1}\ sec^{-1}$ at 30.0°.

Introduction

The mechanism of the reaction

$$2Fe^{2+} + Cl_3^- \text{ (or } Cl_2) \longrightarrow 2Fe^{3+} + 3Cl^- \text{ (or } 2Cl^-) \qquad (1)$$

is of interest because it may proceed through an iron(IV) intermediate

$$Fe^{2+} + Cl_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3Cl^- + Fe(IV) \qquad (2)$$

$$Fe^{2+} + Cl_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2Cl^- + Fe(IV) \qquad (3)$$

$$Fe^{2+} + Fe(IV) \xrightarrow{k_5} 2Fe^{3+} \qquad (4)$$

or as suggested by Taube[1, 2] through a chlorine radical

$$Fe^{2+} + Cl_3^- \underset{k_7}{\overset{k_6}{\rightleftharpoons}} Fe^{3+} + Cl_2^- + Cl^- \qquad (5)$$

$$Fe^{2+} + Cl_2 \underset{k_9}{\overset{k_8}{\rightleftharpoons}} Fe^{3+} + Cl_2^- \qquad (6)$$

$$Fe^{2+} + Cl_2^- \xrightarrow{k_{10}} Fe^{3+} + 2Cl^- \qquad (7)$$

Carter and Davidson[3] have reported that the reaction path $Fe^{2+} + Br_3^- \rightarrow Fe^{3+} + Br^- + Br_2^-$ is preferred to the reaction path $Fe^{2+} + Br_3^- \rightarrow Fe(IV) + 3Br^-$. Connick and Awtrey[4] have made preliminary studies of the iron(II)–chlorine reaction and reported a second-order rate constant approximately the same as for the iron(II)–bromine reaction, although no attempt was made to identify the active chlorine species or to establish the existence of an iron(IV) intermediate. Connochioli, Hamilton, and Sutin[5] have begun a study of the oxidation of iron(II) by 2-equivalent oxidants, including chlorine. Their experiments using chlorine in 3.0 *F* perchloric acid with no added chloride are incomplete, but iron(IV) is suggested as an intermediate in the reactions of Fe(II) with HOCl and O_3. We have measured the rate of reaction 1 in chloride media by observing the increase with time of the concentration of the iron(III) ion spectrophotometrically when the reagents are present at concentrations in the range $10^{-5}–10^{-4}\ F$. The kinetic results have been interpreted as demonstrating the existence of two active chlorine species, Cl_2 and Cl_3^-, but we are not able to identify the intermediate iron species involved in the reaction.

Experimental Section

Materials.—Ferrous ammonium sulfate (0.2 g) was dissolved in 500 ml of 1.00 *F* HCl; the solution was degassed with dry nitrogen and stored under nitrogen in a storage buret. This

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[1] H. Taube, *J. Am. Chem. Soc.*, **65**, 1876 (1943); *ibid.*, **68**, 611 (1946).

[2] I. L. Hochhauser and H. Taube, *ibid.*, **69**, 1582 (1947).

[3] P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

[4] Results quoted by P. R. Carter and N. Davidson in ref 3.

[5] T. J. Connochioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).