[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STEVENS INSTITUTE OF TECHNOLOGY]

Mechanism of Organic Oxidation in Aqueous Solution. II. Effect of Initial Persulfate Concentration on the Rate of Oxidation of Isopropyl Alcohol[1]

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The rate of oxidation of isopropyl alcohol by potassium persulfate at 60° in aqueous solution of *p*H 8.0 and ionic strength 0.5 is first order with respect to the measured disappearance of persulfate. The rate constant is proportional to initial alcohol concentration at low concentrations but becomes independent of it at higher concentrations. The variation of the pseudo first-order constant with initial persulfate concentration, using 0.02 *M* isopropyl alcohol and initial concentrations of persulfate ranging from 0.00125 to 0.06 *M*, has now been investigated, and it is found, rather surprisingly, that a limiting initial rate is also attained at the higher initial persulfate concentrations, similar to that observed when initial alcohol concentration is varied. The rate equation $-\mathrm{d}P/\mathrm{d}t = kP = [k_{\max}A_0P_0/(b + A_0)(c + P_0)]P$ (where b and c are empirical constants) relates the observed rate constant k to the initial alcohol and persulfate concentrations (A_0 and P_0). This equation is in excellent agreement with the data for 18 kinetic runs. The analogy between persulfate oxidation kinetics and enzyme kinetics is pointed out.

Introduction

We have found previously[3] that the rate of oxidation of isopropyl alcohol by $K_2S_2O_8$ in aqueous solution of *p*H 8.0 and ionic strength 0.5 is first order with respect to the measured disappearance of persulfate. A limiting rate was reached at higher initial concentrations of alcohol, where the rate became independent of the initial alcohol concentration. Similar results have been observed in the persulfate oxidation of mercaptans,[4,5] of diethyl and diphenyl sulfoxides[6,7] and of thiodiglycol sulfoxide.[8]

The variation of the pseudo first-order rate constant with varying initial persulfate concentration has now been investigated at 60° using 0.02 *M* isopropyl alcohol and initial concentrations of persulfate ranging from 0.00125 to 0.06 *M*.

Experimental

All kinetic runs were carried out at 60.0° with an initial concentration of 0.02 *M* isopropyl alcohol (Eastman Kodak Co. "spectro" grade). The *p*H was maintained at 8.0 by a phosphate buffer, and the ionic strength was brought up to 0.5 by the addition of K_2SO_4. The course of the reactions was followed by iodometric titration.

The buffer solution and solution for titration of the samples were prepared in the same manner as that previously described,[6] and the experimental procedure also was identical.

Results

It is evident from the accompanying graphs (Figs. 1 and 2) of the logarithm of the persulfate concentration *vs.* time that the reactions are first order with respect to the measured disappearance of persulfate. The rate constant for a given run was calculated in the usual manner from the extrapolated half-time obtained from the logarithmic plot of the data. The reproducibility of the value for the rate constant in duplicate experiments was very satisfactory.[9]

There are points of inflection in the straight lines (Fig. 2 curves A and B) at approximately the concentration for which it would be expected, from the stoichiometry of the oxidation, that all the alcohol should be oxidized to ketone. The rate constant measured for the second portion of these runs is designated k'.

Table I gives the rate constants k observed for the oxidation of 2-propanol at different initial persulfate concentrations. Also included in this table are the corrected rate constants k_c obtained by subtracting from k the value 0.018 hr.$^{-1}$, which is the first-order rate constant for the disappearance of persulfate when no alcohol is present in the solution.[6] For the two runs in which the persulfate concentration was greater than that of the alcohol, Table I also shows the corrected rate constants k_c' for the portion of reaction after the inflection points. That this represents the rate of oxidation of the resulting acetone is supported by a separate run with 0.02 *M* acetone as the substrate, for which k_c was found to be 0.084 hr.$^{-1}$. These data are presented graphically in Fig. 3, where k_c is plotted *vs.* $[S_2O_8^{=}]_0$.

TABLE I

PSEUDO FIRST-ORDER RATE CONSTANTS FOR THE PERSULFATE OXIDATION OF 0.02 *M* 2-PROPANOL AT 60° IN AQUEOUS SOLUTION OF *p*H 8.0 AND IONIC STRENGTH 0.5

$[K_2S_2O_8]_0$	$t_{1/2}$, hr.	k, hr.$^{-1}$	k_c, hr.$^{-1}$	k_c', hr.$^{-1}$
0.00125	1.45	0.48	0.46	...
.00250	1.25	.55	.53	...
.00500	1.03	.67	.65	...
.0200	0.82	.84	.82	...
.0400	.79	.88	.86	0.073
.0600	.81	.85	.83	0.092

Discussion

It is obvious from Fig. 3 that a limiting initial rate is also attained above a certain initial persulfate concentration (approximately 0.02 *M*). This is similar to the effect observed when initial alcohol concentration is varied and the persulfate concentration is held constant. At lower initial persulfate

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[1] This paper was given at the New York Meeting of the A.C.S., September, 1957.

[2] Taken, in part, from the M.S. Thesis of E. R. Malinowski.

[3] L. S. Levitt and E. R. Malinowski, THIS JOURNAL, **77**, 4517 (1955); **78**, 2018 (1956).

[4] R. L. Eager and C. A. Winkler, *Can. J. Res.*, **B26**, 527 (1948).

[5] L. S. Levitt, *ibid.*, **31**, 915 (1953).

[6] E. Howard, Jr., and L. S. Levitt, THIS JOURNAL, **75**, 6170 (1953).

[7] L. S. Levitt and E. Howard, Jr., Abst. of Papers, Dallas Meeting A.C.S., 1956, 51-N.

[8] L. S. Levitt and D. G. Ziebell, Abst. of Papers, Cincinnati Meeting A.C.S., 1955, 41-N.

[9] The same values for k, within 2%, under the same experimental conditions, have been observed by Mrs. B. W. Levitt in this Laboratory; Abst. of papers, Chicago Meeting, A.C.S., 1958, 5-P.

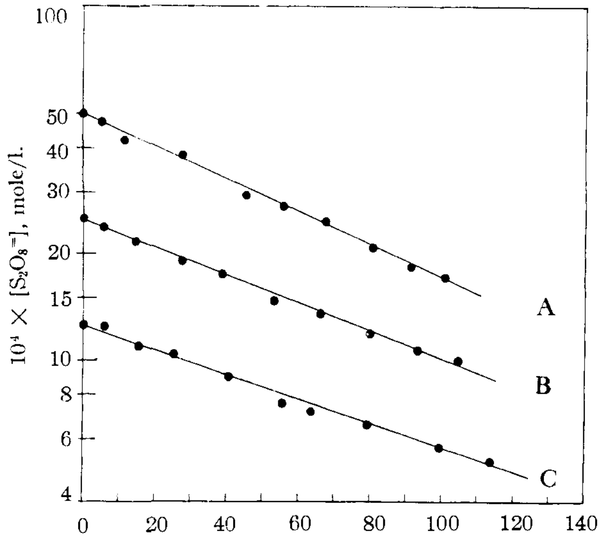

Fig. 1.—Rate of persulfate oxidation of 0.02 *M* isopropyl alcohol at 60° with different initial persulfate concentrations: A, 0.005 *M*; B, 0.0025 *M*; C, 0.00125 *M*.

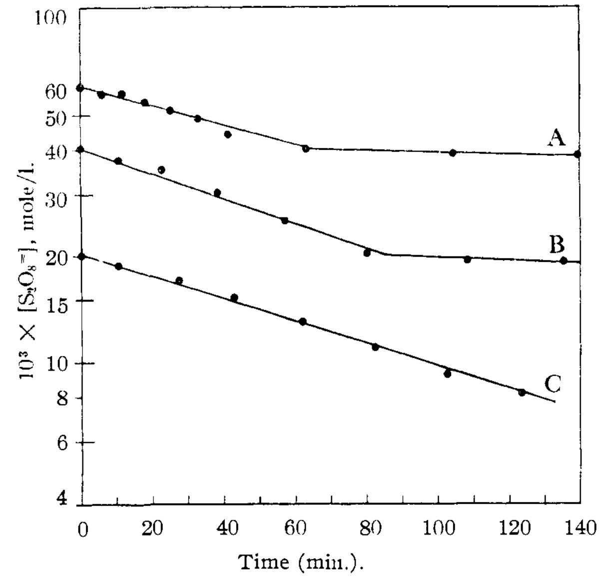

Fig. 2.—Rate of persulfate oxidation of 0.02 *M* isopropyl alcohol at 60° with different initial persulfate concentrations: A, 0.06 *M*; B, 0.04 *M*; C, 0.02 *M*.

concentrations the rate falls off sharply and becomes proportional to the initial persulfate concentration. In the limiting region the rate constant is independent of initial persulfate concentration.

Experimental Rate Law.—The rate may be formulated by the empirical expression

$$-\frac{d[S_2O_8^=]}{dt} = k[S_2O_8^=] = k_{\max(p)}\,[S_2O_8^=]\left(\frac{[S_2O_8^=]_0}{c + [S_2O_8^=]_0}\right) \quad (1)$$

where c is an empirical constant, and the subscript zero refers to initial concentration.

This rate equation means that any single kinetic run obeys the integrated first-order rate law, which shows that the rate of disappearance of persulfate is first order with respect to *time*. The initial rate varies, however, with the *square* of the initial persulfate concentration at low values of the later and with the first power of the initial persulfate concentration at high values. With respect to *concentration*, then, the reaction is either second order or first order in persulfate, or somewhere between these two extremes for intermediate persulfate concentrations. The fundamental difference between the order with respect to time and that with respect to concentration has been pointed out by Letort.[10]

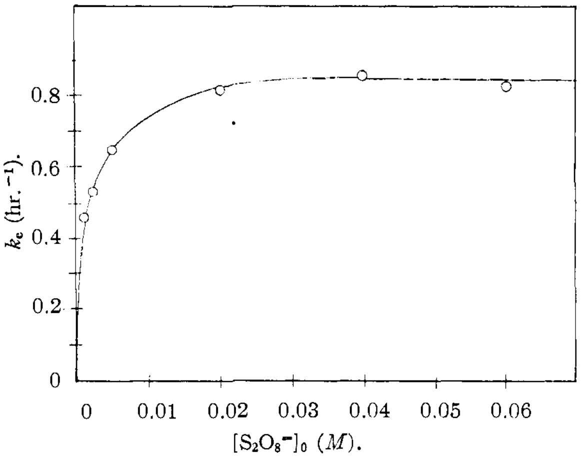

Fig. 3.—Variation of k_c with initial concentration of persulfate; temp. 60°; initial isopropyl alcohol concentration 0.02 *M*.

It is seen from eq. 1 that at high initial persulfate concentrations for which $[S_2O_8^=]_0 >> c$

$$k = k_{\max(p)} \quad (2)$$

and, therefore, the rate constant is independent of initial persulfate concentration. At low initial persulfate concentration $[S_2O_8^=] << c$, and

$$k = k_{\max(p)}\frac{[S_2O_8^=]_0}{c} \quad (3)$$

and, thus, the rate constant is proportional to the initial persulfate concentration.

Evaluation of Empirical Constants.—Equation 1 may be rearranged to give

$$\frac{[S_2O_8^=]_0}{k_c} = \frac{c}{k_{\max(p)}} + \frac{[S_2O_8^=]_0}{k_{\max(p)}} \quad (4)$$

A plot of $[S_2O_8^=]_0/k_c$ *vs.* $[S_2O_8^=]_0$ results in a straight line with slope $1/k_{\max(p)}$ and intercept $c/k_{\max(p)}$. From such a plot (Fig. 4) the slope and the intercept are evaluated, and eq. 1 becomes

$$k_c = \frac{0.87[S_2O_8^=]_0}{0.0015 + [S_2O_8^=]_0} \quad (5)$$

The observed initial rate constant for any initial persulfate concentration can be predicted from this equation as is shown in Table II.

It is seen that the agreement between the observed and calculated values is quite satisfactory.

Dependence of Rate on Substrate Concentration.—The variation of the rate constant with initial isopropyl alcohol concentration under the same experimental conditions, but holding the

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[10] M. Letort, *J. chim. phys.*, **34**, 206 (1937); *Bull. soc. chim. France*, **9**, 1 (1942). See also K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 17.

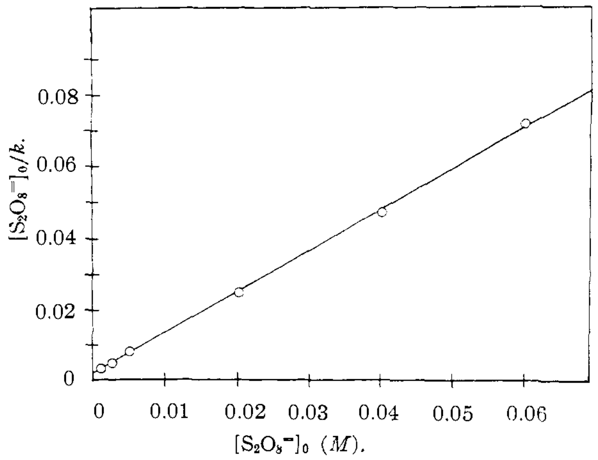


Fig. 4.—Test of equation 4.

initial concentration of persulfate fixed, was previously found to obey a similar expression[3]

$$k = k_{\max(A)} \frac{[\mathrm{ROH}]_0}{(b + [\mathrm{ROH}]_0)} \qquad (6)$$

from which it was found that

$$k = \frac{1.10[\mathrm{ROH}]_0}{0.0070 + [\mathrm{ROH}]_0} \qquad (7)$$

A more general equation which shows the dependence of the rate upon both initial reactant concentrations, and essentially combines eq. 1 and 6, is

$$k = k_{\max} \frac{[\mathrm{ROH}]_0[S_2O_8^=]_0}{(b + [\mathrm{ROH}]_0)\,(c + [S_2O_8^=]_0)} \qquad (8)$$

TABLE II

OBSERVED RATE CONSTANTS FOR THE OXIDATION OF 0.02 *M* 2-PROPANOL AND THOSE CALCULATED FROM EQ. 5

$[S_2O_8^=]_0$ *M*	k_c, hr.$^{-1}$ Obsd.	Calcd.
0	0	0
0.00125	0.46	0.40
.0025	.53	.53
.0050	.65	.67
.0200	.82	.81
.0400	.86	.84
.0600	.83	.85

For a series of kinetic measurements at constant initial persulfate concentration $[S_2O_8^=]_0/(c + [S_2O_8^=]_0)$ = constant, and eq. 8 reduces to eq. 6 where

$$k_{\max(A)} = k_{\max} \frac{[S_2O_8^=]_0}{c + [S_2O_8^=]_0} \qquad (9)$$

On substitution of the appropriate values for *c*, $[S_2O_8^=]_0$ and $k_{\max(A)}$ eq. 9 becomes

$$1.10 = k_{\max} \left(\frac{0.02}{0.0015 + 0.02}\right) \qquad (10)$$

from which one finds $k_{\max} = 1.18$.

For a series of kinetic measurements at constant initial alcohol concentration $[\mathrm{ROH}]_0/(b + [\mathrm{ROH}]_0)$ = constant, and eq. 8 reduces to eq. 1 where

$$k_{\max(p)} = k_{\max} \frac{[\mathrm{ROH}]_0}{b + [\mathrm{ROH}]_0} \qquad (11)$$

On substituting the appropriate values for *b*, $[\mathrm{ROH}]_0$ and $k_{\max(p)}$, eq. 11 becomes

$$0.87 = k_{\max} \left(\frac{0.02}{0.0070 + 0.02}\right) \qquad (12)$$

from which one again finds $k_{\max} = 1.18$.

Therefore, eq. 8 may be written

$$k = 1.18 \left(\frac{[\mathrm{ROH}]_0}{0.0070 + [\mathrm{ROH}]_0}\right)\left(\frac{[S_2O_8^=]_0}{0.0015 + [S_2O_8^=]_0}\right) \qquad (13)$$

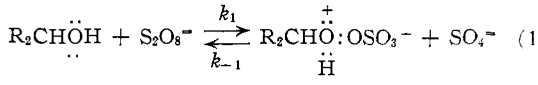
Table III shows the excellent agreement between the observed rate constants and those calculated from eq. 13 for various initial reactant concentrations.

TABLE III

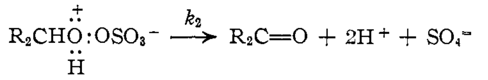
OBSERVED RATE CONSTANTS FOR THE OXIDATION OF 2-PROPANOL BY PEROXYDISULFATE AND THOSE CALCULATED FROM EQ 13

$[S_2O_8^=]_0$ *M*	$[\mathrm{ROH}]_0$ *M*	k_c, hr.$^{-1}$ Obsd.	Calcd.
0.020	0.003	0.32	0.33
.020	.005	.46	.46
.020	.006	.53	.51
.020	.010	.63	.65
.020	.015	.71	.75
.020	.020	.82	.82
.020	.025	.88	.86
.020	.040	1.03	.94
.020	.100	1.05	1.03
.020	.150	1.05	1.05
.020	.200	1.05	1.06
.00125	.020	0.46	0.40
.0025	.020	.53	.53
.005	.020	.65	.67
.040	.020	.86	.84
.060	.020	.83	.85
.010	.010	.54	.60
.005	.010	.50	.53

A Possible Mechanism.—A rate equation of similar (though not exactly the same) form as eq. 13, but one which *does* predict a limiting rate with respect to each of the two reactants, may be derived from the mechanism



$$\mathrm{R_2CH\underset{..}{\ddot{O}}H + S_2O_8^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2CH\underset{\ddot{H}}{\overset{+}{\ddot{O}}}{:}OSO_3^- + SO_4^{=}} \qquad (14)$$



$$\mathrm{R_2CH\underset{\ddot{H}}{\overset{+}{\ddot{O}}}{:}OSO_3^- \xrightarrow{k_2} R_2C{=}O + 2H^+ + SO_4^{=}} \qquad (15)$$

It is assumed (eq. 14) that the alcohol combines with sulfur tetroxide by displacing sulfate ion from persulfate, thus forming reversibly a monopersulfate ester whose subsequent heterolytic decomposition[11] (eq. 15) gives rise to the reaction products. This mechanism is similar to that proposed in our previous paper[3] but avoids assuming that persulfate ion itself first dissociates into sulfur tetroxide and sulfate ion, since there is good evidence[12] that such dissociation is too slow to account for the rate of oxidation observed here.

The steady-state concentration of intermediate complex will be designated *X*. Then

$$dX/dt = k_1[\mathrm{ROH}][S_2O_8^=] - k_{-1}[SO_4^=]X - k_2X = 0 \qquad (16)$$

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[11] L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

[12] K. B. Wiberg and H. B. van der Heyde, Jr., in private communications to the authors.

The concentrations of alcohol and persulfate will not correspond to their initial values, however, since certain amounts will have undergone reaction, and certain quantities of alcohol and sulfur tetroxide will be bound in the complex. Therefore, we set [ROH] = $[\mathrm{ROH}]_0 - X$ and $[\mathrm{S_2O_8^=}] = [\mathrm{S_2O_8^=}]_0 - X$. Making this substitution in eq. 16 and neglecting the presumably small term in X^2, we find for X

$$X = \frac{k_1[\mathrm{ROH}]_0[\mathrm{S_2O_8^=}]_0}{k_{-1}[\mathrm{SO_4^=}] + k_2 + k_1([\mathrm{ROH}]_0 + [\mathrm{S_2O_8^=}]_0)} \quad (17)$$

Finally, setting the over-all rate equal to k_2X and dividing through by k_1, we obtain the rate expression

$$\text{initial rate} = \frac{k_2[\mathrm{ROH}]_0[\mathrm{S_2O_8^=}]_0}{[\mathrm{ROH}]_0 + [\mathrm{S_2O_8^=}]_0 + (k_2 + k_{-1}[\mathrm{SO_4^=}])/k_1} \quad (18)$$

which, as was stated above, is quite similar in form to the empirical expression (eq. 8), predicting a limiting rate with respect to both alcohol and persulfate, and yet differs sufficiently from eq. 8 to make it incorrect. Indeed, it is rather difficult to see how a rate equation of the exact required form can be derived from purely mechanistic considerations.

Analogy with Enzyme Kinetics.—A very interesting fact which remains to be pointed out is that eq. 8 is similar to, and eq. 18 identical with, the complete Briggs and Haldane equation for variation of the rate of enzymatic reactions with initial concentration of enzyme and substrate[13]

$$\text{initial rate} = \frac{k_2S_0E_0}{S_0 + E_0 + (k_2 + k_{-1})/k_1} \quad (19)$$

where S_0 and E_0 are, respectively, the initial substrate and enzyme concentrations, and $(k_2 + k_{-1})/k_1$ is the Michaelis constant, K_m.

Thus persulfate oxidations seem to follow kinetic laws similar to those obeyed by enzyme systems, with the persulfate concentration taking the place of the enzyme concentration in these equations, although, needless to say, the persulfate is not regenerated and hence does not actually function catalytically as does an enzyme.

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[13] See, for example, K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 281.

HOBOKEN, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Thiourea Derivatives. IV. The Methylated Thioureas. Conclusions[1]

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

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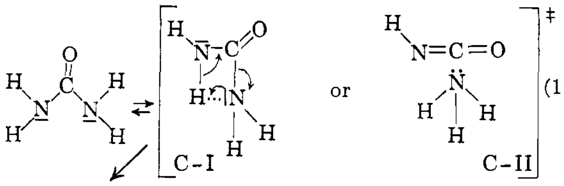
Kinetic data on urea, thiourea and the methylated thioureas have been assembled and compared. The dissociations of these compounds in low *p*H water solutions at elevated temperatures are all first-order, ionic strength independent reactions. Transition states formed by hydrogen transfer and loosening of a C–N bond are assumed. For thiourea and its methyl derivatives these activated complexes are visualized as being composed of two parts: an amine or ammonia-like fragment, and an isothiocyanate-like fragment (either isothiocyanic acid-like or methyl isothiocyanate-like). One important generalization presented is that if transition states with identical amine fragments are compared, substitution of methyl for hydrogen in the thiocyanate fragment increases the rate by a factor of 2.2. If the rate-determining step is assumed to involve rupture of a C–N bond by removal of the nucleophilic amine fragment from the electrophilic isothiocyanate fragment, a consistent interpretation is possible. Under this assumption the relative reactivities of all the methylated thioureas can be rationalized in terms of hyperconjugative electron release by methyl groups and steric strain. The observation that urea is 244 times more reactive than thiourea is attributable to the sulfur atom's superior ability to withdraw electrons. Other aspects of the kinetic behavior of these compounds are discussed.

Introduction

Results of kinetic studies with urea,[2] thiourea[3] and the methylated thioureas,[4-6] in aqueous media at elevated temperatures have been reported. These data have now become extensive enough to warrant their collection, comparison and detailed examination for significant interrelationships.

Discussion

It has been suggested that urea and its derivatives decompose *via* intramolecular hydrogen transfer and dissociation of the activated complex. Applied to urea the postulated mechanism can be formulated as



(1)

$$\mathrm{NH_3} + \mathrm{HNCO} \rightleftarrows \mathrm{NH_4^+} + \mathrm{NCO^-} \quad (2)$$

Similar mechanisms have been proposed for thiourea, the dimethylthioureas and trimethylthiourea. Two slightly different activated complexes are represented in the above scheme. Within the framework of the assumed mechanism they are indistinguishable *a priori* since both represent different configurations that might be encountered along the reaction coördinate. A discussion of the relative merits of the two representations will be presented in a subsequent paragraph after pertinent data on derivatives has been reviewed.

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[1] Presented before the Division of Physical and Inorganic Chemistry, 133rd National Meeting of the American Chemical Society held in San Francisco, California, April, 1958.

[2] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

[3] W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

[4] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 2681 (1957).

[5] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 3683 (1957).

[6] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 4329 (1957).