negligible for $[H^+] \geq 0.04$ M compared to 26.6 M^{-1} sec^{-1}, the coefficient of the rate term $[Cu^{2+}][V^{2+}]$. According to this point of view the lack of a dominant k_{OH}/k_{H_2O} value does *not*, in this instance, constitute an indication of an outer-sphere mechanism, but rather the inverse $[H^+]$ term is negligible owing to the concentration of $CuOH^+$ being very small compared to Cu^{2+} with both metal ions having nearly the same reactivity. Another example of this effect is the reaction of $Co(NH_3)_5OH_2{}^{3+}$ with V^{2+},[14] where the lack of dependence of rate on $[H^+]$ also does not constitute evidence for an outer-sphere mechanism, for an inner-sphere reaction of $Co(NH_3)_5OH^{2+}$ and V^{2+} could not possibly compete with the acid-independent term, owing to the limiting effect of $V(H_2O)_6{}^{2+}$ substitution.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SWARTHMORE COLLEGE, SWARTHMORE, PENNSYLVANIA,
AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Kinetics and Mechanism of the Reduction of Molybdenum(V) by Tin(II) in Concentrated Hydrochloric Acid Solutions[1,2]

BY A. A. BERGH AND G. P. HAIGHT, JR.[3]

Received July 24, 1968

The kinetics and mechanism of the reduction of Mo(V) by Sn(II) have been investigated in 9 and 12 M hydrochloric acid solutions. The reaction is stoichiometrically a simple 2-equiv process in both reagents: $Sn(II) + Mo(V) \rightarrow Mo(III) + Sn(IV)$. The complicated kinetics are best fit by the law

$$\frac{-d[Sn(II)]}{dt} = \frac{-d[Mo(V)]}{dt} = \frac{k_1[Mo(V)][Sn(II)]}{k_2 + k_3[Mo(V)] + k_4[Sn(II)] + k_5[Mo(III)]} \qquad (1)$$

No significant intermediates are detectable in visible and uv absorption spectra or with esr during the reaction. A mechanism is postulated involving reaction of the predominant Sn(II) and Mo(V) species with solvent-activated forms of each other. Data are consistent with the attack of $SnCl_3{}^-$ on $MoOCl_5{}^{2-}$ and the attack of $SnCl_4{}^{2-}$ on the open position *trans* to the $Mo{\equiv}O$ bond in $MoOCl_4{}^-$ to form Cl^--bridged intermediates. The activation energy for the reaction is about 10 kcal.

Introduction

Potentiometric titrations of Sn(II) with Mo(VI) in hydrochloric acid[4] led to the discovery of a slow reaction between Mo(V) and Sn(II) to give Mo(III) and Sn(IV) in hydrochloric acid of acid concentration >9 M. Shaffer[5,6] has remarked that many complementary 2-equiv redox reactions are fast. However this reaction is slow enough to study without employing special mixing techniques.

Experimental Procedure

Reagent grade chemicals were used without further purification. Mo(III) solutions were prepared by reduction of Mo(VI) with mercury and were stored over mercury. Hg_2Cl_2 produced by the oxidation of mercury was removed by filtration. No effect on the reaction under study due to mercury or its ions could be detected. Mo(V) solutions produced by reduction of Mo(VI) with Sn(II) gave the same kinetics as those prepared using reduction by Hg. Mo(V) was prepared by oxidation of Mo(III) with Mo(VI), stock solutions retaining about 6% Mo(III). $SnCl_2$ was dissolved in 12.3 M HCl and standardized before and after each series of runs. Hydrochloric acid was standardized acidimetrically using sodium bicarbonate.

All spectrophotometric and kinetic measurements were carried out using a Beckman Model DU spectrophotometer, with 10.0-mm cells. The reagents were mixed in the cell before each measurement, and the cell compartment was kept at a constant temperature of 25 ± 0.05°, unless otherwise stated.

The absorption spectra of Mo(V) and Mo(III) in 12.0 N hydrochloric acid are shown in Figure 1. The spectrum of Mo(V) has two and the spectrum of Mo(III) three maxima in the visible region.

The rate of the reaction $Mo(V) + Sn(II) \rightleftharpoons Mo(III) + Sn(IV)$ was followed either at 720 mμ by the disappearance of Mo(V) or at 528 mμ by the formation of Mo(III). The same rate was found at both wavelengths, indicating the absence of an intermediate of different spectrum in detectable quantities during the run.

Kinetics Results

The rate law for this reaction was determined in 9 and 12 M hydrochloric acid. It is rather complex, so that analysis of the experimental data will be given in some detail, that its derivation may be clear.

Results in 9 M HCl. Kinetics with $[Sn(II)] = [Mo(V)] = a$.—All runs with equimolar Sn(II) and Mo(V) in this medium started out with good first-order dependence on either reagent but not on both. There appeared to be a slight indication that the first-order constant was low during the first minute or two,

---

[1] Research was supported by U. S. Army through a grant to Swarthmore College from the Office of Ordnance Research, Durham, N. C., and by a grant from the U. S. Public Health Service to the University of Illinois.

[2] The data on which this paper is based were taken mainly from the doctoral thesis submitted in 1959 by A. A. Bergh to the Graduate School of the University of Pennsylvania.

[3] To whom correspondence should be addressed at the University of Illinois, Urbana, Ill.

[4] G. P. Haight, Jr., and A. A. Bergh, *Inorg. Chem.*, **1**, 688 (1962).

[5] P. A. Shaffer, *J. Phys. Chem.*, **40**, 1021 (1936).

[6] P. A. Shaffer, *Cold Spring Harbor Symp. Quant. Biol.*, **7**, 50 (1939).

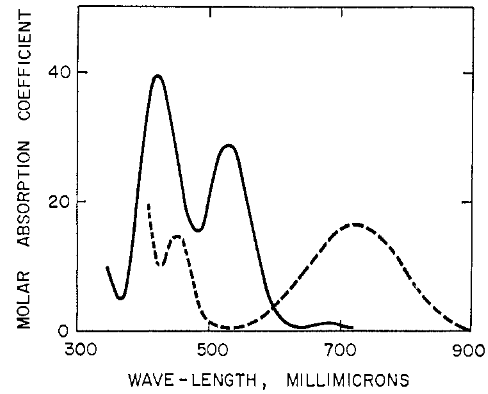


Figure 1.—Absorption spectra for Mo(V) (dashed line) and Mo(III) (solid line) in concentrated hydrochloric acid.

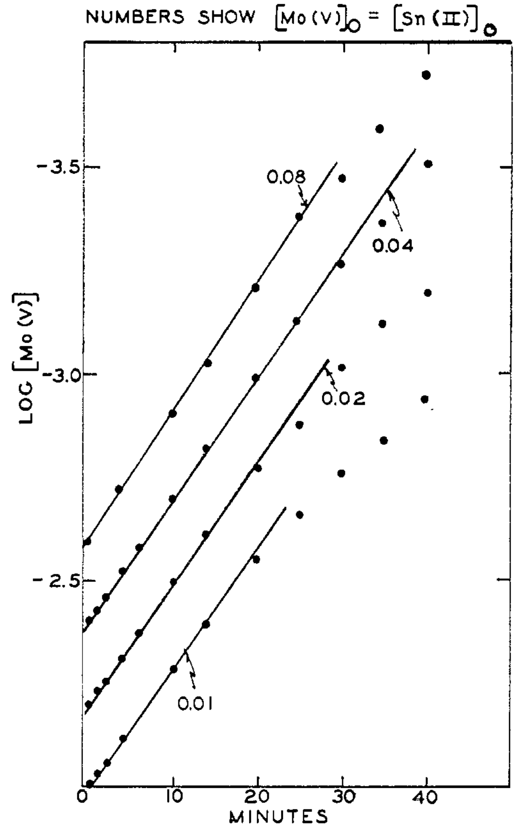


Figure 2.—Runs for [Sn(II)] = [Mo(V)] = a in 9 M HCl, showing deviations from first-order plots late in each run. Numbers by the curves indicate $[\mathrm{Mo(V)}]_0 = [\mathrm{Sn(II)}]_0$. Curves for 0.02, 0.04, and 0.08 M runs are displaced 0.5, 1.0, and 1.5 units upward, respectively.

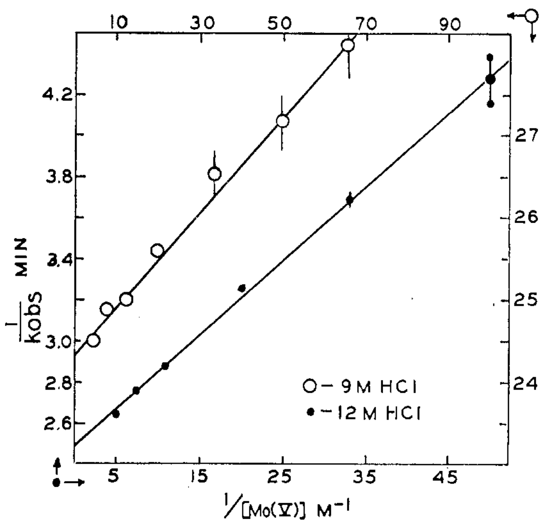


Figure 3.—Runs with excess Mo(V). From slope and intercept constants k_1/k_3 and k_1/k_2 given in the text are calculated.

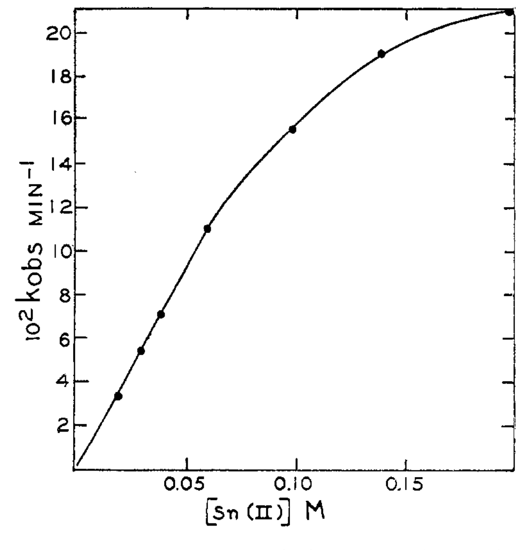


Figure 4.—Runs with excess Sn(II) in 9 M HCl, showing linear increase in k_{obsd} with [Sn(II)] at low excess of Sn(II) followed by leveling off at high [Sn(II)].

but this observation is not conclusive. Results are shown graphically in Figure 2. Departure from first-order dependence occurs at low a primarily because of a tendency to become second order at low concentrations. At high a, Mo(III) which inhibits the reaction builds up during the run.

For initial rates where Mo(III) inhibition can be ignored

$$\text{rate} = 5.5 \times 10^{-4} a\ \text{sec}^{-1} \qquad (2)$$

Kinetics with Excess Mo(V).—Addition of Mo(V) in excess makes every run first order in [Sn(II)] throughout the run. With Mo(V) in excess, a limiting rate is reached which is not very much greater than that observed with [Sn(II)] = [Mo(V)]. The results are consistent with the rate law

$$\frac{-\mathrm{d}[\mathrm{Sn(II)}]}{\mathrm{d}t} = \frac{k_1[\mathrm{Sn(II)}][\mathrm{Mo(V)}]}{k_2 + k_3[\mathrm{Mo(V)}]} \qquad (3)$$

Figure 3 shows a plot of $1/k_{\mathrm{obsd}}$ *vs.* $1/[\mathrm{Mo(V)}]$. The change in k_{obsd} is small giving considerable scatter to the points. The value k_3/k_1 = 1458 sec is accurate since it is obtainable from the limiting k_{obsd} at high [Mo(V)]. The value of k_1/k_2 can only be approximated from the plot.

Effect of Excess Sn(II).—If the rate law given by eq 3 were the result of complex formation between Mo(V) and Sn(II), it would be expected that a similar rate law with [Sn(II)] substituted for [Mo(V)] and

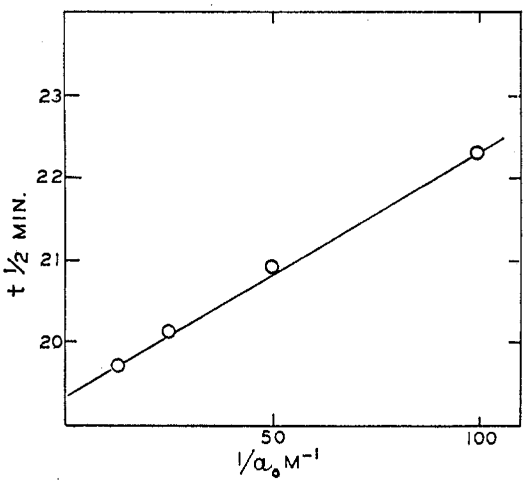


Figure 5.—Half-time plotted against $1/a_0$ for a = [Sn(II)] = [Mo(V)] and $[\mathrm{Mo(III)}]_0 = 0$.

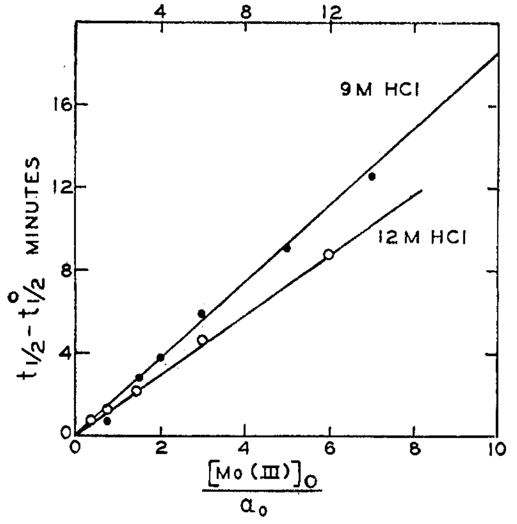


Figure 6.—The effect of changing $[\mathrm{Mo(III)}]_0$ on the half-time at constant a_0: open circles, 12 M HCl; closed circles, 9 M HCl.

d[Mo(V)] substituted for d[Sn(II)] would hold when Sn(II) is in excess. Such is not the case. The runs only approach first order in [Mo(V)] (*cf.* Table I) but the first-order constant increases linearly with [Sn(II)] at low [Sn(II)] and appears to approach a limit at high [Sn(II)] as shown in Figure 4.

This indicates a first-order reaction in Sn(II) with inhibition at high Sn(II), giving a composite rate law

$$\frac{-\mathrm{d[Mo(V)]}}{\mathrm{d}t} = \frac{k_1[\mathrm{Mo(V)}][\mathrm{Sn(II)}]}{k_2 + k_3[\mathrm{Mo(V)}] + k_4[\mathrm{Sn(II)}]} \qquad (4)$$

A value of 190 sec for k_4/k_1 gives a good fit to the data in Figure 4. Strict first-order dependence on Mo(V) is not observed except at very high [Sn(II)] and very low [Mo(V)]. From eq 2 and 4, $k_1/(k_3 + k_4)$ is observed to be 5.5×10^{-4} sec^{-1}. Values given for k_1/k_3 and k_1/k_4 lead to a value of 6.0×10^{-4} sec^{-1} if k_2 is ignored. A term, k_2, is needed in the denominator to keep the rate from going to infinity at low [Mo(V)] and [Sn(II)].

TABLE I

INCREASE OF OBSERVED FIRST-ORDER RATE CONSTANT[a] DURING RUNS WITH EXCESS Sn(II) IN 9 M HCl AT 298°K

	$[\mathrm{Sn(II)}]_0$, M					
	0.060		0.100		0.14	
Time, min	[Mo(V)], M	10^4k_0, sec^{-1}	[Mo(V)], M	10^4k_0, sec^{-1}	[Mo(V)], M	10^4k_0, sec^{-1}
0	0.020		0.020		0.020	
2	0.0166	1.57	0.0153	2.22	0.0145	2.70
4	0.0137	1.59	0.0115	2.38	0.0101	3.05
6	0.0111	1.76	0.0086	2.42	0.0068	3.28
8	...	...	0.0063	2.61	...	...
10	0.0072	1.80				

[a] $k_0 = k_{\mathrm{obsd}}$ (first order).

TABLE II

TYPICAL RUNS FOR [Sn(II)] = [Mo(V)] IN 12 M HCl

Time, min	[Mo(V)], M	10^2k,[a] sec^{-1}	10^2k,[b] M^{-1}, sec^{-1}	[Mo(V)], M	10^2k,[a] sec^{-1}	10^2k,[b] M^{-1} sec^{-1}
0	0.0200			0.079		
2	0.0137	0.316	19.2	0.0496	0.421	6.25
4	0.0099	0.268	23.2	0.0329	0.343	8.50
6	0.0075	0.230	26.7	0.0240	0.261	9.10
8	0.0060	0.188	27.5	0.0178	0.251	12.20
10	0.0051	0.134	25.5	0.1046	0.167	10.30
16	0.0035	0.123	24.7	0.0090	0.134	11.80

[a] Observed first-order rate constant. [b] Observed second-order rate constant.

Evaluation of k_2/k_1.—If eq 4 is integrated and solved for $t_{1/2}$ for the case where [Mo(V)] = [Sn(II)] = a, we have

$$t_{1/2} = \frac{k_3 + k_4}{k_1}\ln 2 + \frac{k_2}{k_1 a_0} \qquad (5)$$

Figure 5 shows that a plot of $t_{1/2}$ *vs.* $1/a_0$ gives a straight line, the slope of which gives $k_2/k_1 = 1.9$ M sec.

The Effects of Products on Reaction Rate.—Mo(III) inhibits the reaction. Given the case where [Mo(V)] = [Sn(II)] = a and $[\mathrm{Mo(III)}]_0 = C$ at $t = 0$, a plot of C/a_0 *vs.* $t_{1/2} - t^0_{1/2}$ gives a straight line through the origin for constant a_0 (Figure 6) where $t^0_{1/2} = t_{1/2}$ when $C = 0$. Such a function is consistent with our final rate law

$$\frac{-\mathrm{d[Mo(V)]}}{\mathrm{d}t} = \frac{k_1[\mathrm{Mo(V)}][\mathrm{Sn(II)}]}{k_2 + k_3[\mathrm{Mo(V)}] + k_4[\mathrm{Sn(II)}] + k_5[\mathrm{Mo(III)}]}$$

$$t_{1/2} = \frac{k_3 + k_2 - k_5}{k_1}\ln 2 + \frac{k_5}{k_1 a_0} + \frac{k_5}{k_1}\left(\frac{C}{a_0}\right) + \frac{k_5}{k_1} \qquad (6)$$

Figure 6 gives $k_5/k_1 = 108$ sec. Sn(IV) has no effect on the reaction rate.

Results in 12 M HCl.—In 12 M HCl, the data are less precise owing to a marked increase in the rate of reaction. It also proved very difficult to reach limiting conditions which gave simplified rate laws. However, patterns were such as to confirm the rate law derived for runs in 9 M HCl.

Runs with [Sn(II)] = [Mo(V)] = a.—At very low reagent concentration the runs approach a second-order rate law. Table II summarizes several runs showing how they deviate sharply toward first-order at high a though no limit is reached.

Runs with Mo(V) in Excess.—All runs with greater than twofold excess Mo(V) appeared to be first-order in Sn(II). Figure 3 shows a plot of data for $1/k_{\mathrm{obsd}}$ *vs.* 1/[Mo(V)]. A straight line and intercept are found consistent with the rate law as given in eq 3.

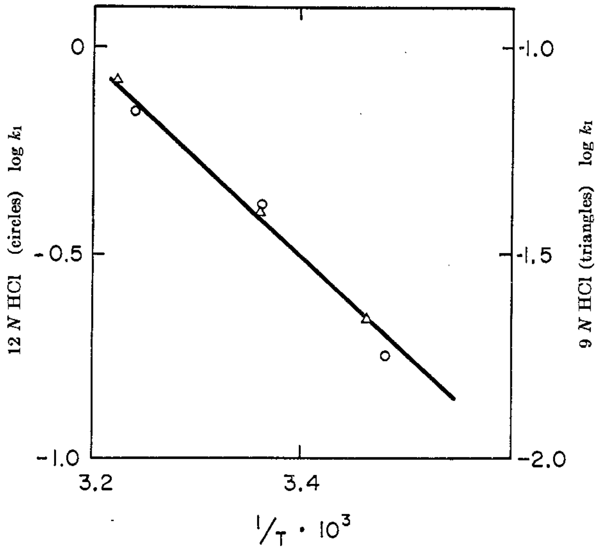


Figure 7.—Arrhenius plots for runs with excess Mo(V) showing constancy of E_a in the two acidities studied.

Runs with Sn(II) in Excess.—Runs become first order in Mo(V) with Sn(II) in excess by 0.02 *M* or more. k_{obsd} was higher than with corresponding excess of Mo(V). At high [Sn(II)] the order in Sn(II) decreases below 1. The deviation is consistent with the rate law observed in 9 *M* HCl if k_4/k_1 = 102 sec (*cf.* eq 4).

Effect of Adding Mo(III).—The same effect as observed in 9 *M* HCl is observed here though in lesser degree as Figure 6 shows. Thus we find the same rate law holding in both 9 *M* HCl and 12 *M* HCl. In both cases k_1 is inaccessible. Only ratios of k_1 with k_2, k_3, k_4, and k_5 are obtainable from the data. Table III gives comparative values of the ratios in the two media. The major effect is seen to be on k_3 with k_3/k_1 increasing tenfold if one dilutes 12 *M* HCl to 9 *M* while other ratios increase by a factor of 2. The ratios are used to calculate k_{obsd} under various conditions and are compared with measured values in Tables IV and V.

TABLE III

RATIOS OF CONSTANTS

[HCl], *M*	k_2/k_1, *M* sec	k_3/k_1, sec	k_4/k_1, sec	k_5/k_1, sec	Temp, °K
9	1.86	1458	180	108	298
12	1.02	144	102	44	298
12	1.86	263	186	70	287
12	0.42	60	42	18	315

Effect of Temperature on Reaction Rate.—Figure 7 shows the effect of changing temperature on pseudo-first-order rate constants in 9 and 12 *M* HCl. The plot should measure the effect on k_1/k_3 in each case. As constructed, the plot shows the same slope for both sets of data indicating that we are probably observing the same reaction with the same activated complex and the same activation energy of 10 kcal in each case.

TABLE IV

OBSERVED AND CALCULATED RATE CONSTANTS

9 *M* HCl AT 298°K

10^3[Mo(V)], *M*	10^3[Sn(II)], *M*	10^3[Mo(III)], *M*	$60k_{obsd}$, sec^{-1} Measd[a]	Calcd[b]
10	10	0	0.028	0.032
5	5	5	0.024	0.025
4	4	6	0.020	0.021
10	10	10	0.035	0.031
10	10	30	0.032	0.029
80	80	0	0.032	0.036
40	40	40	0.036	0.034
40	40	0	0.032	0.035
20	20	20	0.035	0.0355
30	30	10	0.035	0.038
30	30	50	0.030	0.033
30	20	0	0.032	0.036
20	10	10	0.036	0.037
200	20	0	0.041	0.041
100	20	0	0.037	0.039
90	10	10	0.040	0.041
20	200	0	0.182	0.180
10	190	10	0.210	0.217
10	20	10	0.054	0.052

[a] Pseudo-first-order constants obtained from contiguous points in a run. [b] Initial *k*'s are low.

TABLE V

OBSERVED AND CALCULATED RATE CONSTANTS IN 12 *M* HCl

10^3[Mo(V)], *M*	10^3[Sn(II)], *M*	10^3[Mo(III)], *M*	$60k_{obsd}$, sec^{-1} Measd[a]	Calcd
10	10	...	0.166	0.156
20	20	...	0.195	0.200
40	40	...	0.23	0.27
79	79	...	0.25	0.33
3	3	7	0.064	0.064
10	10	10	0.155	0.155
10	10	30	0.118	0.118
10	10	69	0.092	0.092
40	40	39	0.204	0.209
15	15	64	0.107	0.114
20	200	...	0.51	0.51
10	190	10	0.51	0.52
200	20	...	0.37	0.37
185	5	15	0.38	0.38
85	5	15	0.355	0.336
100	20	...	0.33	0.36
20	40	...	0.306	0.312

[a] Pseudo-first-order constants.

By assuming that the chief effect of temperature will be on k_1, the measured effect on k_3/k_1 was assumed to apply to the other ratios. The values obtained were tested on runs where [Mo(V)] = [Sn(II)] in both 9 and 12 *M* HCl and excellent fits to data obtained. Values of all constants are accurate to ±10% of measured values.

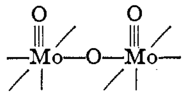
Discussion

Nature of Reactants and Products in Concentrated Hydrochloric Acid. Mo(V).—The visible absorption spectrum of Mo(V) is the same in 9 *M* HCl as in 12 *M* HCl. The dominant factor in the spectrum is the Mo≡O bond.[7] Salts of both $MoOCl_5^{2-}$ and $MoOCl_4^-$ have been isolated,[8] and we find qualitatively that reflectance spectra of such salts match the Mo(V) absorption spectrum in concentrated HCl. It is probable that bonding *trans* to oxygen in the Mo(V) octahedron is quite weak. $MoOCl_5^{2-}$ hydrolyzed to form a dimer containing the

---

(7) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

(8) R. H. James and W. Wardlaw, *J. Chem. Soc.*, 2145 (1927).



group.[9] This enhances absorbance in the visible region but does not change the position of the bands at 460 and 720 mμ.

Sn(II).—Stannous ion forms $SnCl_n^{2-n}$ complexes with n varying from 1 to 4. In 9–12 M HCl the chances are that $SnCl_4^{2-}$ is the dominant species unless complexes of $n > 4$ exist.[10] Evidence has accumulated[11,12] that $SnCl_3^-$ is often the most active reducing agent of the various $SnCl_n^{2-n}$ complexes. $SnCl_3^-$ has also been observed recently to ba a rather good coordinating ligand.[13]

Kinetically active species of Sn(II) involving five and seven chloride ions have been postulated to explain Cl^- catalysis of the Sn(II)–methyl orange reaction[14] at $0.1 < [Cl^-] < 4.0$ M.

Mo(III).—Both $MoCl_6^{3-}$ and $MoCl_5H_2O^{2-}$ salts may be crystallized from concentrated hydrochloric acid. The solution spectrum matches $MoCl_6^{3-}$ more closely but there can be little doubt that reversible anation and aquation involving these two ions is very rapid.

Sn(IV).—Salts of $SnCl_6^{2-}$ crystallize out of Sn(IV) solutions in 9–12 M HCl. In fact, formation of $(NH_4)_2SnCl_6$ solid interfered with our studies when Mo(V) was prepared from $(NH_4)_2MoO_4$.

Changes in the Absorption and Esr Spectra of Mo(V).—During the reaction the visible and near-ultraviolet absorption spectra of solutions of Mo(V) and Sn(II) are pure mixtures of Mo(V) and Mo(III) spectra. No effects on these or on esr signals for Mo(V) are observed in the presence of each other or of Sn(II) or Sn(IV). We must conclude that no intermediate complex of Sn(II) and Mo(V) forms to a measurable extent. The empirical law can be derived if one assumes Sn^{II}–Mo^{V} and $(Sn^{II})_2Mo^{V}$ complexes form to a significant degree. In the absence of physical evidence for complexes we must reject such a mechanism.

Inferences to be Drawn from the Rate Law.—If a complex intermediate involving Sn(II) and Mo(V) formed k_3 and k_4 would be the same. The difference in k_3 and k_4 implies that inhibition by reagents results from trapping of solvent-activated forms of one reagent by the other. The fact that Mo(III) inhibits the reaction while Sn(IV) does not suggests that Mo(III) in its final form $MoCl_6^{3-}$ or $MoH_2OCl_5^{2-}$ is produced in the rate-determining step whereas $SnCl_6^{2-}$ is formed in a subsequent step. Two paths of reaction are suggested.

Path I.—The most important path is suggested by reactions becoming zero order in Mo(V) at high [Mo(V)]

$$SnCl_4^{2-} \rightleftharpoons SnCl_3^- + Cl^- \qquad (I)$$

$$2H^+ + SnCl_3^- + MoOCl_5^{2-} \rightleftharpoons SnCl_3^+ + MoOH_2Cl_5^{2-} \qquad (II)$$

$$SnCl_3^+ + 3Cl^- \longrightarrow SnCl_6^{2-} \qquad (III)$$

$$\text{rate}_{I} = \frac{k_{I}k_{II}k_{III}[SnCl_4^{2-}][MoOCl_5^{2-}]}{k_{III}k_{-I} + k_{III}k_{II}[MoOCl_5^{2-}] + k_{-I}k_{-II}[MoOH_2Cl_5^{2-}]} \qquad (7)$$

This path particularly dominates at lower HCl concentrations which favor $SnCl_3^-$ over $SnCl_4^{2-}$.

Path II.—The decrease in order of rate in Sn(II) suggests a second path

$$MoOCl_5^{2-} \rightleftharpoons MoOCl_4^- + Cl^- \qquad (IV)$$

$$2H^+ + SnCl_4^{2-} + MoOCl_4^- \rightleftharpoons SnCl_3^+ + Mo[H_2O]Cl_5^{2-} \qquad (V)$$

$$SnCl_3^+ + 3Cl^- \longrightarrow SnCl_6^{2-} \qquad (III)$$

$$\text{rate}_{II} = \frac{k_{III}k_{IV}k_{V}[SnCl_4^{2-}][MoOCl_5^{2-}]}{k_{III}k_{-IV} + k_{III}k_{V}[SnCl_4^{2-}] + k_{-IV}k_{-V}[MoOH_2Cl_5^{2-}]} \qquad (8)$$

In eq 7 and 8 cross terms have been omitted from the denominator.

The two paths combined would give the observed rate law if cross terms involving Mo(III), Mo(V), and Sn(II) in the denominator are not significant.

Activation Parameters.—The change in rate with temperature is consistent with an activation energy of 10 kcal. Using the value of k_1/k_2 as a bimolecular rate constant a $\Delta S^{\ddagger}$ value of about -24 cal mol^{-1} deg^{-1} is calculated. Such a complicated rate law renders such activation parameters difficult to interpret.

We can deduce the following possible factors as contributing to the mechanism of the reaction. (1) There is charge repulsion of the negative reactant ions. (2) There is inertia of the $Mo{\equiv}O$ bond in Mo(V). Bonding *trans* to the oxygen is very weak in similar species such as VO^{2+}. Protonation of this oxygen is undetectable though required during the course of reaction. (3) $SnCl_4^{2-}$ and $SnCl_6^{4-}$ are the most likely Sn(II) species to be present,[15] yet $SnCl_3^-$, $SnCl_5^{3-}$, and $SnCl_7^{5-}$ are the kinetically active species[14] of Sn(II) in Cl^- media. (4) Paired electrons on Sn(II) must be transferred (and unpaired) to the t_{2g} orbitals in Mo(V) to form Mo(III).

Whether $SnCl_n^{2-n}$ species coordinate to Mo(V) in the activated state through the lone pair of electrons on Sn(II) or *via* one or more chloride ion bridges is an interesting question to consider. It is attractive to postulate that active $SnCl_3^-$, $SnCl_5^{3-}$, and/or $SnCl_7^{5-}$ have electron pairs at the corners of regular polyhedra

---

[9] G. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 673 (1962).

[10] G. P. Haight, Jr., J. Zoltewicz, and W. Evans, *Acta Chem. Scand.*, **16**, 659 (1962).

[11] F. R. Duke and N. C. Peterson, *J. Phys. Chem.*, **63**, 2076 (1959).

[12] G. P. Haight, Jr., and C. von Frankenberg, *Acta Chem. Scand.*, **16**, 221 (1962).

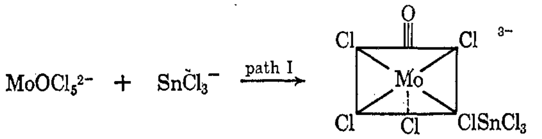
[13] R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963).

[14] L. Johansson and G. P. Haight, Jr., unpublished results.

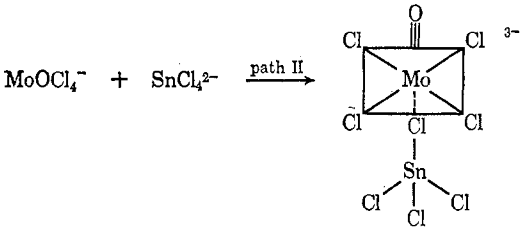
[15] G. P. Haight, Jr., "Halogen Chemistry," Vol. 2, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967.

lacking one chloride ion each. These electron pairs could "bond" to the empty position *trans* to Mo≡O in $MoOCl_4^-$ while effecting a two-electron transfer. Arguing against this reasoning is the fact that $SnCl_3^-$ coordinates only to Ahrland b-type metals.[16] $SnCl_3^-$ does not form σ bonds to H^+ even in concentrated HCl. Alternatively $SnCl_3^-$ could form Cl^--bridged intermediates to $MoOCl_5^{2-}$, the principle Mo(V) species present. Electron transfer could then take place through such bridges. Many such halogen-bridged intermediate reactions involving one-electron transfer have activation parameters comparable to those of the reaction under study.[17]

It is also plausible that the alternative path could result from $MoOCl_5^{2-}$ being the major Mo(V) species present. If $MoOCl_4^-$ formed in small quantity and could form a Cl^- bridge with any $SnCl_n^{2-n}$ species at the position *trans* to the Mo≡O bond, it would account for path II. The position *trans* to the Mo≡O bond is an inferior bonding site. Bridges involving equatorial chlorines would be both more probable and more effective once formed. It is possible to postulate two activated complexes, both of which, assisted by two protons, yield the same products

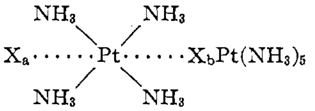


(9)



(10)

Further analogy may be drawn with a two-electron exchange through a halogen-bridged intermediate observed in the $Pt(NH_3)_4^{2+}$-catalyzed *trans*-substitution of halide ion for ammonia on $Pt(NH_3)_5X^{3+}$.[18] The intermediate



has $\Delta S^{\ddagger}$ values ranging from 10 to 29 depending on the species X_a and X_b and $\Delta H^{\ddagger}$ from 6 to 18. This involves reaction of two positive (3+ and 2+) ions. Our reaction with similar activation parameters appears to involve two negative ions forming a halide bridge between two metal ions. It appears that a tenuously stronger case for this can be made than for any other form of intermediate.

Acknowledgments.—The authors wish to thank Dr. Tracy Huang, who made the esr measurements, Professor James K. Beattie (University of Illinois), and Professor Philip George (University of Pennsylvania) for helpful discussions and advice.

---

[16] S. Ahrland, J. Chatt, an N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[17] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

[18] W. R. Mason and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).