

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

REACTIVITY OF HALIDE COMPLEXES OF TIN(II) I. The Reduction of Methyl Orange

Lars Johansson^a; G. P. Haight Jr.^a

^a Department of Chemistry, University of Illinois, Urbana, Illinois

To cite this Article Johansson, Lars and Haight Jr., G. P.(1971) 'REACTIVITY OF HALIDE COMPLEXES OF TIN(II) I. The Reduction of Methyl Orange', *Journal of Coordination Chemistry*, 1: 2, 155 – 160

To link to this Article: DOI: 10.1080/00958977108070757

URL: <http://dx.doi.org/10.1080/00958977108070757>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

REACTIVITY OF HALIDE COMPLEXES OF TIN(II)

I. The Reduction of Methyl Orange

LARS JOHANSSON and G. P. HAIGHT, Jr.

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

(Received March 12, 1971)

Halide ion is required for the reduction of methyl orange by Sn(II). Equilibrium data on the formation of SnCl_n^{2-n} and SnI_n^{2-n} combined with kinetic data indicate that SnCl_3^- and SnI_3^- form activated complexes with protonated methyl orange. The data also suggest pathways involving $\text{SnCl}_4^{=}$, SnCl_5^{3-} , SnI_5^{3-} and SnI_7^{5-} .

In 1959, Duke and Peterson¹ showed that SnCl_3^- was the only tin(II) species which has kinetic significance in the reduction of methyl orange in dilute hydrochloric acid. In their systems, Sn^{++} , SnCl^+ , and SnCl_2 were the dominant species of tin(II). In 1961, Haight and von Frankenberg², postulated that SnCl_3^- was the kinetically active Sn(II) species in the molybdate catalyzed reduction of perchlorate ion in solutions of high chloride concentration where SnCl_2 , SnCl_3^- , and $\text{SnCl}_4^{=}$ were the dominant species. Since chloride ion effects on the molybdate catalyst could not be ruled out, the lability of $\text{SnCl}_4^{=}$ and higher complexes as reducing agents remained in doubt.

Recent work on the stability of halide complexes of $5s^2$ and $6s^2$ ions Sn(II), Pb(II), Bi(III), etc.,^{3,4,5,6} has shown that complexes of MX_n where M is metal, X is halide ion, distinctly favor $n = 2, 4, 6$ and perhaps 8 vs. 3, 5, 7. Other work has shown that SnCl_3^- is an important Lewis base toward soft metal ions such as Pt(II).^{7,8} It is not a good ligand toward hard ions. It does not form HSnCl_3 in strong acid. Rather it acts as an acid forming $\text{SnCl}_4^{=}$ in aqueous hydrochloric acid.³

In this paper we extend the work of Duke and Peterson to higher concentrations ($<4\text{M}$) of chloride ion and examine the behavior of SnI_n^{2-n} complexes toward the reduction of methyl orange. We have also determined the effect of changing acidity on reaction rates in each system.

Experimental. Kinetics. Experiments were designed such that $d[\text{MeO}]/dt$ could be followed where $[\text{MeO}]$ is concentration of methyl orange. Concentrations of all other reagents $[\text{H}^+]$, $[\text{Sn(II)}]$,

$[\text{Cl}^-]$ were held constant during any individual run. All runs exhibited first order decay in methyl orange over several half-lives. Analysis of first order rate constants k_{obs} as functions of $[\text{H}^+]$, $[\text{Sn(II)}]$, and $[\text{Cl}^-]$ or $[\text{I}^-]$ were used as outlined in the theoretical section to elucidate the mechanism.

Reagents. Methyl orange used without further purification was dissolved in 4M HClO_4 . A 0.25 mM solution gave an absorbance of about 1.25 at 505 nm making it very suitable for kinetic runs.

SnCl_2 solutions were prepared by dissolving clear, fresh crystals of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 3 M HClO_4 to give $[\text{ClO}_4^-] + [\text{Cl}^-] = 4.0\text{ M}$. Tin metal and CO_2 were used to prevent oxidation of Sn(II). $[\text{Sn(II)}]$ was determined by adding excess standard triiodide and titrating with standard thiosulfate solution.

SnI_2 was prepared by simple precipitation, and washed with HClO_4 . A mixture of tin, SnI_2 , and 4 M HClO_4 was bubbled with CO_2 and filtered free of solids.

Oxidation of Sn(II) in perchloric acid was inexorable, requiring the use of fresh solutions. However, $[\text{Sn(II)}]$ did not change measurably in the time required for kinetic runs. The presence of Sn(IV) enhanced the yellow color of all iodide solutions, giving variable limiting absorbances after the disappearance of methyl orange. Scrupulous care with final absorbances as blanks was required for studies involving SnI_n^{2-n} .

All solutions were prepared under CO_2 . All mixing of reagents was performed in a CO_2 atmosphere.

Reactions were performed in a Beckman D. U. Spectrophotometer with cells maintained at $25^\circ \pm 0.5$ with thermospacers.

[Cl⁻] and [I⁻] were corrected for complex formation using the values in Table I.

TABLE I
Stability constants for SnX_n²⁻ⁿ

T = 298° K
β_n = [SnX_n²⁻ⁿ]/[Sn²⁺][X⁻]ⁿ M⁻ⁿ

X	Cl ^{-a}		I ^{-b}
	μ = 2.0	μ = 4.0	μ = 4.0
β ₁	11.4	28	5
β ₂	50.0	224	13.5
β ₃	30.0	291	135
β ₄		204	200
β ₆			390
β ₈			120

^a Ref. 3.

^b Ref. 6.

Theoretical. Our treatment of data is essentially that of Duke and Peterson.¹ Effectively, only methyl orange changes concentration during a given run and in all cases good first-order kinetics was obtained over several half-lives. Furthermore, reactions are first-order in total Sn(II) and in H⁺. The pseudo first-order rate constants *k*_{obs} are therefore given by:

$$k_{obs} = [H^+](k_0[Sn^{2+}] + k_1[SnX^+] + \dots + k_n[SnX_n^{2-n}]) \quad (1)$$

where X is Cl or I.

$$\text{If we define } \beta_n = \frac{[SnX_n^{2-n}]}{[Sn^{2+}][X^-]^n}$$

equation (1) becomes:

$$k_{obs} = \frac{[H^+][Sn(II)](k_0 + k_1\beta_1[X^-] + k_2\beta_2[X^-]^2 + \dots + k_n\beta_n[X^-]^n)}{1 + \beta_1[X^-] + \beta_2[X^-]^2 + \dots + \beta_n[X^-]^n} \quad (2)$$

The denominator, designated P by Duke and Peterson,¹ of equation (2), is calculated for each run using the constants in Table I. The quantity F([X⁻]) = *k*_{obs}P/[Sn(II)] at constant [H⁺] may then be examined by various iterative techniques to obtain values for the various rate constants.

$$F([X^-]) = [H^+] \sum_0^n k_n \beta_n [X^-]^n \quad (3)$$

RESULTS

A. SnCl_n²⁻ⁿ; μ = 2.0. Duke and Peterson¹ simply plotted log F([Cl⁻]) vs. log [Cl⁻]. They report a straight line of slope 3 and conclude that only

SnCl₃⁻ of all SnCl_n²⁻ⁿ complexes reacts with methyl orange at a competitive rate. We found that higher complexes do participate and accordingly re-examined Duke and Peterson's data. Results of our re-examination are found in Table II. P and

TABLE II
Analysis of Duke and Peterson's data

[Cl ⁻] M	F[Cl ⁻] ^a $\frac{k_{obs}P}{[Sn(II)]}$	F[Cl ⁻] (equation 3)
0.0169	0.047	0.0261
0.0522	0.691	0.635
0.0881	3.29	3.28
0.0930	6.65	3.95
0.1255	10.0	10.1
0.1620	22.8	22.9
0.181	31.0	32.8
0.187	26.9	36.7
0.1965	50.0	43.0
0.468	788.0	820

^a Calculations of Duke and Peterson corrected by the author using μ = 2.0 data.

F[Cl⁻] were very insensitive to the changes in β values from those at μ = 3.0 previously employed to those at μ = 2.0 which we used.

The quantity, F[Cl⁻]/[Cl⁻]^m is corrected for estimates of all terms *k*_nβ_n[Cl⁻]ⁿ where *n* ≠ *m* + 1 for successive iterations until plots of F[Cl⁻]/[Cl⁻]^m vs. [Cl⁻] (primed in Figure 1) give straight lines through the origin.

The fit is quite good considering the obvious scatter on plotted points.

Figure 1 shows the results of plotting F[Cl⁻]/[Cl⁻]^m vs. [Cl⁻]. β₀ = 1. The intercept of

each raw plot should give the value of β_m*k*_m[H⁺]. The slope of the final iteration should give [H⁺]β_{m+1}*k*_{m+1}. It is clear that *k*₀ and *k*₁ are each zero and that Sn²⁺ and SnCl⁺ are each unreactive toward methyl orange. However, the *m* = 2 curve gives strong indication that both higher and lower SnCl_n²⁻ⁿ complexes than *n* = 3 participate in the reduction of methyl orange. (Were Duke and Peterson's interpretation completely valid, the *m* = 2 curve would be a straight line through the origin.) There are obviously two or three badly skewed data points and one may in good conscience limit interpretation to include SnCl₃⁻ and SnCl₄⁼ by not accepting the point at lowest [Cl⁻]. We

have chosen to do this to keep these results in line with our own findings at higher ionic strengths and much higher $[\text{Cl}^-]$ than those employed by Duke

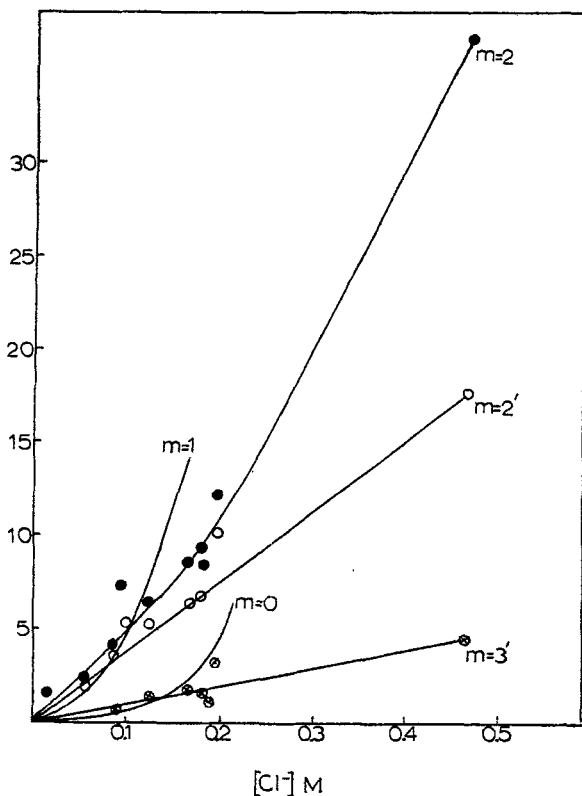


FIGURE 1 Curves $m = 0, 1, 2$ are direct plots of $F([\text{Cl}^-])/[\text{Cl}^-]^n$. Curve $m = 2'$ is for $\frac{F([\text{Cl}^-]) - 9400[\text{Cl}^-]^n}{[\text{Cl}^-]^2}$ vs. $[\text{Cl}^-]$. Curve $m = 3'$ is for $\frac{F([\text{Cl}^-]) - 4000[\text{Cl}^-]^3}{[\text{Cl}^-]^3}$ vs. $[\text{Cl}^-]$.

Several iterations led to curves $m = 2'$ and $m = 3'$. If the data point at lowest $[\text{Cl}^-]$ is accurate, $k_2\beta_2 \approx 100$ is required, giving $k_2 \approx 2 \text{ min}^{-1}\text{M}^{-2}$ or $0.03 \text{ sec}^{-1}\text{M}^{-2}$. We regard this only as an upper limit. Data points are shown for $m = 2$, solid dots; $m = 2'$, open circles; and $m = 3'$, crossed circles.

and Peterson. At $\mu = 2.0 = [\text{H}^+]$ we find from Figure 1:

$$F[\text{Cl}^-] = 3600[\text{Cl}^-]^3 + 9400[\text{Cl}^-]^4 \quad (3a)$$

$$k_o = k_1 = k_2 = 0$$

$$[\text{H}^+]k_3\beta_3 = 3600\text{M}^{-4}k_3 = 58 \text{ min}^{-1}\text{M}^{-2} = 0.97 \text{ sec}^{-1}\text{M}^{-2}$$

$$[\text{H}^+]k_4\beta_4 = 9400\text{M}^{-4}k_4 > 300 \text{ min}^{-1}\text{M}^{-2} = 5 \text{ sec}^{-1}\text{M}^{-2}$$

where β_4 is assumed to be $< 0.5 \beta_3$.

We assume H^+ is first-order at $\mu = 2.0$ since it

will be shown to be so at $\mu = 4.0$. This gives the rate equation at 298°K .

$$-\frac{d[\text{MeO}]}{dt} = [\text{MeO}][\text{H}^+](0.97 \text{ sec}^{-1} \text{M}^{-2}[\text{SnCl}_3^-] + \frac{78 \text{ sec}^{-1}\text{M}^{-2}}{\beta_4} [\text{SnCl}_4^{2-}]) \quad (4)$$

B. SnCl_n^{2-n} ; $\mu = 4.0$.

We have extended this study to higher concentrations of chloride ion. Data given in Table III

TABLE III

Chloride System: $\mu = 4.0$ $[\text{H}^+] = 4.0 \text{ M}$ $[\text{MeO}]_0 = 0.025 \text{ M}$

C_{Cl}	$[\text{Cl}^-]$	$k_{\text{obs}} \cdot 10^3$	$\frac{k_{\text{obs}}P}{[\text{Sn(II)}]}$	
M	M	sec ⁻¹	Observed sec ⁻¹ M ⁻¹	Calculated sec ⁻¹ M ⁻¹
$C_{\text{Sn}} = 5.7 \cdot 10^{-3} \text{ M}$				
.0410	.0370	.155	0.064	0.063
.0760	.070	.71	0.519	0.520
.109	.101	1.58	1.80	1.63
.142	.134	2.78	4.50	4.02
.176	.163	3.85	8.73	8.09
.209	.200	5.14	15.8	15.9
$C_{\text{Sn}} = 1.00 \times 10^{-3} \text{ M}$				
$= [\text{Cl}^-]$.270	1.43	45.4	45.1
↓	.536	3.70	525	520
	.803	5.90	2.38×10^3	2.42×10^3
	1.070	8.35	7.59	7.64
	1.336	11.1	1.97×10^4	1.92×10^4
	1.60	12.5	3.94	4.05
	1.87	14.4	7.43	7.87
	2.14	16.25	1.34×10^5	1.39×10^5
	2.40	20.1	2.42	2.36
	2.67	22.2	3.96	3.73

C_{Sn} = Total Sn(II) present in M

C_{Cl} = Total Cl^- present in M

$[\text{Cl}^-]$ = Free Cl^- present in M

were analyzed by reiteration of plots shown in Figure 2. $F(\text{Cl}^-)$ was calculated from the equation:

$$F(\text{Cl}^-) = 1250[\text{Cl}^-]^3 + 3350[\text{Cl}^-]^4 + 1300[\text{Cl}^-]^5 \quad (3b)$$

From these data the rate constants of interest are found to be:

$$k_3 = 1.07 \text{ sec}^{-1} \text{M}^{-2}$$

$$k_4 = 4.10 \text{ sec}^{-1} \text{M}^{-2}$$

$$\beta_3 k_5 = 325 k_5 > 3.25 \text{ sec}^{-1} \text{M}^{-2} \text{ assuming } \beta_5 < 100 \text{ M}^{-5}$$

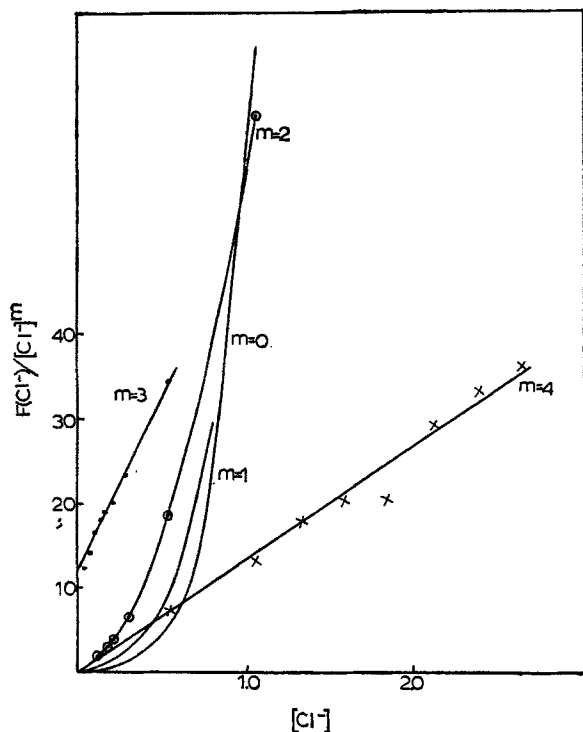


FIGURE 2 Curves $m = 0, 1, 2, 3$ are direct plots of $F([\text{Cl}^-])/[\text{Cl}^-]^m$. These show zero intercepts requiring $k_0 = k_1 = k_2 = 0$. The $m = 3$ curve (only linear portion shown) shows an intercept for $k_3\beta_3 = 1260$. The initial slope of 4000 = β_4k_4 was decreased by correction for a β_5k_5 term to 3350. The $m = 4$ curve is a plot of $(F([\text{Cl}^-]) - \beta_3k_3[\text{Cl}^-]^3 - \beta_4k_4[\text{Cl}^-]^4)/[\text{Cl}^-]^4$ vs. $[\text{Cl}^-]$ for the final iteration. For $m = 3$ and $m = 4$, multiply abscissa by 100. Data points are shown for $m = 2$, circles; $m = 3$, dots; and $m = 4$, crosses.

The rate constants k_3 and k_4 are remarkably close to those obtained from Duke and Peterson's data. The mean activity coefficient γ_{HCl} for $\mu = 4.0$ is roughly twice its value at $\mu = 2.0$. Furthermore, Duke and Peterson used equilibrium data obtained at $\mu = 3.0$ in analyzing kinetic data at $\mu = 2.0$. The absence of a $k_5\beta_5$ term in their study is due to the fact that significant effects due to the term could have been applied only to their point at highest $[\text{Cl}^-]$. Since no $k_4\beta_4$ term is required in the iodide study described below we attempted to fit our chloride data to a law containing only $k_3\beta_3$ and $k_5\beta_5$ terms. A much poorer fit was obtained than when the $k_4\beta_4$ term was included.

Order in hydrogen ion. The results shown in Figure 3 establish the reaction as first-order in H^+ .

The rate equation at $\mu = 4.0$ becomes

$$\frac{d[\text{MeO}]}{dt} = [\text{MeO}][\text{H}^+](1.07[\text{SnCl}_3^-] + 4.10[\text{SnCl}_4^{2-}] + \frac{325}{\beta_5}[\text{SnCl}_5^{3-}]) \quad (4a)$$

C. Iodide System. SnI_n^{2-n} ; $\mu = 4.0$.

We have recently obtained data⁶ on equilibria for the formation of SnI_n^{2-n} in which no evidence for complexes of odd $n > 3$ is found (see Table I). We have, therefore, investigated the behavior of

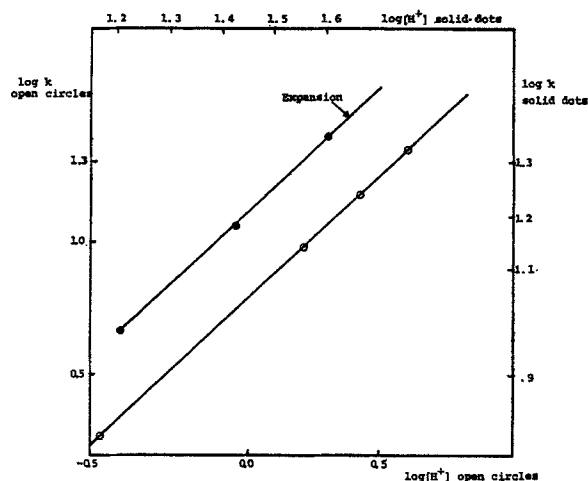


FIGURE 3 Hydrogen Ion Effect.

$$[\text{Cl}^-] = 2.67 \text{ M}; [\text{Sn(II)}] = 0.83 \text{ mM} \\ [\text{H}^+] + [\text{Na}^+] = 4.0 \text{ M}; [\text{ClO}^-] = 1.33 \text{ M}$$

SnI_n^{2-n} complexes toward reduction of methyl orange. Results are given in Tables IV and V. For $[\text{I}^-] < 0.1$, SnI_3^- is the only species of kinetic importance. (Cf. Figure 4.) We cannot give actual rate constants for k_5 and k_7 but only the product $k_n\beta_n$. SnI_n^{2-n} complexes for $n > 3$ and odd appear to be extremely reactive, both to disproportionation and to reduction of methyl orange. Iodide complexes of odd n reduce methyl orange at rates at least an order of magnitude greater than corresponding chloride complexes. The apparent reactivity of SnCl_4^- vs. non-reactivity of SnI_4^- is difficult to explain.

From measurements at higher $[\text{I}^-]$ we conclude that SnI_5^{3-} contributes only 1% at 0.1 M $[\text{I}^-]$. The value $k_3\beta_3 = 6.75 \times 10^4 \text{ M}^{-5} \text{ sec}^{-1}$ is obtained (at $[\text{H}^+] = 1.0 \text{ M}$).

As in the chloride case, reactions are first order

TABLE IV

Iodide System: $C_I < 100$ mM; $C_H = 1$ M, $C_{Na} = 3M(ClO_4^-)$
 $C_{Sn} = 0.714$ mM; $[MeO]_0 = 0.025$ mM
 $\mu = 4.0$ M $\approx [ClO_4^-]$; k_{obs} in sec^{-1}

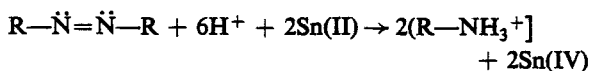
C. mM	[I ⁻] mM	P	$\frac{Pk_{obs}}{C_{Sn}} = F(I^-)$	$\log F(I^-)$	$\log [I^-]$
22.1	22.0	1.118	.464	0.334	1.372
32.1	31.9	1.178	1.365	0.135	1.503
52.1	51.8	1.314	6.32	0.800	1.714
72.1	71.7	1.483	16.5(0)	1.217	1.855
82.1	81.6	1.579	25.4	1.404	1.911
92.1	91.5	1.684	35.4	1.548	1.961

$\log F(I^-)$ versus $\log [I^-]$ is a straight line with slope 3.03.
See Fig. 4.

in hydrogen ion. (Tables 4 and 5.) The rate equation is:

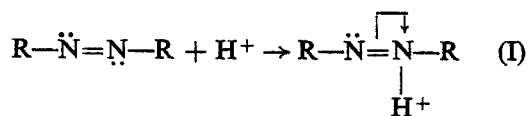
$$\frac{d[MeO]}{dt} = [MeO][H^+](500[SnI_3^-] + \frac{8.38 \times 10^4}{\beta_5} [SnI_3^{3-}] + \frac{3.93 \times 10^4}{\beta_7} [SnI_7^{5-}]) \quad (5)$$

Mechanism The overall reaction involves reduction of the diazo link in methyl orange.

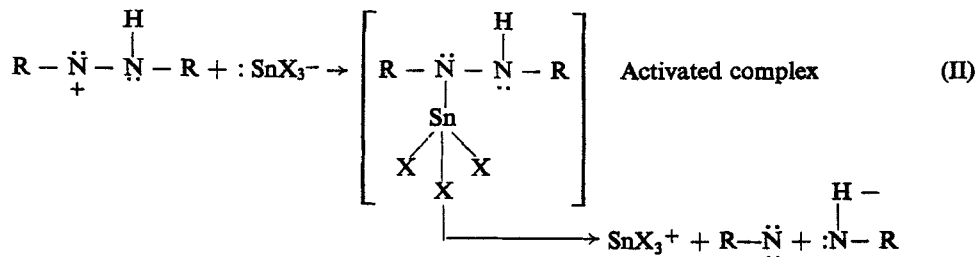


The activated complex includes one diazo group, one proton and one Sn(II). We postulate the sequence:

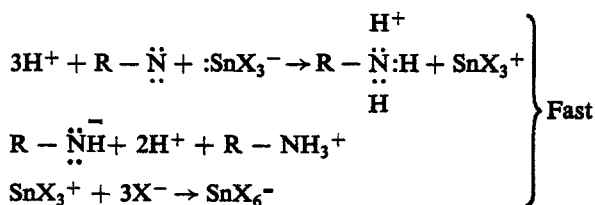
Protonation



Electron pair transfer (slow step):



The fragments all form products rapidly by the following conjectured processes.



II is the rate determining step.

Aquated Sn(II) does not react with methyl orange.¹ Halide or other ligands are essential.

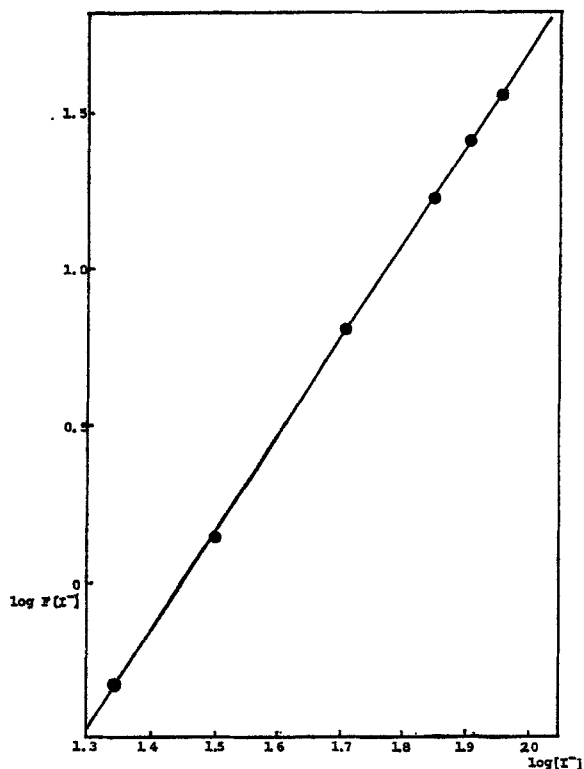


FIGURE 4 A plot of $\log F([I^-])$ vs. $\log [I^-]$ for $[I^-] < 0.1$ giving a very accurate straight line of slope 3.02.

TABLE V
Iodide System: High $[I^-]$
Ionic Strength 4M $C_{MeO} \approx 0.01$ mM

$C_I \approx [I^-]$ M	$10^3 \cdot k_{obs}$ $C_{Sn} = 0.24$ mM $C_H = 0.067$ M sec ⁻¹	$10^3 \cdot k_{obs}$ $C_{Sn} = 0.58$ mM $C_H = 0.267$ M sec ⁻¹	P	Pk_{obs}/C_{Sn} observed M ⁻¹ sec ⁻¹	Pk_{obs}/C_{Sn}^a calculated M ⁻¹ sec ⁻¹
.267	3.76		7.00	0.255	.258
.533	5.05		52.6	2.58	2.55
.800	4.40		287.1	12.25	12.00
1.067	3.55		1200	41.3	42.7
1.333	3.05	29.2	4270	1.257×10^2	1.300×10^2
1.600	2.60	24.3	1.36×10^4	3.37	3.50
1.867	2.25	23.2	3.74	8.41	8.54
2.133		20.6	9.28	1.91×10^3	1.91×10^3
2.400		18.0	2.08×10^5	3.74	3.95
2.933		15.8	9.13	1.44×10^4	1.443×10^4
3.467		14.6	30.6	4.47	4.34

$$Pk_{obs} = [H^+]C_{Sn}(k_3\beta_3[I^-]^3 + k_5\beta_5[I^-]^5 + k_7\beta_7[I^-]^7)$$

^a The results were obtained with:

$$k_3\beta_3 = 6.75 \times 10^4 \quad k_3 = 500 \text{ M}^{-2}\text{sec}^{-1}$$

$$k_8\beta_8 = 8.38 \times 10^4$$

$$k_7\beta_7 = 3.93 \times 10^4$$

Evidently, only negative complexes such as SnX_3^- , SnX_4^- , and SnX_5^{3-} can attack protonated diazo groups which must be positively charged. It appears that $k_5 > k_4$ for Cl^- complexes. Probably ionic attraction binds tin(II) to $HMeO^+$ until reduction occurs. SnX_3^- is a soft base, unlikely to form strong σ bonds to nitrogen. SnX_n^{2-n} species are soft acids as well as bases when n is two or more. The increased covalent character of SnX_n^{2-n} for $n = 3$ or more suggests that in the higher complexes the lone pair finds itself in localized hybrid orbitals, more susceptible to attack than if it remained in the $6s^2$ orbital of the Sn atom.

Conclusions Sn(II) requires three halide ions to be coordinated to it to render it reactive toward methyl orange. Higher complexes become kinetically important at higher halide concentrations. This suggests that the retardation of the Sn(II) reduction of NH_3OH^+ by high $[Cl^-]$ is due to reactions of HCl with the Mo(VI) catalyst rather than to unreactivity of $SnCl_4^{2-}$, $SnCl_5^{3-}$, etc.

It should be noted that interpretation of data depends completely on results of equilibrium studies concerning the formation of SnX_n^{2-n} complexes. Results on SnI_n^{2-n} equilibria suggest the presence of SnI_6^{4-} and SnI_8^{6-} in solutions employed in this study. The high charge makes both species doubtful. Further, I^- is too large to pack $8I^-$ around an Sn^{2+} ion. At present, no other explanation will account for the equilibrium data, however.

It is perhaps worth noting that k_{obs} decreases at high $[I^-]$ according to a very simple law.

$$k_{obs} = \frac{k_3}{1 + K_4[I^-]}$$

where $K_4 = \beta_4/\beta_3$.

This law fits quite well the assumptions that:

- Only SnI_3^- reacts with methyl orange.
- SnI_4^- is the complex of highest n .

β_3 and β_4 as given in Table I for SnI_n^{2-n} fits these assumptions very well. We feel assured as to the demonstrated reactivity of SnX_3^- species but must report apparent reactivity of $SnCl_4^-$, SnX_5^{3-} and SnI_7^- with some reservations.

REFERENCES AND NOTES

- F. R. Duke and N. C. Peterson, *J. Phys. Chem.* **63**, 2076 (1959).
- G. P. Haight and Carl von Frankenberg, *Acta Chem. Scand.* **15**, 2026 (1961).
- G. P. Haight, Jr., J. Zoltewicz, and W. Evans, *Acta Chem. Scand.* **16**, 311 (1962).
- G. P. Haight, Jr., and J. Peterson, *Inorg. Chem.* **4**, 1073 (1965).
- G. P. Haight, Jr., C. H. Springer and Ole J. Heilmann, *Inorg. Chem.* **3**, 195 (1964).
- G. P. Haight, Jr., and Lars Johansson, *Acta Chem. Scand.* **22**, 961 (1968).
- R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt and U. G. Stolberg, *J. Am. Chem. Soc.* **87**, 685 (1965).
- R. V. Lindsay, Jr., G. W. Parshall and U. G. Stolberg, *Inorg. Chem.* **5**, 109 (1966).