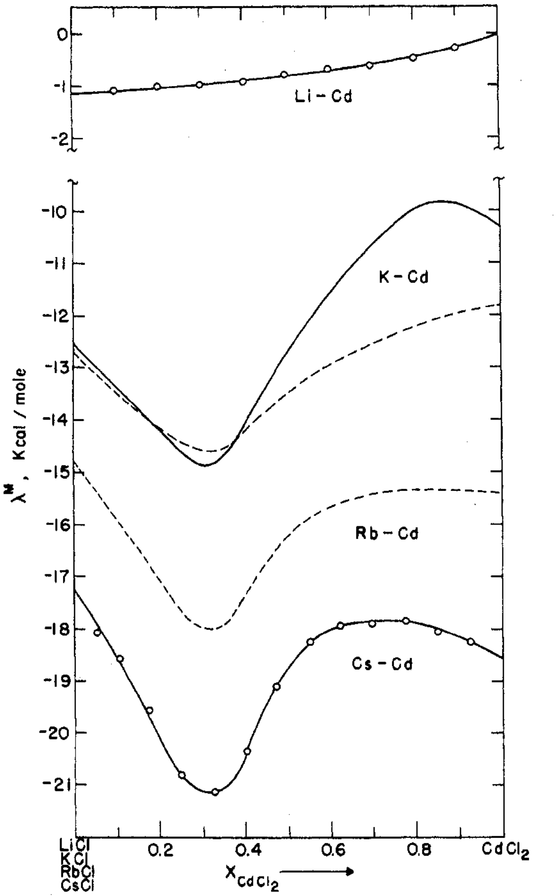

Figure 1.—Experimental enthalpy interaction parameters $\lambda^M = \Delta H^M/X_1(1 - X_2)$ *vs.* X_{CdCl_2} at 690° for the mixtures of $CdCl_2$ with LiCl and CsCl. Dotted curves give calculated values of λ^M for $CdCl_2$–RbCl and for $CdCl_2$–KCl. Solid curve for the latter system was calculated by Bredig[12] from the partial enthalpy data at 780° of Metzger, Brenner, and Salmon.[10]

Mg; A, A′ = K, Rb, Cs). For example, for the binaries of $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, and $MgCl_2$, with CsCl and RbCl, the ratios λ^M(Cs–M)/λ^M(Rb–M) at $X_{MCl_2} = {}^1/_3$ are 1.17, 1.15, 1.18, 1.17, and 1.19, respectively. In Table II we list some average values of the

TABLE II

	X_{MCl_2}			
	0	$^1/_3$	$^1/_2$	1
λ^M(Cs–M)/ λ^M(Rb–M)	1.16 ± 0.04	1.17 ± 0.02	1.17 ± 0.02	1.25 ± 0.05
λ^M(Cs–M)/ λ^M(K–M)	1.37 ± 0.07	1.44 ± 0.03	1.42 ± 0.06	1.58 ± 0.09

ratios λ^M(Cs–M)/λ^M(Rb–M) and λ^M(Cs–M)/λ^M(K–M), evaluated at different compositions of the mixture. If we assume that these ratios hold also for the $CdCl_2$–ACl binaries, we can use them to calculate the interaction parameters λ^M(Cd–Rb) and λ^M(Cd–K), from the curve for the $CdCl_2$–CsCl system. The calculated curves for λ(Cd–Rb) and λ(Cd–K) are given as dotted lines in Figure 1.[14] In this figure we give also the "experimental" interaction parameter curve for the $CdCl_2$–KCl system at 780°, calculated by Bredig[13] from the partial enthalpy data of Metzger, Brenner, and Salmon.[10] We see that there is quite good agreement between the two interaction parameter curves at mole fraction of $CdCl_2$ below about 0.5. However, the agreement is less satisfactory at higher contents of $CdCl_2$, where the difference between the two curves is as large as about 2.5 kcal/mol at $X_{CdCl_2} \approx 0.85$.

Due to the "intermediate" character of the NaCl–MCl_2[4] binaries the λ^M(Cs–M)/λ^M(Na–M) ratios (and the λ^M(Cs–M)/λ^M(Li–M) ratios) vary as much as 50% for the different MCl_2–ACl systems. Thus a reliable estimate of λ^M for the $CdCl_2$–NaCl mixtures is not possible.

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[14] The dotted curves drawn in Figure 1 are the result of a somewhat more laborious calculation of the λ^M(Cs–M)/λ^M(A–M) ratios, including compositions other than those listed in Table II.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF IOWA, IOWA CITY, IOWA 52240

Mechanistic Implications of the Role of Phenol in the Uranium (IV)-Chlorine(III)-Phenol Reaction

BY EUGENE B. GRIMLEY, ROBERT BUCHACEK, AND
GILBERT GORDON*[1]

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Evidence has been reported for the presence of a reactive chlorine intermediate in the reaction of uranium(IV) with chlorine(III) in acidic aqueous solution.[2] When phenol is added to this system as an initial reactant, the resultant kinetics, stoichiometry, and product identification indicate that an intermediate chlorine species has been scavenged by phenol. The purpose of this note is to discuss the results of the present study which was aimed at the determination of the scavenged intermediate chlorine species in the above reaction.

The stoichiometry of the uranium(IV)–chlorine(III) reaction was reported to be variable in the absence of phenol. The criterion for monitoring reactant stoichiometry was the $([Cl(III)]/[U(IV)])_{consumed}$ ratio. In the absence of phenol, this ratio was found to vary from 1.5 to 2.5, depending upon reaction conditions. The reaction was accompanied by the production of chlorate ion as one of the products. The formation of chlorate ion under the strongly reducing conditions imposed by uranium(IV) and a greater than expected consumption of chlorine(III) are two unusual features of the reaction

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[1] To whom correspondence should be addressed.

[2] G. Gordon and F. Feldman, *Inorg. Chem.*, 3, 1728 (1964).

that are consistent with the mechanism

$$\mathrm{U(IV) + Cl(III) \longrightarrow U(VI) + Cl(I)} \qquad \text{slow} \tag{1}$$

$$\mathrm{Cl(I)} + x\mathrm{Cl(III)} \longrightarrow y\mathrm{Cl^-} + z\mathrm{ClO_3^-} \qquad \text{fast} \tag{2}$$

$$\mathrm{U(IV)} + (1 + x)\mathrm{Cl(III)} \longrightarrow \mathrm{U(VI)} + y\mathrm{Cl^-} + z\mathrm{ClO_3^-} \tag{3}$$

The first step of the overall reaction is rate determining and produces chlorine(I) by a two-electron-transfer process which is effected by oxygen atom transfer[3] from chlorine(III) to uranium(IV). Chlorine(I) refers to hypochlorous acid which would be the predominant species in the acid range of 0.18–1.50 *M* perchloric acid. (The use of chlorine(I) eliminates the necessity to differentiate between the species HOCl, OCl^-, and Cl^+.) The reaction between hypochlorous acid and chlorine(III) has been reported by Emmenegger and Gordon to be rapid.[4] Therefore, the chlorine(I) formed in reaction 1 could react rapidly in a second step with chlorine(III) to produce the observed stoichiometry and chlorate ion.

Feldman and Gordon[2] reported that the reactant stoichiometry is reduced to 1:1 when phenol is initially added to the uranium(IV)–chlorine(III) reaction in the range of 0.18–1.5 *M* $HClO_4$ at 25°. Gordon and Buchacek[5] have determined the simplified rate law for the uranium(IV)–chlorine(III)–phenol reaction in 0.11–1.5 *M* perchloric acid at 25° to be

$$-\frac{\mathrm{d[U(IV)]}}{\mathrm{d}t} = k_{\mathrm{obsd}}\frac{\mathrm{[U(IV)][Cl(III)]}}{\mathrm{[H^+]}} \tag{4}$$

In 2 *M* ionic strength and 0.1 *M* phenol, the value of k_{obsd} is 13.1 ± 0.2 $\mathrm{sec^{-1}}$ at 25°.

The apparent role of phenol is to scavenge an intermediate chlorine species. What is the chlorine-containing species? In order to answer this question, a rate comparison must be made to determine which of the known chlorine species are able to react with phenol rapidly enough to account for the observed scavenger reaction.

Table I summarizes the results found[2,6,7] for the reaction of known chlorine oxidants with phenol. The reaction comparison is made under conditions of 1.00 *M* perchloric acid, unit ionic strength, and 25°, except where noted.

A comparison of calculated half-lives extrapolated from the work of Emmenegger and Gordon[4] on the reactions of hypochlorous acid with chlorous acid and of chlorine with chlorous acid are shown in Tables II and III. The extrapolated half-lives are calculated under the same conditions used for comparison of the potential scavenger reactions. The chlorine–chlorous acid reaction was assumed to be first order in both reactants.

TABLE I

A COMPARISON OF ESTIMATED HALF-LIVES FOR REACTIONS BETWEEN PHENOL AND CHLORINE OXIDANTS WITH 0.100 *M* PHENOL

Oxidant in reaction with phenol[a]	Estd half-lives, sec	Conditions and remarks	Ref
ClO_4^-	$>10^6$	No reaction in 1 month	2, 6
ClO_3^-	$>10^5$	No reaction in weeks	2, 6
ClO_2	15	$[C_6H_5OH]_0 \gg [ClO_2]$	6
ClO_2^-	$>10^3$	No reaction in hours	2, 6
$HClO_2$	>180		2, 6
$[Cl_2O_2]$[b]	<0.0001	Indirect evidence	2, 6
HOCl	14	Ag^+ present[c]	7
Cl_2	0.0003[d]	$[C_6H_5OH] \gg [Cl_2]$	6

[a] The following reactivity order with phenol is established: $[Cl_2O_2] \approx Cl_2 \gg HOCl \approx ClO_2 > HClO_2 > ClO_2^- \approx ClO_3^- > ClO_4^-$. [b] Not directly observed but implied by indirect evidence. [c] Silver perchlorate was present to suppress the formation of chlorine from hypochlorous acid dissociation. [d] Predicted half-life at 5°.

TABLE II

CALCULATION OF SECOND-ORDER RATE CONSTANTS FROM THE CHLORINE(0)–CHLORINE(III) INTERACTION DATA IN 0.8 *M* PERCHLORIC ACID AT 23°

10^3[Cl(III)], *M*	10^3[Cl(0)], *M*	Reported half-lives,[a] sec	Calcd rate constants × 10^{-4}, M^{-1} $\mathrm{sec^{-1}}$
2.54	1.27	0.030 ± 0.002	1.06
1.27	0.64	0.060 ± 0.003	1.06
1.27	1.27	0.063 ± 0.002	1.25
		Av	1.1 ± 0.1

[a] Half-lives are reported[4] for the production of chlorine dioxide.

TABLE III

CALCULATION OF SECOND-ORDER RATE CONSTANTS FROM THE CHLORINE(I)–CHLORINE(III) INTERACTION DATA IN 0.2 *M* PERCHLORIC ACID AT 25°

$10^3[HClO_2]$, *M*	10^3[HOCl], *M*	Temp, °C	Reported half-lives,[a] sec	Calcd rate constants[b] at 25°, M^{-1} $\mathrm{sec^{-1}}$
0.29	0.29	23	3.5	985
18.0	0.15	23	0.84	46
0.90	9.0	11	0.08	∽1900
0.50	0.50	11	6.2	∽540
0.90	9.0	1	0.15	∽2000

[a] Reported[4] half-lives were for the production of chlorine dioxide. [b] Based on an activation energy of ~11 kcal/mol and a preexponential factor of 10^{11}.

An important factor in the rate comparison is the effect of chloride ion on the reaction with hypochlorous acid, as illustrated by the equation

$$\mathrm{HOCl + Cl^- + H^+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cl_2 + H_2O}$$

Eigen and Kustin have reported[8] k_f for the forward reaction to be 1.8 × 10^4 M^{-2} $\mathrm{sec^{-1}}$ at 20°. At 5°, the third-order rate constant has been determined in this laboratory[6] by means of a stopped-flow experiment to

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[3] Oxygen transfer from chlorine(III) to the uranium(VI) product rules out the possibility of a uranium(V) intermediate for the primary pathway: *cf.* D. M. H. Kern and G. Gordon in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, Oxford, 1964, p 655; G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).

[4] F. Emmenegger and G. Gordon, *ibid.*, **6**, 633 (1967).

[5] R. J. Buchacek and G. Gordon, to be submitted for publication.

[6] E. Grimley and G. Gordon, to be submitted for publication.

[7] P. B. D. de la Mare, A. D. Ketley, and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

[8] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).

be ~$1.1 \times 10^4\ M^{-2}\ \mathrm{sec}^{-1}$. An estimated value of $2.1 \times 10^4\ M^{-2}\ \mathrm{sec}^{-1}$ at 25° is consistent with the values reported at 5 and 20°.

For purposes of comparison, the reaction of 0.035 *M* uranium(IV) with 0.035 *M* chlorine(III) in the presence of 0.054 *M* phenol at 25° and 1.00 *M* perchloric acid has a half-life of about 2.2 sec. The reaction[2,9] of 0.035 *M* uranium(IV) and 0.034 *M* hypochlorous acid in 1.00 *M* perchloric acid at 25° has a half-life of about 27 sec. The reaction of 0.054 *M* phenol with 0.034 *M* hypochlorous acid in 1.00 *M* perchloric acid at 25° has a half-life of about 26 sec. This comparison shows that chlorine(III) reacts faster with uranium(IV) than does hypochlorous acid and that the phenol–hypochlorous acid reaction is not fast enough markedly to inhibit the reaction of hypochlorous acid with uranium(IV).

The hypochlorous acid–chlorine(III) interaction is fast enough such that the hypochlorous acid reaction with phenol *cannot* account for the scavenger reaction. The reaction between phenol and the scavenged chlorine species *must* be competitive with the hypochlorous acid–chlorine(III) interaction and *must* be much faster than the uranium(IV)–chlorine(III) reaction.

However, the reaction of chlorine with phenol can be competitive with the hypochlorous acid–chlorine(III) interaction if a sufficient chloride ion concentration is present in the reaction mixture to produce chlorine from hypochlorous acid. (Reagent grade sodium chlorite used in these reactions was analyzed and found to contain 0.47% sodium chloride.) For purposes of comparison, the extent of formation of chlorine and its subsequent fate, along with the extent of formation of the chlorine-containing $[Cl_2O_2]$ intermediate,[4,10,11] have been calculated for two sets of conditions.

The first comparison is made for a solution of 0.035 *M* chlorous acid, 1.0 *M* perchloric acid, 0.1 *M* phenol, and 0.035 *M* uranium(IV) at 25°. The hypochlorous acid formed upon reduction of chlorine(III) by uranium(IV) could react with chlorine(III) to give the $[Cl_2O_2]$ intermediate or it could react with chloride ion to give chlorine. Under these conditions, the half-life for the reaction of hypochlorous acid with chlorine(III) has a lower limit of 0.01 sec. The chloride ion concentration, due to the sodium chloride impurity in the sodium chlorite, is $2.6 \times 10^{-4}\ M$. From this chloride ion concentration, an upper limit of 0.1 sec for the half-life for production of chlorine due to the hypochlorous acid–chloride ion reaction is calculated. Once formed, chlorine will react faster with phenol than with chlorine(III) by a factor of approximately 14, but some $[Cl_2O_2]$ will be formed owing to the competitive chlorine(III)–hypochlorous acid reaction.

The second comparison is made for a solution of $10^{-3}\ M$ chlorous acid, 1 *M* perchloric acid, 0.054 *M* phenol, and $5 \times 10^{-3}\ M$ uranium(IV) at 25°. Under these conditions, the half-life for the reaction of hypochlorous acid with chlorine(III) has a lower limit of 0.35 sec. The chloride ion impurity in the sodium chlorite is $7 \times 10^{-6}\ M$. From this chloride ion concentration, an upper limit of 4 sec for the half-life for production of chlorine due to the hypochlorous acid–chloride ion reaction is calculated. Once formed, the chlorine will again react faster with phenol than with chlorine(III) by a factor of approximately 20, but once again, reasonable concentrations of $[Cl_2O_2]$ will have been formed.

It is evident from these results, summarized in Table IV, that at least 10% of the hypochlorous acid formed by the reduction of chlorine(III) by uranium(IV) would react with chloride ion to form chlorine. The remainder of the hypochlorous acid would be involved in the formation of $[Cl_2O_2]$ owing to the hypochlorous acid–chlorine(III) reaction. Concomitantly, the chlorine and $[Cl_2O_2]$ formed would react with phenol to produce *o*- or *p*-chlorophenol. Thus, the intermediate species scavenged by phenol must be chlorine *and* $[Cl_2O_2]$. It is to be emphasized, however, that the chloride ion concentration could not be so high such that chlorine could account for the entire amount of chlorine species scavenged by phenol. (Concentrated uranium(IV) solutions, ~0.18 *M*, have been shown to have less than $5 \times 10^{-4}\ M$ chloride ion present.) The fact that neither chlorine(V) nor chlorine dioxide is formed under these conditions implies that direct reaction of the $[Cl_2O_2]$ intermediate must occur with phenol. Furthermore, at a pH greater than or equal to 1, the scavenged species must be almost entirely the $[Cl_2O_2]$ intermediate.

TABLE IV

COMPARISON OF HALF-LIVES FOR REACTIONS POTENTIALLY INVOLVED IN THE SCAVENGER REACTION OF PHENOL IN THE URANIUM(IV)–CHLORINE(III)–PHENOL REACTION IN 1.00 *M* PERCHLORIC ACID AT 25°

Reaction	Calcd half-life, sec	
	For 0.035 *M* chlorous acid[a]	For 10^{-3} *M* chlorous acid[b]
$HOCl + HClO_2 \longrightarrow [Cl_2O_2]$	≥ 0.01[c]	≥ 0.35
$HOCl + Cl^- \longrightarrow Cl_2$	≤ 0.1[d]	≤ 4
$Cl_2 + HClO_2 \longrightarrow [Cl_2O_2]$	≥ 0.002	≥ 0.06
$Cl_2 + C_6H_5OH \longrightarrow ClC_6H_4OH$	0.00015	0.0003

[a] The calculated half-lives for reaction of 0.035 *M* uranium(IV) with 0.035 *M* chlorine(III) in the presence of 0.1 *M* phenol. [b] The calculated half-lives for reaction of $5 \times 10^{-3}\ M$ uranium(IV) with $10^{-3}\ M$ chlorine(III) in the presence of 0.054 *M* phenol. [c] The calculated half-life is a minimum value based on the data calculated from Table II. [d] The maximum $t_{1/2}$ is calculated from the amount of NaCl impurity in Matheson Coleman and Bell reagent grade sodium chlorite. Analysis shows >99% $NaClO_2$ with 0.47% NaCl. The remaining impurity is assumed to be due to $NaClO_4$. It should be noted that this amount of chloride ion in reactions containing chlorous acid is a minimum, not accounting for chloride ion produced during the reaction.

Based on these arguments, the following mechanism is presented

$$U(IV) + Cl(III) \longrightarrow U(VI) + Cl(I) \qquad \text{slow} \qquad (5)$$

$$Cl(I) + Cl(III) \longrightarrow [Cl_2O_2] \qquad t_{1/2}^{a} \qquad (6)$$

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[9] R. A. Silverman and G. Gordon, to be submitted for publication.
[10] H. Taube and H. Dodgen, *J. Amer. Chem. Soc.*, **71**, 3330 (1949).
[11] H. Dodgen and H. Taube, *ibid.*, **71**, 2501 (1949).

$$\mathrm{Cl(I)} + \mathrm{Cl}^- \longrightarrow \mathrm{Cl_2} \qquad t_{1/2}^{\mathrm{b}} \qquad (7)$$

$$[\mathrm{Cl_2O_2}] + \mathrm{C_6H_5OH} \longrightarrow \mathrm{ClC_6H_4OH} + \mathrm{H}^+ + \mathrm{Cl(III)} \qquad \text{fast} \qquad (8)$$

$$\mathrm{Cl_2} + \mathrm{C_6H_5OH} \longrightarrow \mathrm{ClC_6H_4OH} + \mathrm{H}^+ + \mathrm{Cl}^- \qquad \text{fast} \qquad (9)$$

where $t_{1/2}^{\mathrm{a}} \leq (0.1)t_{1/2}^{\mathrm{b}}$.

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