For fields varying in direction this reduction fails. For example in a radial field we have potential and ion densities functions of r only. Let the radial component of $\bar{E}$ be $\bar{R}(r)$, the others vanishing. Then it can be shown that the radial component of (5) reduces to

$$\frac{D}{8\pi r^4}\frac{\mathrm{d}}{\mathrm{d}r}(r^2\bar{R})^2 = \frac{\mathrm{d}p}{\mathrm{d}r}$$

This relation between p and $\bar{R}$ cannot be integrated without knowledge of the manner in which one of them depends upon r.

Summary

The Poisson–Boltzmann equation for solutions of electrolytes is derived by postulating a state of balance between the electrostatic forces and the thermal pressure due to the Brownian movement of the ions. The same assumption is required as in the usual derivation, namely, that the average force on any ion can be calculated from the average field. Using this approximation, the average interionic force on the contents of any specified volume can be derived from a stress tensor identical in form with that familiar in electrostatic theory, except that its components involve the squares of the average field components rather than the average of their squares. In the case of a uni-directional problem such as that of the forces on a plane phase boundary, the method leads at once to a first-order differential equation for the average potential.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Chain Mechanisms for the Reaction of Chlorine and Oxalic Acid

BY HENRY TAUBE

In an earlier paper,[1] it was shown that certain reducing agents and oxidizing agents which are capable of acting by one-electron changes induce the addition of chlorine to maleic acid by a chain mechanism. Numerous data on the kinetics of the reaction and observations on the effect of various substances as inhibitors made it appear likely that atomic chlorine[2] and an organic free radical were the chain carrying substances.

Similar effects can be expected in other reactions of chlorine with reducing agents. The present paper contains the results of a study of the mechanism of the reaction[3]

$$Cl_2 + H_2C_2O_4 \longrightarrow 2H^+ + 2Cl^- + 2CO_2$$

induced by Fe^{++}. At sufficiently high concentrations of hydrogen ion and chloride ion, the spontaneous reaction of chlorine and oxalic acid[3] becomes slow enough so that the induced reaction can be studied conveniently.

Many of the observations reported here are analogous to those made in the earlier study[1] and the general conclusions reached there are confirmed. All the data on the Fe^{++} induced reaction of chlorine and oxalic acid are consistent with the following steps.

Chain initiating step

$$Fe^{++} + Cl_2 \longrightarrow Fe^{+++} + Cl_2^- \text{ or } FeCl^{++} + Cl \quad (1)$$

Chain carrying steps

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \text{ (rapid equilibrium)}$$

$$Cl + HC_2O_4^- \xrightarrow{k_2} H^+ + Cl^- + C_2O_4^- \quad (2)$$

$$C_2O_4^- + Cl_2 \xrightarrow{k_3} Cl + Cl^- + 2CO_2 \quad (3)$$

Chain breaking steps

$$Cl + C_2O_4^- \xrightarrow{k_4} Cl^- + 2CO_2 \quad (5)$$

$$Cl + Cl \xrightarrow{k_5} Cl_2 \quad (4)$$

Whether reaction (4) or (5) predominates as the chain-breaking step depends on the ratio of the chlorine and oxalic acid concentrations.

Substances which were observed to affect the rate of addition of chlorine to maleic acid by the chain mechanism are found to affect also the rate of the chain reaction of chlorine with oxalic acid. A striking difference in behavior is observed however. Co^{++}, Ce^{+++}, Mn^{++}, Vo^{++} and other ions all inhibit the induced addition of chlorine to maleic acid. While some of these inhibit the induced reaction of chlorine and oxalic acid, some enhance the rate of the reaction and some in fact enhance the rate under certain conditions, and reduce the rate under others. These observations can be explained in terms of simple, chemically reasonable reactions. The explanation advanced furthermore finds support in extensive work to be published later.

Experimental Methods

The experimental method differed from that employed in the previous work only in some details. Two stopcocks

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[1] Taube, THIS JOURNAL, **65**, 1876 (1943).

[2] Taube and Bray, *ibid.*, **66**, 3369 (1940), presented evidence that at 0° and chloride ion concentrations in excess of 0.01 *M*, atomic chlorine is largely associated with Cl^-. This evidence was not conclusive, and since the present work contributes no further data bearing on this point, the powerful one-electron oxidizing agent in the system under study is for simplicity called atomic chlorine and is represented by Cl.

[3] Griffith and McKeown have published results on the spontaneous reaction: *Trans. Faraday Soc.*, **28**, 518 (1932). Their data are consistent with a mechanism involving as slow step the reaction of $HC_2O_4^-$ with HOCl.

in series were used in the inductor buret, thus making convenient a wide variation in the rate of addition of the inducing agent solution. Certain refinements in the handling of the chlorine solution and in the procedure led to increased precision.

As before, inducing agent was added slowly, with violent stirring of the cell contents, to the solution containing chlorine, the oxalic acid and other substances, all at known concentrations. The quantities measured were: initial and final concentrations of chlorine (hence the final concentration of oxalic acid since the initial concentration was known) volume of inducing agent solution of known strength and the time taken for the reaction.

The chlorine concentration was determined iodometrically. A complication, which in most experiments was trivial, is introduced because the oxidation of I^- by Fe^{+++} is incomplete within the time of analysis when the concentration of oxalic acid is high. For experiments in which the amount of ferrous ion added was appreciable as compared to the total amount of chlorine consumed, the procedure was modified. Dipotassium hydrogen phosphate solution was added to the solution for analysis, in amount sufficient to stabilize the system with respect to the oxidation of I^- by Fe^{+++}. The titration of the iodine liberated under these conditions gives the total decrease in chlorine: that consumed in oxidizing both Fe^{++} and oxalic acid. The amount of Fe^{++} added was measured, and therefore the change in the amount of oxalic acid could be computed.

Materials.—Chemicals were c. p. quality, used without further purification. The solutions were made up using conductivity water. The solutions of oxalic acid and hydrochloric acid were given a preliminary treatment before use: chlorine was added and they were left exposed to laboratory light for several days.

Conditions.—Unless otherwise stated, the solutions in the cell were made 2 *M* with respect to hydrochloric acid. The majority of the data were obtained at 25.0°; some experiments at 0.2° are also reported.

Definitions and Units

Time, *t*, is expressed in minutes, concentration in moles per liter. (Oxalic) refers to concentration of the total oxalate present.

Δ represents the change in (oxalic) produced by the induced reaction. *R* represents the average rate of addition of the ferrous ion, expressed in moles per liter per minute. *A* represents the number of moles of ferrous ion added per liter of solution. The chain length is defined as the change in total oxalate, divided by *A*. *K* represents the first dissociation constant for oxalic acid.

The correction for the spontaneous reaction, usually less than 5% of the total effect, has been applied to all the data reported.

Results and Discussion

Table I contains a body of data on the kinetics of the induced reaction for the range of relatively high values of $(Cl_2)/(\text{oxalic})$ at 2 *M* hydrochloric acid. The specific rate *k* is defined by the relation

$$-\,d(\text{oxalic})/dt = k(R)^{1/2}(\text{oxalic}) \qquad \text{(I)}$$

If, as is true in the experiments of Table I, the fractional change in the concentration of oxalic acid is small, the corresponding integrated form is

$$\Delta R^{1/2}/\overline{(\text{oxalic})}A = k \qquad \text{(II)}$$

This form was used in testing the validity of the rate law.

Examination of the data in Table I shows that over wide ranges of the variables (oxalic), (Cl_2), *R* and *A* and for the consequent great variations in chain length, the rate law represents the data with considerable fidelity. Under extreme conditions, deviations do occur (Experiments 4 and 14). It will be shown, however, that the rate law as well as the deviations from it are consistent with the mechanism proposed in the introduction. The average value for *k*, excluding experiments in which the rate law fails, or those for which experimental accuracy is low, is 0.405. This value is regarded as fixed within 1 to 2%.

TABLE I

THE INDUCED REACTION AT HIGH VALUES OF (Cl_2)/(OXALIC)

HCl = 2 *M*; temp. 25°; *R* = rate at which Fe^{++} is added in moles per liter per min.; *A* = amount of Fe^{++} added in moles per liter; Δ = change in total oxalate concentration; *k* is defined in the text.

No.	(Cl_2) × 10^2	$\overline{(\text{Oxalic})}$	$\Delta \times 10^3$	*A* × 10^4	*R* × 10^4	Chain length	*k*
1	3.5	0.176	4.85	6.03	0.778	8.1	0.043
2	1.68	.207	1.67	4.04	4.04	6.6	.401
3	1.68	.217	3.25	4.70	1.58	6.9	.402
4	0.68	.205	1.20	13.8	30.7	8.7	.236
5	.68	.207	1.74	1.91	0.820	9.1	.403
6	.68	.210	1.59	0.583	.0955	27.3	.401
7	.68	.190	0.967	.187	.0220	5.2	.403
8	.68	.198	.748	.0690	.00553	108	.405
9	.68	.363	1.86	.871	.497	21.3	.414
10	.68	.0927	1.71	1.73	.145	9.9	.406
11	.68	.106	1.25	0.523	.0337	23.9	.414
12	.68	.0606	1.27	1.83	.118	6.9	.394
13	.68	.0200	0.485	1.93	.0965	25.1	.384
14	.14	.211	1.081	0.575	.0925	18.8	.269
15	.14	.0675	0.291	.144	.0190	20.2	.413
16	.14	.0341	.205	.231	.240	8.9	.405
17	.14	.0171	.121	.229	.0173	5.3	.407
18	.14	.00686	.139	.960	.0362	1.4	.402

A reaction scheme consisting of the steps 1, 2, 3, 5 and the rapid acid equilibrium, under the condition that the rate of atomic chlorine production by step 1 is given by *R*, leads to the form of rate law experimentally observed with the over-all specific rate *k* equal to $\dfrac{k_2K}{\sqrt{k_5}\,(H^+ + K)}$.[4]

The above-mentioned condition will be fulfilled if ferrous ion does not accumulate appreciably during the reaction, if it is fairly uniformly distributed throughout the solution before reaction with chlorine, and if the only reaction it undergoes is reaction 1.

Since the duration of the reaction in all cases exceeded twenty seconds, it seems certain that the first requirement was always fulfilled. That the second requirement was also fulfilled was demonstrated by the observations that at the stirring rates employed a threefold change in the rate of stirring did not appreciably alter the value of *k* measured, nor was the value altered noticeably by substituting a cell with fluted walls for the one most commonly employed.

Internal evidence that the third requirement was also met is the agreement of the results over a

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[4] The rate of reaction 5 is defined as $k_5(Cl)^2$.

wide range of the values of R. However, at sufficiently high values of R, with other variables appropriately set, there is a deviation from the rate law (experiment 4) consistent with the reaction of Fe^{++} with reactive intermediates, Cl or $C_2O_4^-$, as well as with chlorine. Table II presents additional data bearing on this point. Experiment 4 of Table I is included in Table II under the same number.

TABLE II

THE INDUCED REACTION AT HIGH VALUES OF R

$(HCl) = 2\ M$; temp. = 25.0°

No.	(Cl_2) × 10^2	(Oxalic)	Δ × 10^3	A × 10^4	R × 10^4	k
1	0.69	0.0841	0.848	13.2	16.4	0.310
2	.69	.0840	0.527	13.9	41.3	.290
3	.69	.210	1.67	11.3	15.0	.272
4	.68	.205	1.20	13.8	30.7	.236
5	1.72	.214	1.88	13.7	33.0	.368

On the basis of the mechanism presented, reaction of Fe^{++} with the reactive intermediates is expected at sufficiently high values of R. This follows from a consideration of the variation with R of the stationary concentration of Fe^{++} and Cl or $C_2O_4^-$ for the range of values of R in which reaction 5 remains the principal chain breaking step. It can be seen that the rate of reaction 5 varies directly with R; however, the rate of reaction of Cl or $C_2O_4^-$ with Fe^{++} varies with $R^{3/2}$, since (Fe^{++}) varies directly with R and (Cl) or $(C_2O_4^-)$ with $R^{1/2}$. At high values of R, the contribution by reaction of Fe^{++} to the chain breaking process will therefore increase, and the observed values of k in this range will decrease.

The data of Table II require that $C_2O_4^-$ rather than Cl reacts with Fe^{++} to break chains. This somewhat surprising conclusion follows since the deviation of k from the normal value increases with the ratio $(oxalic)/(Cl_2)$, and an increase in this ratio means that $(C_2O_4^-)$ increases relative to (Cl). Comparison of the present results with those presented[1] for the reaction of chlorine and maleic acid supports the conclusion reached above. In the latter work, no decrease of an analogous "k" was observed at values of R considerably higher than those of the present work. Since atomic chlorine is common to both systems at corresponding concentrations, the organic radicals must be responsible for the difference in the behavior of the systems.

It seems unlikely that the specific rate of reaction of $C_2O_4^-$ with Fe^{++} is greater than that of Cl with Fe^{++}, and the predominance of the first reaction must mean that $C_2O_4^-$ is present at a higher concentration in the system than is Cl.

k is observed to decrease also at very low values of R. The value of R at which the decrease sets in varies from one set of solutions to another, and the effect is therefore not an intrinsic characteristic of the system under study. It can be attributed to the reaction of atomic chlorine with residual inhibitors; such a reaction will increase in importance relative to reaction 5 at low values of R since it is of lower order with respect to atomic chlorine concentration. If the solutions are subjected to the photochemical chlorine treatment before use, much lower values of R are tolerated before the effect sets in than is otherwise the case. Solutions left exposed to air fairly rapidly accumulate the inhibitor. It seems likely that NH_4^+, which below is shown to decrease the induced effect, is an important one of the residual inhibitors in the solutions. The same substance may have been responsible for the failure of the analogous rate law at low value of R reported for the induced reaction of chlorine and maleic acid.[1]

When the ratio $(Cl_2)/(oxalic)$ decreases, rate law I fails (Table I, experiment 14) and the rate law

$$-d(\text{oxalic})/dt = k'[R(Cl_2)(\text{oxalic})]^{1/2} \qquad \text{(III)}$$

becomes valid. Data for the region of low values for $(Cl_2)/(oxalic)$ are presented in Table III. k' was calculated from the experimental data using the integrated form of rate law III

$$\frac{2\,[(Cl_2)_0{}^{1/2} - (Cl_2)_t{}^{1/2}]\,R^{1/2}}{(\text{oxalic})^{1/2}A} = k' \qquad \text{(IV)}$$

In an experiment, (oxalic) but not (Cl_2) remains substantially constant.

TABLE III

THE INDUCED REACTION AT RELATIVELY LOW VALUES OF $(Cl_2)/(OXALIC)$

$(HCl) = 2M$; temperature = 25.0°

No.	$(Cl_2)_0$ × 10^4	$(Cl_2)_t$ × 10^4	(Oxalic)	A × 10^5	R × 10^6	k'
1	10.85	3.05	0.387	2.95	10.65	5.5
2	10.70	5.58	.387	1.30	12.60	6.0
3	5.89	1.63	.387	2.22	11.00	5.5
4	13.25	8.79	.388	.565	2.42	6.0
5	5.00	2.80	.200	.666	2.17	5.6

The data at low values of $(Cl_2)/(oxalic)$ are not as reproducible as those for higher values of the ratio. The contribution of the spontaneous reaction appears to be erratic and the cause of this behavior was not discovered. The rate law proposed appears however to be reasonably well obeyed over the limited range investigated.

The explanation for the change in rate law from form I to form III as the ratio of chlorine to reducing agent decreases is presumably the same as that advanced for the similar effect previously reported.[1] On this basis k' is to be identified with $\left[\frac{k_2k_3}{2k_4}\frac{K}{K + (H^+)}\right]^{1/2}$.

It seems worthwhile to mention explicitly that the variation in order with respect to reactant concentration established for the present and previous systems is quite different from the case in which independent paths for a reaction vary in order with respect to a given reactant. In the latter case, the over-all order with respect to the given reactant increases as the concentration of reactant increases; in the present cases, a decrease in order as reactant concentration increases is observed.

From two experiments comparable to no. 10 of Table I in all respects except that the solution was 0.98 M rather than 2.00 M with respect to the concentration of hydrochloric acid, a mean value for k of 1.01 was obtained. Using for the first dissociation constants of oxalic acid in 1 and 2 M hydrochloric acid the values of 0.075 and 0.060,[5] $k_2/\sqrt{k_5}$ at the lower acidity becomes 14.2 and at the higher acidity, 14.0. These results provide the justification for formulating the reaction of atomic chlorine as being more rapid with $HC_2O_4^-$ than with oxalic acid. A small contribution by the latter process, as well as one involving $C_2O_4^=$ is not ruled out by the data, however.

The close agreement of the values of $k_2/\sqrt{k_5}$ at the two acidities may be fortuitous to some extent. The effect on K of a high concentration of potassium chloride may be different from that of hydrochloric acid, and the effect of ionic strength on the reaction was not settled. Results of the latter type are difficult to obtain since the small amounts of various metal ion impurities introduced with even a pure sample of potassium chloride can vitiate the results. The single experiment performed on this aspect of the problem led to no unambiguous conclusion and is omitted.

Table IV contains a summary of results on the induced reaction at 0.2°.

TABLE IV

THE INDUCED REACTION AT 0.2° C.

Ratio of (Cl_2/(oxalic) relatively high; (HCl) = 2 M.

No.	$(Cl_2)_0 \times 10^3$	(Oxalic)	$\Delta \times 10^3$	$A \times 10^4$	$R \times 10^6$	k
1	6.63	0.112	0.495	0.501	2.47	0.138
2	6.62	.107	0.871	1.93	10.72	.143
3	8.10	.152	1.36	1.37	4.79	.144
4	15.9	.152	1.35	1.19	3.81	.144
5	6.6	.110	1.07	1.50	5.01	.144
					Mean	.142

The rate of reaction is observed to decrease almost threefold when the temperature changes by 25°. It is of interest to discuss the variation of the rate with temperature in terms of the variations of the specific rates k_2 and k_5, which together with K compose the over-all specific rate k. From the results of Drucker[6] it appears that K does not vary markedly with temperature; the values he measured for K in freezing point experiments and in conductivity experiments at 18° agree fairly closely. The variation of k with temperature is therefore attributed solely to the variations of k_2 and k_5. Applying the average values for k of 0.142 and 0.405 at 0.2 and 25°, respectively, to the Arrhenius equation, the over-all activation energy, $E_2 - (E_5/2)$ is found to be 6,900 cal. The activation energy of reaction 5 is probably very small, and an activation energy of about 7,000 cal. can therefore be ascribed to reaction 2. Comparison of this value for the activation of energy of reaction 2 with 15,000 cal. for the reaction of $HC_2O_4^-$ and hypochlorous acid,[3] and 18,000 for the reaction of I and $C_2O_4^=$[7] is of interest.

At 25° and $\mu = 2$, $k_2/\sqrt{k_5}$ is 14.0 and the pz factor for reaction 2 divided by the square root of the pz factor for reaction 5 is 1.4×10^6. If the pz factor for reaction 5 is assumed to have the "normal" value of about 10^{13}, that for reaction 2 becomes 5×10^{12}, which is also in the range of normal values.

The experiments reported in the remainder of the paper were devoted to a study of the effect at low concentration of various substances which themselves do not react rapidly with Fe^{++}, Cl_2 or $H_2C_2O_4$ (except possibly to form complexes with $H_2C_2O_4$) on the rate of the induced reaction. The experiments were limited to the range of chlorine, oxalic acid concentration ratios for which reaction 5 is the principal chain breaking step in the absence of inhibitors.

Table V contains the results of experiments with NH_4^+, VO^{++}, Ce^{+++} and Mn^{++} as the added substances.

In every case except experiment 24 of Table V, a decrease in k below the normal value of 0.40 is observed on addition of the ions listed.

The data will be discussed with reference to the mode of action of an "ideal" inhibitor, that is, one that behaves simply. The inhibitors, some of which are difficulty oxidizable substances, may be presumed to react with atomic chlorine as follows

$$Cl + In \longrightarrow Cl^- + In^+ \qquad (6)$$

and it is assumed that the higher valence state, In^+, of the added substance is regenerated rapidly by reaction with Fe^{++} or $C_2O_4^-$. If this simple situation is realized, $k_6/\sqrt{k_5}$ can be calculated from the data by applying the equation:

$$k_6/\sqrt{k_5} = R - \left(\frac{\Delta}{k(\text{oxalic})t}\right)^2 \frac{k(\text{oxalic})t}{2\Delta(\text{In})}$$

The constancy of the function on the right, f_{In}, as (Cl_2), (oxalic), (In) and R are varied will test the mechanism as applied to any particular substance as inhibitor.

For VO^{++}, alone out of the four inhibitors considered in Table V, does the value of f_{In} remain constant as the parameters mentioned above are varied. It seems justifiable to identify the average value of 42 observed for f_{In} in this case with $k_6/\sqrt{k_5}$ for VO^{++}.

The results with NH_4^+ are chiefly of interest in demonstrating that this substance, which is present at low concentration in the materials used, is indeed an inhibitor, and that its action as

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[5] Dawson, *J. Chem. Soc.*, 1889 (1929), reports the above values of K at 25° in 1 and 2 M potassium chloride, respectively.

[6] Drucker, *Z. physik. Chem.*, **96**, 404 (1920).

[7] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 394 (1933).

TABLE V

THE EFFECT OF NH_4^+, VO^{++}, Ce^{+++} AND Mn^{++}, EACH AT VARYING CONCENTRATION, ON THE RATE OF THE INDUCED REACTION

HCl = 2 *M*; temp., = 25.0°

No.	In	(In) × 10^4	$(Cl_2)_0$ × 10^3	(Oxalic)	Δ × 10^3	t	R × 10^6	k	f_{In}
1	NH_4^+	2.12	7.0	0.108	0.840	8.72	16.1	0.223	12.1
2	NH_4^+	2.14	6.6	.109	.604	18.60	5.25	.130	15.
3	NH_4^+	2.12	3.4	.108	.990	9.50	14.6	.254	9
4	VO^{++}	2.08	6.5	.106	.209	6.00	13.8	.089	39
5	VO^{++}	0.208	6.6	.106	.802	6.97	12.0	.312	43
6	VO^{++}	.208	3.3	.0423	.585	17.65	7.21	.292	43
7	VO^{++}	.208	3.5	.106	.870	13.69	4.90	.272	44
8	VO^{++}	1.02	3.4	.104	.541	2.75	63.2	.238	43
9	VO^{++}	0.515	3.4	.105	.765	8.65	12.9	.236	41
10	Mn^{++}	.104	6.6	.212	1.15	7.17	13.9	.203	270
11	Mn^{++}	.104	6.6	.212	1.10	6.37	16.7	.199	300
12	Mn^{++}	.103	6.6	.210	1.12	3.28	66.2	.200	600
13	Mn^{++}	.102	6.6	.209	0.948	1.63	177	.210	930
14	Mn^{++}	.102	6.6	.208	0.905	1.33	228	.217	1000
15	Mn^{++}	.042	6.6	.212	1.45	6.52	15.8	.264	420
16	Ce^{+++}	26	6.7	.106	0.349	16.87	4.25	.094	1.6
17	Ce^{+++}	26	6.6	.104	.344	8.83	18.0	.087	3.7
18	Ce^{+++}	26	6.0	.103	.258	3.08	65.0	.100	6.0
19	Ce^{+++}	26	6.7	.042	.492	13.13	8.1	.315	.3
20	Ce^{+++}	26	3.4	.107	.204	14.0	5.51	.183	3.1
21	Ce^{+++}	26	3.4	.106	.261	2.67	90.0	.098	7.2
22	Ce^{+++}	26	3.5	.042	.198	5.20	36.6	.150	2.7
23	Ce^{+++}	26	3.4	.042	.104	1.65	137	.128	6.4
24	Ce^{+++}	26	3.6	.021	.479	25.1	1.79	.67	...

such may account for the observed decrease in k at extreme low values of R. The data are insufficient to warrant discussion of the respects in which the inhibitory mechanism for NH_4^+ differs from the "ideal" case. Complex results can be expected in view of the numerous possibilities for higher valence states open for nitrogen and the possibility of contributions to the inhibitory effect by chlorinated derivatives of ammonia.

The general features of the variation of f_{In} for Ce^{+++} and Mn^{++} find a simple interpretation. It is known that the higher valence states Ce^{++++} and Mn^{+++} under the conditions of the experiments react rapidly with oxalic acid, and presumably oxidize it by a one-electron change

$$In^+ + H_2C_2O_4 \longrightarrow In + H^+ + HC_2O_4 \quad (7)$$

As the path corresponding to reaction (7) contributes more and more to the reduction of In^+, the efficiency of the inhibitor will decrease. This is consistent with the observation, Table V, that as R decreases the efficiency of the inhibitors as measured by the values of f_{In} decreases also. As R decreases the concentrations of Fe^{++} and $C_2O_4^-$ will decrease relative to oxalic acid, and reaction (7) will become increasingly important relative to reaction of In^+ with Fe^{++} or $C_2O_4^-$. At sufficiently low values of R, the sole fate of the higher valence may become reaction with oxalic acid. Under these conditions, the "inhibitor" may change over to a "positive catalyst" for the reaction, a type of behavior actually realized for Ce^{+++} (compare experiment 24 with others in Table V), and in principle realizable also for Mn^{++}.

At high values of R, as the fraction of In^+ which is reduced by Fe^{++} or $C_2O_4^-$ increases, f_{In} should approach the value of $k_6/\sqrt{k_5}$ for the inhibitor. The law of variation of f_{In} with R depends on whether In^+ is reduced mainly by Fe^{++} or $C_2O_4^-$, and in either case is very complex; consideration of either type of mechanism shows that f_{In} should vary with R, to a power less than 1. When f_{In} for Mn^{++} is plotted against $(1/R)^{1/2}$ the data extrapolate to a value of 1300 for f_{In} at high values of R. For Ce^{+++} the same type of plot yields an extrapolated value for f_{In} of about 9. In the latter case, data were obtained for varying values of (oxalic) and (Cl_2), and are consistent with a single value for f_{In} in the limit. It is suggested that under the conditions of the experiments (25°, 2 *M* hydrochloric acid and in the presence of oxalic acid) the values of $k_6/\sqrt{k_5}$ for Mn^{++} and Ce^{+++} are about 1300 and 9, respectively.

In the experiments with maleic acid in 1 *M* hydrochloric acid, values of $k_6/\sqrt{k_5}$ for Mn^{++}, VO^{++} and Ce^{+++} of *ca.* 800, 9 and 2 were reported. The relative order for the corresponding values in the present work is the same, but all are higher. Part of the discrepancy can be attributed to the differing ionic strengths in the two systems, and part to the influence of oxalic acid, which may form complexes even in the acid solutions. Perhaps the most important point to note is that the values of $k_6/\sqrt{k_5}$ reported in the previous work rested on insufficient data, and were not proved independent of the various concentration parameters and the possibility of some reaction analogous to (7) which would manifest itself in low values for $k_6/\sqrt{k_5}$ was not ruled out except for Mn^{++}.

Of the figures reported in this paper for $k_6/\sqrt{k_5}$ a degree of confidence is attached only to the value for VO^{++}. It seemed of interest to obtain data on the temperature coefficient of the reaction of atomic chlorine with VO^{++} and some experiments were conducted at 0.2° using VO^{++} as inhibitor, with the results recorded in Table VI.

TABLE VI

INHIBITION BY VO^{++} AT 0°; HCl = 2*M*

No.	(In) × 10^3	$(Cl_2)_0$ × 10^3	(Oxalic)	Δ × 10^3	*t*	*R* × 10^6	f_{In}
1	0.214	7.1	0.109	0.950	29.2	6.02	20
2	.642	7.0	.109	.705	28.6	6.59	20
3	1.07	7.5	.109	.590	31.9	6.52	20
4	1.07	7.6	.110	.433	35.9	4.17	21
						Mean	20.2

If the temperature coefficient of reaction 5 is again assumed to be small, the values for $k_6/\sqrt{k_5}$ of 42 and 20 at 25 and 0.2° lead to 4,900 cal. as the activation energy for reaction 6. On the assumption again of 10^{13} for the *pz* factor of reaction 5, that for reaction 6 is 5×10^{11}.

The observation that VO^{++} behaves as a simple inhibitor, while Mn^{++} and Ce^{+++} do not, correlates with the known greater oxidizing powers of the higher valence states for the last two substances. It is to be expected[8] that as the oxidizing power of the upper valence states of the inhibitor increases, the departure from the simple inhibitor behavior will increase. Results with Cu^{++}, Pr^{+++}, Co^{++} and Ni^{++} bear this out. Each of these substances when added to the solution, other conditions being about those fixed for the experiments reported in Table V, actually enhance the speed of reaction. The presumption is that Cu^{+++}, Pr^{++++}, Ni^{+++} and Co^{+++} react sufficiently rapidly with oxalic acid so that the effect of reaction (7) predominates over the effect produced by the reactions with Fe^{++} or $C_2O_4^{-}$. Comparison of Ce^{+++} and Pr^{+++} in this regard is particularly interesting.

The data for Cu^{++}, Pr^{+++} and Ni^{++} are not reported in detail, a few experiments only being recorded in Table VII to give some idea of the order of magnitude of the effects observed.

More complete data are reported for Co^{++}, Table VIII, since these results have a bearing on work to be published later.

TABLE VII

THE EFFECTS OF Cu^{++}, Pr^{+++} AND Ni^{+++} ON THE INDUCED REACTION

(HCl) = 2 *M*, temp. = 25.0°, $(Cl_2)_0 = 6.6 \times 10^{-3}$ *M*, (oxalic) = 0.042 *M*

No.	In	(In) × 10^3	Δ × 10^3	*A* × 10^5	*R* × 10^3	κ
1	Cu^{++}	0.262	0.782	0.772	4.15	0.485
2	Cu^{++}	1.30	.875	.733	4.28	.584
3	Pr^{+++}	1.30	.830	.830	4.66	.510
4	Ni^{++}	2.60	.765	.724	4.26	.507
5	Ni^{++}	5.18	.960	.756	3.96	.595

TABLE VIII

THE EFFECT OF Co^{++} ON THE INDUCED REACTION OF CHLORINE AND OXALIC ACID

HCl = 2 *M*; temp. = 25° except in expt. 11

No.	(In) × 10^2	$(Cl_2)_0$ × 10^{-1}	(Oxalic)	Δ × 10^3	*R* × 10^6	*k*	*k* × (oxalic)$^{1/2}$
1	0.104	0.068	0.085	1.53	5.23	0.50	..
2	5.23	.069	.106	1.73	6.95	.87	0.28
3	12.5	.063	.106	2.60	3.13	.96	.31
4	12.5	.067	.105	2.42	11.7	.81	.26
5	41.3	.068	.106	2.31	4.83	.95	.31
6	41.3	.058	.105	2.18	14.8	.75	.24
7	20.7	.035	.106	1.74	4.10	.75	.24
8	12.5	.069	.0208	1.97	2.90	2.4	.35
9	12.5	.071	.0207	1.18	14.5	1.7	.25
10	4.1	.069	.210	1.37	234	.382	..
11[a]	4.2	.068	.0214	0.06	20.5	.06	..

[a] Temp. = 0.2°; in the absence of Co^{++}, *k* = 0.142.

At sufficiently high values of (Co^{++}), the rate becomes independent of (Co^{++}) (compare experiment 4 with 6 and 3 with 5.) This effect is expected on the basis of the mechanism proposed; after sufficient Co^{++} is present to react with all the atomic chlorine formed, increasing the concentration should exert no further effect.

An attempt to unravel the kinetics of the reaction in the presence of high (Co^{++}) was not completely successful. No simple rate law describes the data under these conditions but some conclusions can be drawn from the trends in *k*.

As *R* increases, *k* decreases (compare experiments 3 with 4 and 5 with 6). This behavior implies that Fe^{++} is involved in breaking chains, possibly by reaction with Co^{+++}. The observation that *k* decreases somewhat as (Cl_2) decreases (compare experiments 5 and 7) is consistent with the conclusion above. At low chlorine concentrations the steady state concentration of Fe^{++} will be higher, and the reaction of Fe^{++} with Co^{+++} to break chains will increase in importance.

At high concentrations of Co^{++}, the rate of reaction is no longer first order with respect to oxalic acid concentration. Comparison of the value of *k* (oxalic)$^{1/2}$ in experiment 9 with 6 and 8 with 3 shows that square root order with respect to oxalic acid concentration probably holds.

Conditions favorable for observing inhibition by Co^{++} should be high *R* and a low temperature. The choice of the first factor follows from previous discussion, the second follows if it is accepted that the relatively slow reaction of Co^{+++}

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[8] The specific rate of the reaction of the upper valence states of the inhibitor with oxalic acid is smaller than it is for the reaction with Fe^{++}, and it presumably has a higher activation energy. It is therefore expected to be more sensitive in general to changes in the strength of the oxidizing agent.

with $H_2C_2O_4$ will have a higher temperature coefficient than the reaction of Co^{+++} with Fe^{++}. The results of experiments 10 and 11 show that inhibition by Co^{++} can indeed be realized by proper choice of conditions.

Two further points of comparison between the work on the reaction of chlorine and maleic acid, and the present work seem worthy of mention. The observation that all of the ions discussed here acted as inhibitors for the former reaction whereas some act as positive catalysts in the present study correlates with the slower reaction of the higher valence states (demonstrated for Ce^{++++}) with maleic acid as compared to oxalic acid. Inhibition by oxygen was marked in the former reaction; no significant effect of oxygen over a wide range of conditions was observed in the reaction under present study however.

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Summary

Results on the rate and kinetics of the reaction of chlorine with oxalic acid induced by ferrous ion, over a wide range of conditions are presented.

The data are interpreted by a chain mechanism involving atomic chlorine; this substance results from the reaction of ferrous ion with chlorine.

As the ratio of chlorine to oxalic acid decreases, the chain breaking step changes from an association of atomic chlorine to a reaction of this substance with the oxalate free radical.

Atomic chlorine reacts more rapidly with $HC_2O_4^-$ than with $H_2C_2O_4$. The activation energy of the former reaction is about 7,000 cal. and its pz factor about 5×10^{12}.

NH_4^+, VO^{++}, Ce^{+++}, Mn^{++}, Co^{++}, Cu^{++}, Ni^{++} and Pr^{+++} affect the rate of the reaction. Under the most usual conditions NH_4^+, VO^{++}, Ce^{+++} and Mn^{++} act as inhibitors, while the remaining ions enhance the induced effect.

Only VO^{++} functions as a simple inhibitor. The kinetics observed prove that atomic chlorine reacts with VO^{++}; the activation energy of this reaction is about 5,000 cal.

For the other metal ions, reaction of the upper valence state of the inhibitors with oxalic acid must also be considered. With Ce^{+++} and Mn^{++}, the effect of the reaction of the upper valence states with Fe^{++} or the oxalate free radical predominates in most of the experiments over the effect produced by reaction with oxalic acid; with Cu^{++}, Ni^{++}, Pr^{+++} and Co^{++}, the reverse is true.

The mechanism predicts conditions under which a negative catalyst can enhance the rate of reaction (observed for Ce^{+++}) and a positive catalyst can become an inhibitor (observed for Co^{++}).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Dipole Moments of Chlorobenzene, Monochlorocyclopropane, and 1,2-Dichlorocyclopropane, with a Calculation of the Exterior Valence Angle of the Cyclopropane Ring[1]

BY BERNARD I. SPINRAD

In recent years, dipole moments have been determined for the most part from radio frequency capacity data. While there is no objection to such procedures so long as dispersion is negligible, it appears that audio frequency bridge methods have been neglected for this purpose, although they form the basis for much of the work of testing engineers.[2] This is despite the fact that the only serious objection to them is that conductance effects, which are hardly ever appreciable in dilute solutions of low dielectric constant, may in rare cases be troublesome. The method, moreover, has several advantages: easy construction of the apparatus, complete elimination of dispersion and stray inductive effects, and simplicity of computation combined with ability to evaluate the effect of small conductance leakages.

During the course of work on physical chemical applications of the Schering Bridge, it was found that the apparatus was a highly accurate audio frequency capacity bridge. The molar polarizations and dipole moments of chlorobenzene, monochlorocyclopropane, and 1,2-*dl*-dichlorocyclopropane were thereupon measured with a view to investigating the convenience of the method. The measured moment of chlorobenzene is a check on the accuracy of the experiment, and the moments of the cyclopropanes are useful in determining whether the dichlorocyclopropane is *dl* or *meso*, and, further, in approximating the angle which the carbon–chlorine bond makes with the plane of the carbon ring.

Experimental

Materials.—1,2-*dl*-Dichlorocyclopropane and monochlorocyclopropane were prepared and purified by Dr. P. G. Stevens of this Laboratory.[3]

Chlorobenzene ("Paragon Labs., Tech.") was purified

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[1] This paper contains material from the dissertation presented by Bernard I. Spinrad to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] See, for example, B. Hague, "A. C. Bridge Methods," Pitman, London, 1938.

[3] See the accompanying paper by Dr. P. G. Stevens.