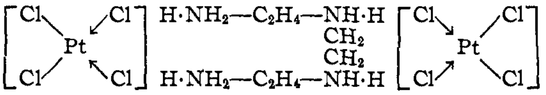
structural formula of [Pt trien][$PtCl_4$]. Attempts were also made to repeat the above procedure for the 2:1 complex of palladium, but it was so insoluble that no reproducible results could be obtained. By analogy to the platinum complex, however, it would seem that the palladium complex also possesses a Magnus-type structure, *viz.*, [Pd trien][$PdCl_4$].

2. **The Complex Compound $Pt_2trienH_4Cl_8$.**—The absorption spectrum of a solution of this salt showed the absorption characteristics of the tetrachloroplatinite ion (see Fig. 1) indicating that its structure is



3. The [Pt(trien)]$^{++}$ and [Pd(trien)]$^{++}$ Ions: A. Attempted Optical Resolution

Experimental.—Several attempts were made to precipitate the [Pt(trien)]$^{++}$ and [Pd(trien)]$^{++}$ ions using a large optically active anion. Saturated solutions of *d*-tartaric acid and *d*-α-bromocamphor-π-sulfonate were added to solutions of the ions. Dry air was blown over the solutions for several hours and the resulting precipitate was tested for platinum. In all instances the tests revealed only the presence of organic material.

Discussion.—Although the 1:1 complex had been isolated for either the Pt(II) or Pd(II) systems, its existence in solution has been shown. By treatment with [$PtCl_4$]$^=$ or [$PdCl_4$]$^=$ ions the corresponding Magnus-type salts precipitate.

If a covalent tetrahedral [Pt trien]$^{++}$ or [Pd trien]$^{++}$ ion were present in solution a large optically active anion should bring about resolution. Since the fractions obtained contained no platinum the resolving agents must be more insoluble than the platinum salts. No structural information can therefore be obtained from these data.

B. Magnetic Behavior

Experimental.—The magnetic behavior of the solid complexes prepared, *viz.*, [Pt trien][$PtCl_4$], $[PtCl_4]_2H_4(trien)\cdot 2H_2O$, and [Pd trien][$PdCl_4$] was investigated on a Curie–Cheneveau type balance.[19,20] The investigation was made at room temperature (25°). Previously boiled distilled water was used to calibrate the balance. In all instances the salts under investigation were found to be diamagnetic. Average mass susceptibilities found for [Pt trien][$PtCl_4$], $H_4(trien)(PtCl_4)_2\cdot 2H_2O$ and [Pd trien][$PdCl_4$] were found to be -0.22×10^{-6}, -0.31×10^{-6} and -0.42×10^{-6} units, respectively.

Discussion.—The diamagnetism exhibited by all of the complexes investigated is in accord with the predictions of theory and constitutes further evidence for the planar structure of bivalent platinum and palladium complexes.[12]

Summary

1. The absorption spectra of the system triethylenetetramine and platinum(II) or palladium(II) ions indicate that one or more complexes are present in these systems.
2. The complex compounds [Pt trien][$PtCl_4$], [Pd trien][$PdCl_4$] and [trienH_4 $(PtCl_4)_2$]$\cdot 2H_2O$ were prepared and their structures determined.
3. Attempts to resolve the [Pt trien]$^{++}$ and [Pd trien]$^{++}$ ions were unsuccessful.
4. Magnetic investigations of the complex compounds show them to be diamagnetic, indicating planar dsp^2 linkage.

(19) Cheneveau, *Phil. Mag.*, **20**, 357 (1910).

(20) Grey and Farquharson, *J. Sci. Instruments*, **9**, 1 (1932).

NEW ORLEANS, LOUISIANA RECEIVED APRIL 22, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

The Kinetics of the Reaction of Ozone and Chloride Ion in Acid Aqueous Solution

BY LE ROY BROUGH YEATTS, JR.,[1,2] AND HENRY TAUBE

Kinetic investigations of reactions of ozone with reducing agents are in most instances difficult. The reactions are often so rapid that it is difficult to follow the rate, as for example in the reactions with stannous ion, iodide ion or ferrous ion. Often, too, the reaction with the reducing agent induces decomposition of ozone. This is observed in the reactions of ozone with hydrogen peroxide,[3] formic acid,[4] oxalic acid and phosphorous acid.[5] By contrast, in the system under present study, the main net reaction

$$2H^+ + 2Cl^- + O_3 = O_2 + H_2O + Cl_2 \qquad (A)$$

proceeds slowly enough so that the rate may be followed by ordinary methods, and it accounts almost completely for the change in the system. A very slight decomposition of ozone is observed, but since it varies in an erratic way from experiment to experiment it appears to be unrelated to reaction A. Elsewhere[3] it has been shown, and this observation is confirmed by the present work, that the spontaneous decomposition of ozone in acid solution is inhibited by chloride ion.

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[1] From a thesis submitted by Le Roy B. Yeatts, Jr., to the Department of Chemistry, Cornell University, in partial fulfillment of the requirements for the Ph.D. degree.

[2] Present address, Lafayette College, Easton, Penna.

[3] Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

[4] Taube, *ibid.*, **63**, 2453 (1941).

[5] Taube, unpublished observations.

The rate of reaction A has been measured at various concentrations of ozone, chloride ion and hydrogen ion at different temperatures and in the presence of various metal ions that might be expected to act as catalysts.[6] The data on the variation of rate with temperature yield the value of the "a" factor which is of particular interest in the present system. The over-all reaction involves a spin change. It seemed of interest to discover whether an abnormally low "a" factor, as has been predicted[7] for a reaction of this type if the spin change takes place in the rate determining step, would be observed for reaction A.

Experimental Procedure

For each experiment a large supply of a solution of ozone was prepared by bubbling ozonized oxygen through conductivity water acidified with perchloric acid. This solution was maintained at the particular temperature chosen for the experiment. A series of calibrated reaction cells (designed to minimize gas volume, see Fig. 1) previously cooled to the temperature of the bath, and each containing the required amount of chloride ion, was rapidly filled from the reservoir through a tube issuing from its bottom. The cells were then stoppered and placed in the constant-temperature bath shielded from light, withdrawn at intervals and the ozone and chlorine content determined. The initial concentration of ozone was determined by analysing at once the contents of a cell from which chloride ion had been omitted.

In carrying out an analysis, the cell was attached to the analysis train diagrammed in Fig. 1, air was drawn rapidly through the system and the ozone and chlorine removed from the gas stream by neutral potassium iodide contained in tubes C. It was found that the ozone concentration in the reaction cell fell to 40% of its initial value after an aspiration period of one minute. In making analyses, the aspiration was continued for ten minutes. This is sufficiently long to insure complete removal of ozone and of chlorine.

The method for determining chlorine and ozone depends on the fact that both react with iodide ion, and that the reaction of ozone with iodide ion consumes hydrogen ion quantitatively. An excess of acid in known amount was added to the contents of tubes C, and the total oxidizing agent (T. Ox.) determined by titration with standard thiosulfate. Then iodate in excess was added and the liberated iodine again titrated. The second titration measures the amount of acid left after the ozone has reacted with the iodide ion, and on comparing it with amount of acid added, gives the amount of ozone. The precision of the analytical method may be gaged by comparing the figures for T. Ox at zero time with the concentration of ozone at zero time. The latter figure is based on the acidimetric analysis.

The thiosulfate solution was standardized against potassium iodate and against potassium dichromate. The acid was standardized by means of the iodate method used in the analysis.

All solutions were made up using conductivity water. The perchloric acid was 60% C. P. acid. For most of the experiments, hydrochloric acid of special grade, low in heavy metals, was used as the source of chloride ion. For experiments in which the chloride ion concentration exceeded that of the hydrogen ion, C. P. sodium chloride was added to supply chloride ion. The ionic strength was maintained constant in a series by means of sodium perchlorate. A solution of this salt was prepared by neutralizing perchloric acid with sodium carbonate.

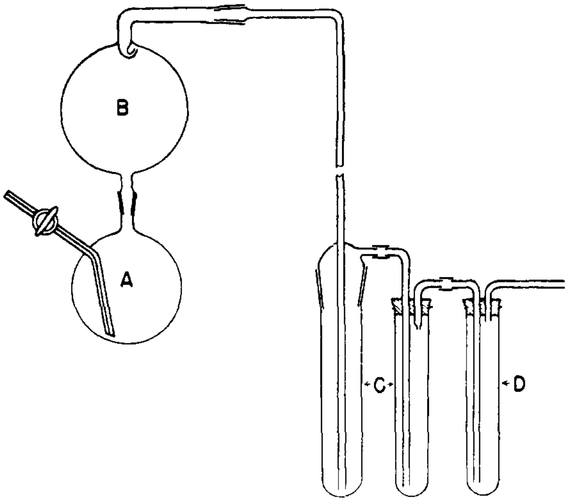

Fig. 1.—Chain used for aspiration of reaction bulbs: A, reaction bulb; B, bulb to prevent entrainment of liquid; C, tubes containing neutral potassium iodide solution; D, trap connected to water aspirator.

An ice-water mixture was used to maintain a temperature of 0°, and a solid dioxane-liquid dioxane mixture for 9.5°.

Throughout the paper, time is expressed in minutes and concentration in moles per liter.

The data are treated with reference to the rate law

$$-\mathrm{d}(\mathrm{O_3})/\mathrm{d}t = k(\mathrm{O_3})(\mathrm{Cl^-}) + k^*(\mathrm{O_3}) \qquad \text{(I)}$$

The second term on the right-hand side allows for the slight decomposition of ozone which accompanies the oxidation of chloride ion. The spontaneous decomposition is first order[8] in the absence of chloride ion, and it was assumed to be first order in the present system also. When this rate law is integrated under the condition that (O_3) is the only concentration variable (other reagents in great excess) it leads to the following form, which is the form applied to the data.

$$k = \frac{2.303}{(\mathrm{Cl^-})_{\mathrm{av}}t}\,\frac{\Delta(\mathrm{Cl_2})}{\Delta(\mathrm{O_3})}\,\log\frac{(\mathrm{O_3})_0}{(\mathrm{O_3})_t} \qquad \text{(II)}$$

It is evident that as long as the decomposition of ozone is slight (*i.e.*, T. Ox. remains almost constant in an experiment), $\Delta(Cl_2) = \Delta(O_3)$ very nearly and the correction factor $\Delta(Cl_2)/\Delta(O_3)$ is nearly unity. Values of T. Ox. have been reproduced in Tables I, IV, V and VI to indicate how nearly this condition is approached in the experiments.

Results

Variation of Rate with Ozone Concentration.—Table I presents some of the data which show how the rate of reaction varies with the concentration of ozone, the other variables being kept almost constant. The concentration of ozone has been varied by using different initial concentration, and by following the natural decrease with time during an experiment.

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[6] G. R. Hill, THIS JOURNAL, **70**, 1036 (1948).

[7] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 324-326.

[8] Sennewald, *Z. physik. Chem.*, **A164**, 305 (1933).

TABLE I

VARIATION OF RATE WITH CONCENTRATION OF OZONE

μ = *ca.* 0.09; temp. = 0° C.

No.	Time, min.	T. Ox. $\times 10^4$	$(O_3)_t$ $\times 10^4$	(Cl^-) av.	(H^+) av.	k
1	0	5.872	5.872	0.04028	0.04940	....
	853	5.799	3.024	.04000		0.0190
	1089	5.823	2.538	.03995		.0190
2	0	17.17	17.08	.04028	.05107	
	2493	17.04	2.569	.03883		.0196
	2533	17.07	2.437	.03882		.0198
	2645	16.99	2.153	.03879		.0202
3	0	15.16	15.16	.04028	.04770	
	747	14.86	8.438	.03961		.0198
	780	14.87	8.238	.03959		.0198
	1033	14.80	6.810	.03944		.0196
	1062	14.68	6.534	.03942		.0201
4	0	15.21	9.205	.04028	.05175	
	450	15.23	6.275	.03999		.0213
	1490	15.26	2.740	.03901		.0205

The data show that over a range three-fold in initial ozone concentration and about eight-fold for the extreme concentrations, the rate of reaction is first order with respect to ozone concentration. In other experiments also (see below) the ozone concentration changed three or four-fold in an experiment. With the exception of a few early experiments, in none was there evidence for deviation from the first order law beyond what might be attributed to experimental error. In a few of the earlier runs, a decrease of specific rate with time was observed. The precise cause of this drift was not discovered, but it disappeared after some details of the analytical procedure were improved, and did not reoccur in any of the later experiments.

Experiment 4 was conducted by permitting the reaction to proceed for ten hours before the first sample was analyzed. In this period of time the concentration of chlorine built up to about two-thirds that of the ozone for the first sample of the series. The rather good agreement of the specific rates in this run with the others shows that there are no important effects caused by accumulation of products, or by the destruction of a catalyst.

Surface Effect.—To investigate the possibility that the cell surfaces might influence the rate of reaction A, the series of experiments presented in Table II was performed. Comparisons of rate were made varying the surface to volume ratio about four-fold, using in one experiment soft glass beads and in the others pyrex tubing. It may be concluded from the data that the observed rate is independent of surface area in the range studied. The slight increase observed for the packed vessels can be entirely attributed to the higher concentration of acid in these experiments (see below)—in performing the experiments the fact that the packing material occupied some of the volume was overlooked when the hydrochloric acid was measured into the cells.

TABLE II

EFFECT OF VARYING THE SURFACE TO VOLUME RATIO, T = 0°C.

Expt.	Rel. surf.: vol. ratio	Time, min.	$(O_3)_t$ $\times 10^4$	$(Cl^-)_{av.}$	$(H^+)_{av.}$	μ	k
1	1	0	18.92	0.04028	0.05044	0.091	....
	1	963	8.588	.03925	.04941	.089	0.0209
	4.1[a]	0	17.85	.05203	.06165	.114	....
	4.1[a]	992	6.135	.05086	.06048	.111	.0212
2	1	0	19.37	.04028	.04853	.089	....
	1	1016	8.805	.03922	.04747	.087	.0198
	1	1046	8.828	.03923	.04748	.087	.0192
	3.4[b]	0	18.97	.04620	.05418	.100	....
	3.3[b]	1075	7.159	.04459	.05259	.097	.0203
	3.4[b]	1103	7.094	.04543	.05339	.099	.0196
3	1	0	19.79	.04028	.04691	.087	....
	1	990	9.286	.03923	.04586	.085	.0195
	1	1018	9.045	.03921	.04584	.085	.0196
	3.4[b]	0	19.12	.04620	.05256	.099	....
	3.3[b]	1051	7.547	.04461	.05099	.096	.0199
	3.4[b]	1082	7.121	.04543	.05177	.097	.0200

[a] Soft glass beads used. [b] Pyrex tubing used.

Variation of Rate with Concentration of Chloride Ion.—Data bearing on the variation of rate with the concentration of chloride ion are presented in Table III. These data show that the rate of reaction A is accurately first order with respect to chloride ion concentration over the four-fold range investigated.

TABLE III

THE EFFECT OF VARYING CHLORIDE ION CONCENTRATION

μ = *ca.* 0.30: T = 0° C.

Expt.	Time, min.	$(O_3)_t$ $\times 10^4$	$(Cl^-)_{av.}$	$\Delta(Cl_2)$ $\times 10^4$	$(H^+)_{av.}$	k
1	0	11.81	0.1004	....	0.1035	....
	137	8.287	.1000	3.503	.1031	.0255
	273	5.894	.0997	5.906[b]	.1029	.0255
	297	5.531	.0998	6.239	.1029	.0255
2	0	8.590	.1004	....	.1027	....
	149	5.878	.1001	2.750[b]	.1024	.0255
	303	3.982	.0999	4.616	.1022	.0254
3	0	10.57	.02509	....	.1029	....
	292	8.813	.02491	1.757	.1027	.0250
	314	8.709	.02464	1.871	.1027	.0252
	581	7.320	.02477	3.200	.1026	.0251
4	0	8.025	.02509	....	.09957	....
	277	6.688	.02496	1.275	.09944	.0252
	656	5.270	.02479	2.706	.09930	.0254
	682	5.224	.02481	2.757	.09929	.0250

Variation of Rate with the Concentration of Hydrogen Ion.—Table IV presents the results of a series of experiments at constant ionic strength by varying values of hydrogen ion concentrations. The averages of the specific rates for each experiment are plotted against the averages of the hydrogen ion concentrations in Fig. 2. The result shows that the rate law has two terms, one independent of hydrogen ion concentration, and the other, first order in hydrogen ion concentration.

$$d(Cl_2)/dt = k_1(O_3)(Cl^-) + k_2(O_3)(Cl^-)(H^+) \quad \text{(III)}$$

At $\mu = 0.30$ and 0°, $k_1 = 0.0128$ l. mole.$^{-1}$ min.$^{-1}$ and $k_2 = 0.124$ l.^{2} mole.$^{-2}$ min.$^{-1}$

TABLE IV

VARIATION OF k WITH HYDROGEN ION CONCENTRATION

$\mu = ca.\ 0.30$; $T = 0°$ C.

Expt.	Time, min.	T. Ox. $\times 10^4$	$(O_3)_t \times 10^4$	$(Cl^-)_{av.}$	$(H^+)_{av.}$	k
1	0	17.36	17.36	0.1004	0.01189	....
	305	17.29	11.33	.0998	.01129	0.0139
	330	17.20	10.91	.0987	.01127	.0139
	583	17.23	7.711	.0993	.01094	.0138
	608	17.18	7.432	.0994	.01092	.0138
2	0	19.17	19.03	.1004	.02820	....
	268	19.00	12.19	.0997	.02752	.0166
	297	19.06	11.82	.0986	.02750	.0163
	532	19.01	8.005	.0993	.02710	.0163
3	0	19.49	19.44	.1004	.07317	....
	285	19.40	10.39	.0995	.07227	.0220
	314	19.46	9.853	.0984	.07227	.0220
	555	19.42	5.866	.0989	.07181	.0218
	583	19.45	5.516	.0990	.07178	.0218
4	0	8.007	8.025	.02509	.09957	....
	277	7.963	6.688	.02496	.09944	.0252
	656	7.976	5.270	.02479	.09930	.0254
	682	7.981	5.224	.02481	.09929	.0250
5	0	20.09	20.08	.1004	.2047	....
	143	19.54	11.32	.0985	.2014	.0382
	243	19.80	7.831	.0991	.2035	.0382
	268	19.77	7.126	.0991	.2034	.0381

Variation of the Rate of Reaction with Temperature.—A series of experiments was carried out at 9.5°, keeping μ at 0.3 and varying the concentration of hydrogen ion. The results are presented in Table V, and are shown in graphical form in Fig. 2 (lower curve). The values of k_1 and k_2 at 9.5° are found to be 0.0379 and 0.366, respectively. Two experiments were carried out also at a higher temperature, 25°. Under these conditions the decomposition of ozone becomes marked, and the initial concentration of ozone is low. These factors make the experimental error so great that further work at this temperature was abandoned. The data indicate that the temperature coefficient in the range 9.5 to 25° does not differ seriously from that in the range 0 to 9.5°.

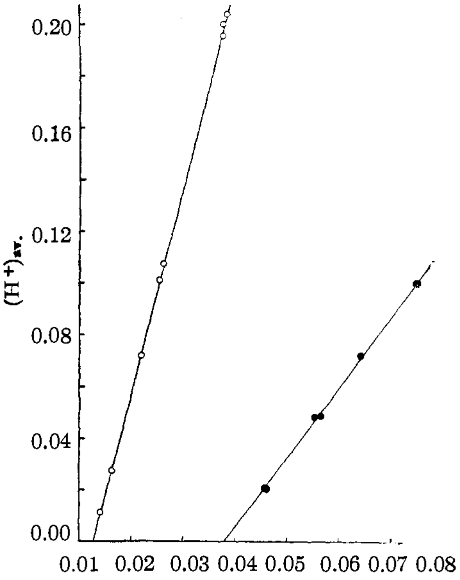

Fig. 2.—Variation of $k_{corr.}$ with $(H^+)_{av.}$ at two different temperatures: ○, 0°; ●, 9.5°; $\mu = ca.\ 0.30$.

TABLE V

VARIATION OF k WITH HYDROGEN ION CONCENTRATION AT A HIGHER TEMPERATURE

$\mu = ca.\ 0.30$; $T = 9.5°$ C.

Expt.	Time, min.	T. Ox. $\times 10^4$	$(O_3)_t \times 10^4$	$(Cl^-)_{av.}$	$(H^+)_{av.}$	k
1	0	11.71	11.68	0.05020	0.02111	....
	147	11.57	8.248	.04987	.02078	0.0459
	207	11.47	7.094	.04976	.02067	.0462
	259	11.43	6.328	.04969	.02060	.0454
2	0	12.69	12.70	.05020	.04874	....
	152	12.44	8.171	.04977	.04863	.0550
	196	12.39	7.177	.04968	.04854	.0554
	243	12.36	6.318	.04960	.04846	.0549
3	0	13.08	13.19	.05020	.07271	....
	87	12.91	9.708	.04988	.07239	.0651
	144	12.83	8.095	.04920	.07230	.0642
	204	12.83	6.698	.04959	.07210	.0634
	259	12.72	5.570	.04948	.07199	.0633
4	0	13.76	13.80	.05020	.1008	....
	152	13.38	7.548	.04962	.1002	.0747
	210	13.37	6.065	.04947	.1001	.0749
	261	13.36	5.005	.04936	.1000	.0749

Applying the Arrhenius equation to the data for the temperatures 0 and 9.5°, the values of the activation energy for the hydrogen ion dependent path and the hydrogen ion independent path are calculated to be 17,500 ± 300 and 17,600 ± 300 cal., respectively; the "a" factors are 1.2×10^{13} $l.^2$ $mole.^{-2}$ $min.^{-1}$ and 1.4×10^{12} l. $mole.^{-1}$ $min.^{-1}$, respectively.

Catalysis by Metal Ions.—The influence of metal ions on the rate of reaction was investigated to some extent. The data obtained in this phase of the study are presented in Tables VI and VII.

In Table VII the observed values of k are compared with those expected if metal ion were omitted but the ionic strength kept the same. This comparison necessitates a slight correction for the difference in ionic strength between the solutions used here and those used for the earlier experiments. The correction was made using the Brönsted relation for the variation of specific rate with ionic strength. A correction presumably is required only for the second term of the rate law. In the most extreme case the correction changed the value of k at $(H^+) = 0.100\ M$ from 0.0252 at $\mu = 0.30$ to 0.0306 at $\mu = 0.152$.

The comparison of columns 7 and 8 of Table VII shows that Cu^{++} and Fe^{+++} at concentrations near 0.01 M do not exert a marked effect on the rate of reaction A. The correction applied for the ionic strength is undoubtedly too great;

TABLE VI

EFFECT OF VARIOUS POSITIVE IONS ON THE RATE OF REACTION, $T = 0°C$.

Expt.	Subst. added	$(M^{+n}) \times 10^4$	Time, min.	T. Ox. $\times 10^4$	$(O_3)_t \times 10^4$	$(Cl^-)_{av.}$	$(H^+)_{av.}$	μ	k
1	$CuCl_2$	98.11	0	20.57	20.51	0.06975	0.1026	0.182	....
			148	20.37	15.17	.06923	.1021		0.0276
			232	20.36	12.89	.06900	.1019		.0284
			320	20.32	10.86	.06880	.1017		.0283
2	$FeCl_3$	96.86	0	21.77	21.73	.07925	.1026	.211	....
			63	21.54	18.62	.07824	.1023		.0294
			113	21.47	16.72	.07877	.1021		.0279
			191	21.34	14.05	.07852	.1019		.0276
			229	21.27	13.01	.07842	.1018		.0271
3	$CoCl_2$	1.088	0	18.17	18.21	.1004	.1030	.204	....
			102	17.96	8.699	.0986	.1021		.0716
			127	17.89	7.289	.0993	.1019		.0705
			155	17.90	5.934	.0992	.1018		.0711
			183	17.75	4.718	.0991	.1017		.0720
4	$CoCl_2$	2.176	0	21.84	21.78	.05057	.1016	.152	....
			52	21.75	12.81	.05001	.1007		.203
			88	21.78	8.951	.04929	.1003		.205
			114	21.74	6.934	.04909	.1001		.204
			138	21.68	5.458	.04895	.1000		.204
5	$CoCl_2$	4.363	0	20.99	20.92	.05100	.0978	.150	....
			83	20.83	4.367	.04935	.0962		.380
			108	20.79	2.723	.04919	.0960		.381

[a] An average value of ionic strength during the course of an experiment.

TABLE VII

RATE CONSTANT DATA IN PRESENCE OF METALLIC IONS, $T = 0°C$.

Expt.	Subst. added	$(M^{+n}) \times 10^4$	$(Cl^-)_{av.}$	$(H^+)_{av.}$	μ	k if non-catalyzed	k	k_3
1	$CuCl_2$	98.1	0.0690	0.102	0.182	0.0295	0.0284	..
2	$FeCl_3$	96.9	.0785	.102	.211	.0282	.0280	..
3	$CoCl_2$	1.09	.0991	.102	.204	.0287	.0713	38.9
4	$CoCl_2$	2.18	.0493	.100	.152	.0306	.204	39.3
5	$CoCl_2$	4.36	.0494	.0961	.150	.0301	.380	39.6

even assuming that the corrected values are as much as 5% too high, the effect of these metal ions is seen to be very slight. By contrast, cobaltous ion at much lower concentration accelerates the reaction markedly. The data for cobaltous ion have been treated under the assumption that to the two terms of equation III must be added the term $k_3(O_3)(Co^{++})$. Not enough experiments have been done to test the rate law rigorously, but it does describe accurately the present data which cover a two-fold change in (Cl^-), a four-fold change in (Co^{++}) and approximately a five-fold change in (O_3). The value of k_3 at 0° is 39.3 l. mol.$^{-1}$ min.$^{-1}$ It is of interest to note that Co^{++} in the presence of Cl^- does not catalyze the decomposition of ozone, as is the case if chloride ion is absent.[3,6]

Discussion of the Results

Rate law III shows that in acid solution there are two paths for reaction A. A reasonable mechanism for the hydrogen ion independent path is

$$O_3 + Cl^- \xrightarrow{k_1} O_2 + ClO^- \text{ (rate determining)}$$
$$2H^+ + Cl^- + ClO^- = Cl_2 + H_2O \text{ (rapid)}$$

The hydrogen ion dependent path may be supposed to differ only in that each activated complex contains one hydrogen ion in addition to the ozone molecule and chloride ion.

Alternative possibilities for the products formed in the rate determining step have been considered. The most reasonable of these are discussed below, and the arguments which have led to their rejection are presented.

$$\text{(a)}\quad Cl^- + O_3 + H_2O \longrightarrow Cl + HO + HO^- + O_2 \qquad (1')$$

This reaction postulates a one-electron oxidation–reduction process for $O_3 + Cl^-$. Calculation shows this step to be endothermic to the extent of about 45 kcal. This value exceeds the observed activation energy by much more than the error in the calculations, hence reaction 1′ may be ruled out as a possibility. The fact that the catalytic decomposition is very slight also argues against reaction 1′ as the slow step. Atomic chlorine initiates a rather pronounced catalytic decomposition of ozone also in water solution[8]; the decomposition observed in the present system is slight and is unrelated to the main reaction.

$$\text{(b)}\quad Cl^- + O_3 \longrightarrow Cl{-}O{-}O^- + O$$

Using bond energy values and thermal data,[9] ΔH for this reaction is estimated as 62 kcal., which is again much in excess of the observed activation energy.

$$\text{(c)}\quad Cl^- + O_3 \longrightarrow ClO_2^- + O$$

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[9] Pauling, "Nature of the Chemical Bond," Cornell University Press, 1939; thermal data from Bichowsky and Rossini, "Thermal Chemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y.

This reaction can be rejected because it is not in agreement with the observed chemistry. If ClO_2^- were formed it would certainly lead to the formation in the system of ClO_2 or ClO_3^-. Furthermore, for this reaction also ΔH (= 41 kcal.) much exceeds the observed activation energy.

It appears that only if a strong oxygen to oxygen bond is maintained in the products (as is the case when O_2 is a product) will the value of ΔH be compatible with the activation energy. ΔH for reaction 1 is -18.9 kcal.

The observed activation energy does not preclude the possibility that the oxygen found in the rate determining step is left in an excited state. Thus for the reaction

$$Cl^- + O_3 \longrightarrow ClO^- + O_2{}^1\Delta$$

ΔH is 3.5 kcal. A formulation of this type ($^1\Sigma$ oxygen is another possibility) may in fact explain why the "*a*" has about the normal value, 1.4×10^{12}, although there is a spin change in the over-all reaction. The spin change may take place after the rate determining step by deactivation of the singlet oxygen. In a study recently published[10] the "*a*" factor in another reaction in which a spin change takes place

$$ClO^- + H_2O_2 \longrightarrow H_2O + O_2 + Cl^-$$

was also found to be normal. In this reaction also the activation energy is high enough so that the oxygen formed as product in the rate determining step may be in an excited singlet state, and the spin change may therefore take place after the rate determining step.

It may be of interest to note that the oxidation of bromine ion by ozone[11] at low hydrogen ion proceeds by a path similar to that of term 1 of equation III. As might be expected, the specific rate of the $Br^- + O_3$ reaction is much greater than that of the $Cl^- + O_3$ reaction, 1600 as compared to 0.28 at 0°.

It seems remarkable that hydrogen ion exerts a catalytic effect by enhancing the "*a*" factor rather than by lowering activation energy. The oxidation of halide ions by hydrogen peroxide is also governed by a rate law similar in form[12] to rate law III. Participation by hydrogen ion in these reactions leads to a decrease in activation energy amounting to 2,860 cal. in the reaction of hydrogen peroxide with chloride ion.

Catalysis of reaction A by cobaltous ion may be explained by the reaction of cobaltous ion with ozone to form cobaltic ion as the slow step. Cobaltic ion is known to react rapidly with chloride ion, thus the catalyst at the steady state will be present mainly in the lower oxidation state. This interpretation gives for the specific rate of the reaction $Co^{++} + O_3$ ($+H_2O$) the value of 39.3 l. mole^{-1} min.$^{-1}$. This reaction is important also in the decomposition of ozone catalyzed by cobaltous ion, and Hill[13] has measured the specific rate in the latter system as 37. Hill has suggested $CoOH^{++} + OH + O_2$ as the products formed in step 3. This formulation is consistent with the present work. HO at high Cl^- in acid is expected to react rapidly to produce Cl, Cl in turn is expected to react rapidly to form Co^{+++}. Thus, the net result of the interaction of one mole of ozone and one mole of cobaltous ion is the production of two moles of cobaltic ion, equivalent to one mole of chlorine. In the absence of chloride ion, each $Co^{++} + O_3 \rightarrow$ act accounts for the net destruction of two molecules of ozone.[6]

The data show that acceleration or inhibition of the reaction by cupric or ferric ions even at 0.01 *M* is inappreciable. It may therefore be concluded that the oxidation of these substances by ozone is very slow. Any catalytic effects to the magnetic moments of these substances are also very slight.

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Summary

The rate law for the reaction of ozone with chloride ion in acid solution is

$$d(Cl_2)/dt = k_1(O_3)(Cl^-) + k_2(H)(Cl^-)(O_3)$$

At 0° and $\mu = 0.3$, k_1 is 0.0128 l. mole^{-1} min.$^{-1}$ and k_2 is 0.124 l.^{2} mole^{-2} min.$^{-1}$. The activation energies and "*a*" factors corresponding to the first and second terms are 17.6 and 17.5 kcal., 1.4×10^{12} and 1.2×10^{13}.

Cupric and ferric ions affect the rate of reaction only slightly, if at all. Cobaltous ion exerts a strong catalytic effect, expressible by adding the term k_3 (Co^{++}) (O_3) to the rate law. The value of k_3 is found to be 39.3 l. mole^{-1} min.$^{-1}$ in agreement with the value obtained by Hill in an independent system.

Mechanisms for the three reaction paths have been proposed.

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(10) Connick, THIS JOURNAL, **69**, 1514 (1947).

(11) Taube, *ibid.*, **64**, 2468 (1942).

(12) Mohammed and Liebhafsky, *ibid.*, **56**, 1680 (1934).

(13) Hill, THIS JOURNAL, **71**, 2434 (1949). The work published earlier (ref. 6) does not give the specific rate since the distribution of the catalyst between upper and lower oxidation states was not measured.