# Iodine Catalysis in the Chlorite–Iodide Reaction[1]

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The reaction $ClO_2^- + 4H^+ + 4I^- = 2I_2 + 2H_2O + Cl^-$ in aqueous solution is catalyzed by the iodine product, and the autocatalysis is inhibited by iodide ion. At 25° and ionic strength 0.5 M over the pH range 4–8, the reaction follows the rate expression $d([I_2] + [I_3^-])/dt = k_1[ClO_2^-][I^-]a_{H^+} + k_2[ClO_2^-][I_2]/[I^-]$ over at least the first half of its course, with $k_1 = 9.2 \times 10^2 \ M^{-2} \ sec.^{-1}$ and $k_2 = 5.1 \times 10^{-3} \ sec.^{-1}$. The second, autocatalytic term is consistent with a rate-determining oxygen transfer reaction between $HClO_2$ and HOI. In the presence of excess chlorite, the exponential rise of the iodine concentration toward the end of the reaction is terminated in an abrupt fall to zero as the iodine is further rapidly oxidized to iodate.

Although oxyhalogen–halide reactions have been the subject of many classical kinetic studies,[4] the first quantitative work on the reaction between chlorite and iodide

$$4H^+ + ClO_2^- + 4I^- = 2I_2 + 2H_2O + Cl^- \quad (1)$$
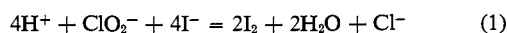
was published only recently by Indelli.[5] This author deduced the rate law[6]

$$d[\Sigma I_2]/dt = -2d[ClO_2^-]/dt = 8.3 \times 10^2[ClO_2^-][I^-][H^+] \quad (2)$$

at 25° in unbuffered solutions of very low ionic strength (ca. $10^{-2} \ M$). Using a different experimental technique, we have established the existence of an autocatalytic term in the rate law, which in its complete form may be written

$$d[\Sigma I_2]/dt = k_1[ClO_2^-][I^-]a_{H^+} + k_2[ClO_2^-][I_2]/[I^-] \quad (3)$$

The second term predominates under most conditions when significant amounts of iodine are present and consequently controls the course of the reaction beyond the initial stages. The catalytic effect of iodine and the inhibitory effect of iodide on the chlorite–iodide reaction long ago were observed qualitatively by Bray.[7] We have found no later references to this phenomenon.

Experimental Section

Reagents. Reagent quality chemicals were used without further purification. Analytical grade sodium chlorite was obtained from Matheson Coleman and Bell. Sodium chlorite stock solutions contained 0.001 M NaOH to retard decomposition; they were made up fresh each day. Potassium iodide and sodium chlorite solutions were made up by weight. Iodine concentra-

tions in the reaction mixtures were calculated from absorbance.

Rate Measurements. The rate of the reaction was measured by following the iodine absorbance as a function of time at 3530 (I_3^- peak) or 4690 Å. (iodine–triiodide isosbestic point). A Bausch and Lomb Spectronic 505 double beam spectrophotometer was employed. This instrument records absorbance directly. A first set of experiments (series I), carried out at ambient room temperatures with direct registration of absorbance on the instrument drum at constant wave length, served to establish the form of the rate law over a wide concentration range. A second set (series II) was aimed at establishing the numerical value of the rate constant with maximum accuracy as a function of temperature. For these runs a thermostat holder was constructed which maintained the cylindrical cells to within ±0.1°. In series II experiments, the absorbance-time curves were registered on a Texas Instrument Servoriter II strip chart recorder in combination with a Spectronic time–rate accessory. This arrangement avoided inaccuracies arising from variations in the Spectronic drum speed. Results are given in Table I.

Extinction Coefficients. The I_2–I_3^- isosbestic point was determined by recording the spectrum of elemental iodine dissolved in $10^{-2} \ M$ $HClO_4$ (to suppress hydrolysis), to which small crystals of KI were successively added. The crossing point occurred at 4690 Å. To measure the extinction coefficient at this wave length, iodine solutions of known concentration were required. Loss of iodine during transfer was avoided by generating iodine in the cell from mixtures of KI (in small excess) and KIO_3 upon addition of concentration $HClO_4$ from a micropipet. After several hours the absorbance of iodine was found to have reached a constant value corresponding to complete consumption of iodate. At 4690 Å. an extinction coefficient of 730 M^{-1} cm.$^{-1}$ was found.

For the triiodide extinction coefficient at 3530 Å. the value of 26,400 M^{-1} cm.$^{-1}$ was used.[8] Chlorite, iodate, and iodine have negligible absorption at this wave length.

The Iodine–Triiodide Equilibrium. The initial concentrations of iodide and iodine mentioned in the text are the analytical concentrations ($I^- + I_3^-$ and $I_2 + I_3^-$, respectively). The iodide and iodine concentrations listed in the tables have been corrected for the presence of I_3^-, since the triiodide ion does not enter into the rate equations. The correction was performed with the aid of the triiodide dissociation constant $K = [I^-][I_2]/[I_3^-]$. The expression of Davies and Gwynne[9] has been employed.

$$\log K = 48.622 + 16.725 \log T + 3018.8(1/T)$$

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(4) J. O. Edwards, *Chem. Rev.*, 50, 455 (1952).
(5) A. Indelli, *J. Phys. Chem.*, 68, 3027 (1964).
(6) The symbol $[\Sigma I_2] \equiv [I_2] + [I_3^-]$.
(7) W. C. Bray, *Z. physik. Chem.*, 54, 741 (1906).
(8) T. L. Allen and R. M. Kiefer, *J. Am. Chem. Soc.*, 77, 2957 (1955).
(9) M. Davies and E. Gwynne, *ibid.*, 74, 2748 (1952).

Table I. Initial ΣI_2 Formation Rates at High $[I^-]^a$

	$[I^-]^b$	$[ClO_2^-]$	pH	$d[\Sigma I_2]/dt$, M sec.$^{-1}$ $\times 10^7$	Rate/a_{H^+} $[ClO_2^-][I^-]$, M^{-2} sec.$^{-1}$ $\times 10^{-3}$
Series A	0.125	0.292	6.85	62.5	1.22
ClO_2^- dependence	0.125	0.0584	6.85	12.6	1.23
	0.125	0.0117	6.85	2.59	1.26
	0.125	0.00233	6.85	0.56^b	1.37^c
Series B	0.250	0.167	6.85	65.6	1.12
I^- dependence	0.167	0.167	6.85	48.3	1.23
	0.125	0.167	6.85	39.4	1.35
	0.083	0.167	6.85	25.8	1.33
Series C	0.125	0.292	6.32	195	1.12
H^+ dependence	0.125	0.292	6.70	95	1.31
	0.125	0.292	6.95	46	1.13
	0.125	0.292	7.82	7.5	1.36

^{a} I_2 initially absent; $26 \pm 1°$; $\mu = 0.5$-$0.6\ M$; $\lambda\ 4690\ \text{Å}$.; 1-cm. cell. ^{b} The iodide range was limited because the influence of the catalyzed path became important at $[I^-] = 0.05\ M$. ^{c} Measured at 3530 Å.

At $25°$, $K = 1.30 \times 10^{-3}$. The equilibrium is insensitive to ionic strength.

pH Measurements. A Beckman expanded-scale meter was used. It was standardized at the temperature of the reaction mixture. The pH of the commercial buffer standard was taken from the manufacturer's table of pH as a function of temperature.

Experimental Technique. In the series I experiments, reactants were mixed by magnetic stirrer in a small beaker and immediately poured into the cell. About 15 sec. elapsed between mixing and the first absorbance measurements. In series II, a 2-cm. cylindrical cell was used. This was almost filled with 7 ml. of iodide or iodine–iodide solution, which had previously been buffered with phosphate to the desired pH and adjusted with $NaNO_3$ to an ionic strength of 0.5 M. The cell was placed in the thermostated holder inside the spectrophotometer cell compartment. Meanwhile a syringeful of chlorite solution, its ionic strength likewise adjusted to 0.5 with $NaNO_3$, was immersed in the thermostat proper after the needle tip had been plugged. After both vessels had come to temperature, the syringe was rapidly dried, the plug removed and the platinum syringe needle inserted into the cell through a small hole in the compartment lid. Chlorite solution (0.5 ml.) was then injected into the iodide solution. To ensure rapid mixing, a spring-loaded[10] device was employed to actuate the syringe plunger. The mixing occurred in less than 1 sec.

Results

A change in $[I^-]$ has a profoundly opposite effect on the two terms of eq. 3, a fortunate circumstance which permitted us to eliminate the influence of either reaction path by a suitable choice of the initial iodide concentration. The iodide dependence was even more disparate than is apparent from the rate law, because high iodide concentrations converted I_2 largely to I_3^- (which is *not* a catalyst), thus exerting a doubly depressing effect on the catalytic term.

The First Term. The form of this term was established by observing the growth of iodine absorbance as a function of time in chlorite–iodide mixtures containing $[I^-] \simeq 0.08\ M$. The iodine absorbance is strong

enough, even at the isosbestic point, for the reaction to be conveniently followed during the very early stages, when the analytical iodine concentration was low and less than 1% of the reactants had been consumed. In this region the absorbance–time curves were strictly linear; the accumulated iodine exerted no catalytic effect on the rate. The data of Table I are the result of preliminary study at ambient room temperatures, which suffice to confirm the law published by Indelli[5] (eq. 2).

The rate measurements were repeated at controlled temperature with a rapid mixing technique. In this second series, one set of starting concentrations was used throughout: $[I^-] = 0.279\ M$, $[ClO_2^-] = 6.95 \times 10^{-3}\ M$, $[NaH_2PO_4] = [Na_2HPO_4] = 0.0465\ M$, $[NaNO_3] = 0.03\ M$. A 2-cm. cell was employed at 3530 Å. The reaction was followed until the triiodide concentration reached $10^{-5}\ M$. At the iodide concentration used, over 99% of the iodine was in the triiodide form. The results are given in Table II. Each k_1 value is the average of three runs with an average deviation of less than 2%.

Table II. Rate Constant k_1 of the Noncatalytic Term as a Function of Temperature ($\mu = 0.5\ M$)

Temp., °C.	$d[\Sigma I_2]/dt$, M sec.$^{-1}$	pH	k_1, M^{-2} sec.$^{-1}$
10.6	1.32×10^{-6}	6.63	0.29×10^3
25.0	4.5×10^{-6}	6.60	0.92×10^3
40.1	13.3×10^{-6}	6.57	2.6×10^3

A comparison between our rate constant, $k_1 = 9.2 \times 10^2\ M^{-2}$ sec.$^{-1}$ at $25°$, and the constant 8.3×10^2 of Indelli[5] must make allowance for the differences in ionic strength and in the manner of expressing the acidity. If a_{H^+} is replaced by $[H^+]$ in eq. 3, with an assumed activity coefficient of 0.7 at ionic strength 0.5 M, then k_1 becomes 6.4×10^2. Adjustment to zero ionic strength would probably increase this figure to a value exceeding 10×10^2, since there is a negative salt effect.[11]

The Second Term. At initial iodide concentrations less than $5 \times 10^{-3}\ M$, the iodine absorption–time runs showed increasing upward curvature as the iodine accumulated, indicating an autocatalytic process.

(10) R. Thompson and G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

(11) See ref. 5, Table II.

	[I⁻], mM	[ClO₂⁻], mM	[I₂], mM	[I₃⁻], mM	pH	d[ΣI₂]/dt, M sec⁻¹ × 10⁷	d[ΣI₂]/dt × [I⁻]/ [I₂][ClO₂⁻], sec⁻¹ × 10³
Series D	3.32	3.55	0.0035	0.00720	6.8	0.241	6.52
I₂ dependence	3.31	3.55	0.0063	0.0131	6.8	0.513	7.60
3530 Å., 1 cm.	3.30	3.55	0.0100	0.0209	6.8	0.688	6.40
	3.29	3.55	0.0130	0.0270	6.8	0.959	6.83
Series E	1.75	1.83	0.0615	0.0665	7.1	4.40	6.85
ClO₂⁻ dependence	1.75	0.731	0.0595	0.0645	7.1	1.72	6.91
4670 Å., 10 cm.	1.75	0.366	0.0591	0.0640	7.1	0.826	6.69
	1.75	0.183	0.0576	0.0624	7.1	0.400	6.65
Series F	9.4	20.0	0.0150	0.0860	7.9[a]	1.84	5.76
I⁻ dependence	6.13	5.00	0.0200	0.0735	7.9[a]	1.05	6.44
4670 Å., 10 cm.	3.09	2.00	0.0340	0.0650	6.3	1.21	5.50
	1.23	0.496	0.0560	0.0420	6.3	1.19	5.27
	0.268	0.097	0.0822	0.0137	6.3	1.59	5.29
Series G	4.90	6.10	0.0214	0.0816	6.34	0.96	5.60
pH dependence	4.90	6.10	0.0202	0.0775	6.88	1.05	6.48
4670 Å., 10 cm.	4.90	6.10	0.0200	0.0762	7.20	1.06	6.60
	4.90	6.10	0.0196	0.0755	7.80	1.04	6.60

[a] The two highest [I⁻] runs in series F were at high pH to repress the uncatalyzed path.

When iodine was present in the initial reaction mixture, the reaction proceeded almost exclusively by the autocatalytic path from the instant of mixing. Examples are shown in Figure 1. A series of runs were carried
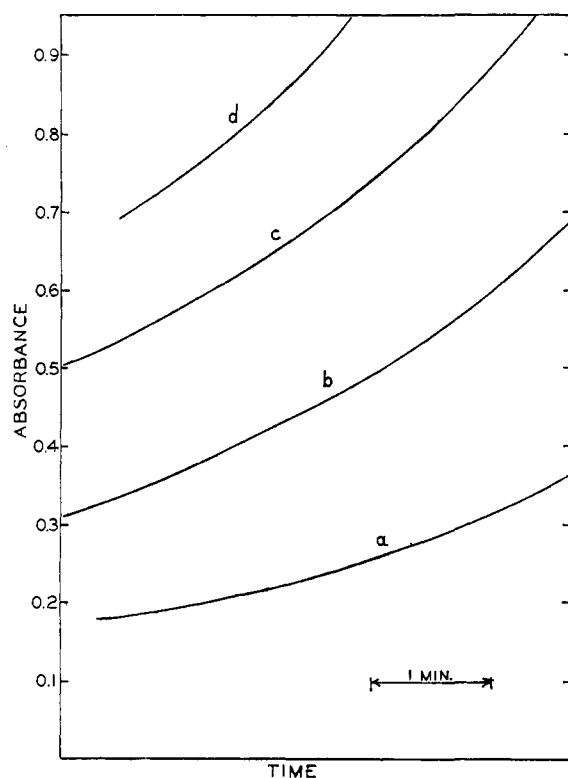

Figure 1. Absorbance–time curves at λ 3530 Å.: cell length, 1 cm., [I⁻] = 3.3 mM, [ClO₂⁻] = 3.5 mM, pH 6.95. Approximate initial [I₂ + I₃⁻]: (a) 1×10^{-5} M, (b) 2×10^{-5} M, (c) 3×10^{-5} M, (d) 4×10^{-5} M (25°).

out at ambient room temperature with iodine initially present (Table III). In some runs, 1-cm. cells were employed at the triiodide peak wave length; other runs were followed in 10-cm. cells at the iodine–triiodide isosbestic point. Rates were determined from the initial slopes. These experiments established the rate law

$$d[\Sigma I_2]/dt = k_2[I_2][ClO_2^-]/[I^-] \qquad (4)$$

in the ranges pH 6 to 8, [I⁻] = 10^{-4} to 10^{-2} M, [ClO₂⁻] = 10^{-4} to 10^{-2} M, [I₂] = 10^{-6} to 10^{-4} M. The rate is independent of pH and of [I₃⁻]. A 50-fold change in the [I₂]/[I₃⁻] ratio (series F, Table III) does not alter the constancy of k_2. In certain runs the contribution of the noncatalytic term was significant and was subtracted out. The correction did not exceed 5%.

A second series of experiments was performed in this case also, with rapid mixing at controlled temperatures, to obtain an accurate measure of k_2 as a function of temperature. The results are summarized in Table IV. The tabulated k_2 values were averaged from the number of runs listed in the third row, the average deviation being again less than 2%. Among the runs at 25° was one at pH 4.60, which after a 7% correction for the contribution of the first term, yielded a k_2 value of 5.18 × 10^{-3}. This considerably extends the pH range over which eq. 4 is valid.

Table IV. Rate Constant k_2 of the Catalytic Term as a Function of Temperature (μ 0.5 M)

Temp., °C.	15.5	25.0	31.7	40.0
$k_2 \times 10^3$, sec.⁻¹	1.12	5.15	15.4	44.5
No. of runs	2	8	3	3

Initial slopes are more difficult to estimate for the second term than the first, because the exponential character of the absorbance–time curve. It was found that a plot of log A against time gave a straight line which permitted an accurate measure of the initial slope. This method was used for all runs listed in Table IV.

From our final results we select $k_1 = 9.2 \times 10^2$ M^{-2} sec.⁻¹ and $k_2 = 5.1 \times 10^{-3}$ sec.⁻¹ at 25° and an ionic strength of 0.5 M. The temperature coefficients lead to the following enthalpies and entropies of activation: $\Delta H_1^* = 12.3$ and $\Delta H_2^* = 26.3$ kcal. mole⁻¹; $\Delta S_1^* = 21$ and $\Delta S_2^* = -3.4$ cal. deg.⁻¹ mole⁻¹.

Table V. Test of Eq. 4 for the First Half of Reaction (μ 0.5 M, 25°)

Time, sec.	Absorbance	$[I_2 + I_3^-]$, 10^{-4} M	$[I^- + I_3^-]$, 10^{-4} M	$[I_2]$,[a] 10^{-4} M	$[I^-]$,[a] 10^{-4} M	$[ClO_2^-]$, 10^{-4} M	$d[\Sigma I_2]/dt$, M sec.$^{-1}$ $\times$ 10^{-6}	$k_2 \times 10^3$, sec.$^{-1}$
0	0.250	1.71	9.31			17.3		
30	0.299	2.05	8.63	1.27	7.86	17.2	1.40	5.01
45	0.333	2.28	8.17	1.46	7.35	17.1	1.63	4.82
60	0.373	2.55	7.63	1.68	6.76	16.9	2.00	4.75
75	0.423	2.90	6.93	1.98	6.01	16.8	2.55	4.62
90	0.491	3.36	6.01	2.42	5.07	16.5	3.88	4.92
105	0.601	4.12	4.49	3.23	3.60	16.1	7.00	4.83
116	0.754 (peak)							

[a] The true I_2 and I^- concentrations in columns 5 and 6 have been calculated from the analytical concentrations in columns 3 and 4 by means of the triiodide dissociation constant.

Indelli[5] obtained an activation energy of 14.4 kcal. mole^{-1} for the first term at lower ionic strength.

It should be remarked that the experimental technique employed by Indelli prevented him from observing the catalytic term. He followed the reaction by titrating the iodine product with thiosulfate as fast as it was formed, thus eliminating iodine buildup. The initial concentrations used in his experiments were approximately $[I^-] = [ClO_2^-] = [H^+] = 5 \times 10^{-4}$ M. According to eq. 3, autocatalysis should have become apparent after a few per cent of reaction if the iodine had been allowed to accumulate. These reaction conditions were examined in this laboratory, and the expected exponential rise in iodine absorbance was in fact observed.
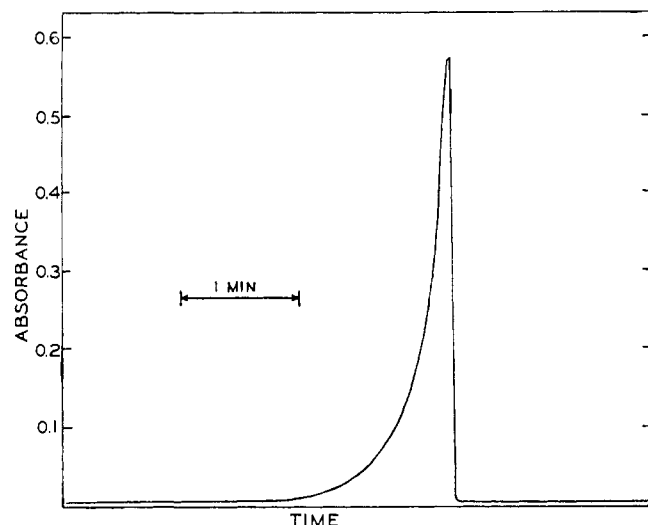

Figure 2. Absorbance–time curve of clock reaction at λ 4670 Å.: cell length 10 cm., $[I^-] = 2.7 \times 10^{-4}$ M, $[ClO_2^-] = 2.5 \times 10^{-3}$ M, pH 5.8, 25°.
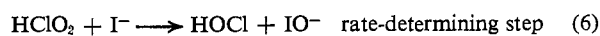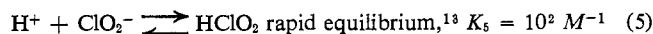
Later Stages of the Reaction. When excess chlorite is added to pure iodide in the pH range 4–7, the initial slow linear increase in iodine absorbance is followed by an exponential rise as the second term of eq. 3 takes over control. The rapid rise in iodine concentration then terminates in a spectacularly abrupt fadeout (Figure 2) which occurs when the iodine has reached 60–80% of the value corresponding to complete oxidation of the iodide. If the reaction mixture is tested with ammoniacal silver solution directly after this fadeout, no precipitate of silver iodide occurs; the iodide has thus

been converted quantitatively to iodate. The processes $I^- \rightarrow I_2$ and $I_2 \rightarrow IO_3^-$ presumably occur simultaneously near the end of the reaction.

A similar peak in the absorbance–time curve is observed when iodine is initially present. In that case the induction period is lacking and the trace resembles the latter portion of the curve in Figure 2. An analysis of such a trace was made under conditions which permitted accurate measurement of the slope of the absorbance–time curve for over 50% of the course of the reaction. The initial mixture contained 1.73×10^{-3} M ClO_2^-, 9.3×10^{-4} M I^-, and 1.7×10^{-4} M I_2 buffered with phosphate at pH 6, with ionic strength adjusted to 0.5. Slopes were measured at constant time intervals; the composition of the solution at these times were calculated from the iodine absorbance and the initial reactant concentrations, assuming stoichiometry according to eq. 1. The data are collected in Table V. The constancy of k_2 in the last column demonstrates that the same mechanism prevails throughout at least the first half of the reaction. A second run with half the initial chlorite concentration gave similar results (10^3k_2 varied between 5.1 and 4.7 during the first 50% of the reaction). During the last 10% of reaction time the chemistry undoubtedly becomes extremely complicated. In the sample of Table V, the peak absorbance falls far short of the value 0.93 corresponding to complete conversion of I^- to I_2. It is hoped to report later on a preliminary study[12] of the kinetics of the reaction between ClO_2^- and I_2.

Discussion

The first term in the rate law (3) corresponds to the mechanism[5]

$$H^+ + ClO_2^- \rightleftharpoons HClO_2 \quad \text{rapid equilibrium,}[13] \quad K_5 = 10^2 \ M^{-1} \quad (5)$$

$$HClO_2 + I^- \longrightarrow HOCl + IO^- \quad \text{rate-determining step} \quad (6)$$
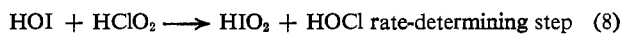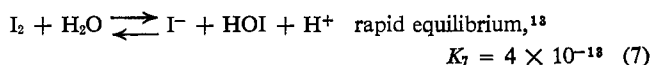
followed by rapid reduction of the products by excess I^-. Under the conditions of our experiments (pH >4), chlorite was present almost exclusively in the unprotonated form. We thus obtain[5] $k_6 = k_1/2K_5 = 5 \ M^{-1}$ sec.$^{-1}$ at 25°. The corresponding activation parameters are $\Delta H_6^* \cong 9$ kcal. mole^{-1} and $\Delta S_6^* \cong 3$ cal. deg.$^{-1}$ mole^{-1}. Indelli[5] had calculated an erroneous value of 17 kcal. for the activation energy of reaction 6, apparently by mistaking the sign of the heat of ionization of chlorous acid.

(12) D. M. Kern and R. E. Arlt, unpublished results.
(13) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants," Part II, The Chemical Society, London, 1958, p. 27.

The autocatalytic term in eq. 3 can be accounted for by the reaction sequence

$$I_2 + H_2O \rightleftarrows I^- + HOI + H^+ \quad \text{rapid equilibrium,}[13]$$
$$K_7 = 4 \times 10^{-13} \quad (7)$$

$$HOI + HClO_2 \longrightarrow HIO_2 + HOCl \quad \text{rate-determining step} \quad (8)$$

In the presence of sufficient iodide, the products of step 8 are promptly reduced, with a net yield of two iodine molecules per chlorite. At very low iodide concentration, HIO_2 is instead oxidized to iodate.

We may now calculate $k_8 = k_2/2K_5K_7 = 6 \times 10^7$ M^{-1} sec.$^{-1}$ at 25°. Since the frequency factor for a reaction between two uncharged species is not expected to lie much above the normal upper limit of about 10^{12} M^{-1} sec.$^{-1}$, we may set an upper limit of about 6 kcal. mole^{-1} on ΔH_8^*. Correspondingly, we have

$\Delta H_7° = \Delta H_2^* - \Delta H_8^* - \Delta H_5° \geq 17$ kcal., where we have taken the required enthalpies for reaction 5 from Latimer.[14] This inequality is inconsistent with the NBS heat of formation for HIO(aq) of -38 kcal., a figure already branded as unreliable by Latimer,[14] so our result tends to confirm his suspicions. Proceeding in the reverse direction, if we accept the NBS figure we get $\Delta H_7° \cong 12$ kcal. and $\Delta H_8^* \sim 11$ kcal., in which case the frequency factor for reaction 8 has to be about 10^{16} M^{-1} sec.$^{-1}$, a very unlikely value.

Reactions of Gaseous Brønsted Acids[1]

M. S. B. Munson

Contribution from the Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. Received July 12, 1965

Gaseous ionic reactions have been observed for a series of oxygenated compounds in the source of a mass spectrometer at pressures up to a few tenths of a torr. The major product ions were the solvated protons. Major differences in relative abundances were observed for the higher solvated protons which suggested differences in stability: no more than two molecules of dimethyl ether, acetaldehyde, or acetone will be strongly bound to a proton, but more highly solvated protons will be stable for methanol (three), formic acid (three), and water (four). There are general areas of agreement between ionic reactions in the gas phase and their macroscopic counterpart. Reactions of protonated molecule ions were observed in methanol, acetaldehyde, and acetone which may be considered as elementary steps of some of the acid-catalyzed reactions which occur in solution. Proton transfer was observed from H_3O^+ to HCOOH, and the decomposition path of lowest energy for $HCOOH_2^+$ is the one which gives H_3O^+ and CO.

Introduction

Most of the recent work from this laboratory concerns mass spectrometric studies of ionic reactions in gaseous hydrocarbons. The work reported here is an extension to oxygenated hydrocarbon derivatives and shows the wealth of chemistry which can be developed. A study has been made of ionic reactions in some simple polar molecules to establish the types of reaction products which could be observed, with a primary concern for clustering of the polar molecules and reactions of the protonated species. A complete analysis of all of the reactions was not attempted, and only the dominant

processes are discussed. Individual reaction rate constants were not calculated since the pressures within the source of the mass spectrometer were not known with sufficient accuracy.

Experimental Section

The mass spectrometer and experimental procedure have been reported previously,[2,3] and will not be discussed in detail. The source temperature was 200°. A scan of the mass spectrum was made after the introduction of each successive pressure of the gases. The pressures were estimated from calibrations of structurally related compounds[4] or were taken as proportional to the pressures indicated on the ionization gauge in the envelope surrounding the source. The same qualitative behavior was observed using both pressures. To a reasonable approximation the rate constants for all of the reactions which are reported in this paper are very large, of the order of 10^{-9} cc./molecule sec.

The compounds which were used in these experiments were obtained from several commercial sources and were purified by several single-stage distillations within the gas-handling system. The purities are not accurately known, but they should be about 99%, except for formic acid, which was somewhat less pure. No significant contamination was observed in preliminary experiments. Each compound will be discussed separately.

Results

H₂O. Ionic reactions were studied in pure water at pressures up to about 0.4 torr with electrons of

(1) Supported in part by Project SQUID under Contract Nonr-2623 (S-18).

(2) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).
(3) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).
(4) F. H. Field and M. S. B. Munson, paper presented at the ASTM E-14 Meeting on Mass Spectrometry, San Francisco, Calif., May 1963.