tions in mind an exchange run was made with 0.196 *M* butyl chloride in formic acid containing 10% water by volume. The results are given in Table II where *r* is the ratio of the activity in the chloride ion to that in the control.

TABLE II

$t_{\text{sec.}}$	r	Cl^-
281	0.94	0.022
600	.94	.042
902	.96	.061
1283	1.02	.078

It is apparent that to within experimental error there is no exchange, indicating that there is no appreciable exchange due to a bimolecular collision between the butyl chloride and chloride ion and that there is no appreciable reassociation[6] during the course of hydrolysis.

Acknowledgment.—The apparatus used in this research was built with the aid of a grant from the Research Corporation.

Summary

Exchanges between radio-chloride ion and *t*-butyl chloride have been studied in formic acid and it was found that the exchange proceeded through the equilibrium established between butyl chloride, isobutylene and chloride ions. There was no appreciable contribution to the exchange from a bimolecular collision between butyl chloride and chloride ion. The constant corresponding to rate of ionization was found to be in good agreement with the constant for the rate of hydrolysis under similar conditions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

II. Chain Reactions of Ozone in Aqueous Solution. The Interaction of Ozone and Formic Acid in Aqueous Solution

BY HENRY TAUBE

In a previous article[1] experimental results on the reaction between ozone and hydrogen peroxide and the catalytic decomposition of ozone induced by this reaction were shown to be consistent with a mechanism involving the free radicals HO and HO_2 as intermediates. It was also found that other reducing agents (formic acid,[2] certain metal ions) also catalyze the decomposition of ozone. In this paper more detailed experimental results on the interaction of ozone and formic acid are presented, and the results are correlated with those obtained in the ozone–peroxide system.

Two equations[3] are necessary and sufficient to express the stoichiometric results

$$\text{HCOOH} + O_3 = CO_2 + O_2 + H_2O \qquad \text{(A)}$$

$$2O_3 = 3O_2 \qquad \text{(B)}$$

No evidence was found for oxidation of formic acid by oxygen; even when the ratio of $(\text{HCOOH})/(O_3)$ was as high as ten, the corresponding consumption ratio was less than unity. Neither peroxides nor oxalic acid could be detected as end-products of the reaction.

It was found convenient to represent the rates by the following differential equations

$$\frac{-d(\text{HCOOH})}{dt} = k_A(\text{HCOOH})(O_3)$$

and

$$-\left[\frac{d(O_3)}{dt} - \frac{d(\text{HCOOH})}{dt}\right] = k_B(O_3)^2$$

where k_A and k_B[4] are not constants. k_A was calculated from the measured concentrations of formic acid by using the approximate equation

$$k_A = \frac{2.3}{\overline{(O_3)}\,t}\log\frac{(\text{HCOOH})_0}{(\text{HCOOH})_t}$$

where

$$\overline{(O_3)} = \frac{(O_3)_0 + (O_3)_t}{2}$$

k_B was calculated from the expression

$$k_B = \frac{\Delta B}{(O_3)_0(O_3)_t\,t}$$

$$\Delta B = \Delta(O_3) - \Delta(\text{HCOOH})$$

Materials.—Formic acid solutions were prepared by acidifying C. P. sodium formate with perchloric acid solution.

The solutions of ozone in dilute perchloric acid were pre-

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[1] Taube and Bray, THIS JOURNAL, **62**, 3357–73 (1940).

[2] Ref. 1, p. 3366.

[3] Analogous reactions in the peroxide–ozone and the formic acid–ozone systems are given the same numbers. Arrows are used throughout to represent rate-determining steps.

[4] This definition of k_B differs from that used in the published experiments, ref. 1, p. 3366, and may be converted by multiplying by the factor $(\text{HCOOH})/(O_3)$. When expressed in the same units, the published results agree with the present ones to within 5–10%.

TABLE I

EFFECT OF CHLORIDE ION ON THE RATES OF A AND B

$(HCOOH)_0 = 3.97 \times 10^{-4}$ (some expts. differ by 2%); $(HClO_4) = 0.104$ *M*

No.	$(Cl^-) \times 10^6$	t^5, min.	$(O_3)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	$\Delta B \times 10^4$	k_A	k_B	k_B'	k_B' (In) $\times 10^5$
1	None	26	15.24	0.75	2.11	5.60	4.20		
2	5	40	14.96	.75	1.14	3.65	1.42	2.15	1.18
3	10	49	16.99	1.02	1.03	3.70	1.01	1.26	1.26
4	10	52	12.85	0.79	0.62	3.40	0.99	1.23	1.23
5	25	58	14.31	.89	.41	3.20	.38		
6	100	65.5	14.66	.98	.17	3.03	..		
7	1000	67.5	12.90	.92	.03	3.23	..		
8	3000	69.5	13.77	1.03	.02	3.18	..		

TABLE II

EFFECT OF ACETIC ACID ON THE RATES OF A AND B

$(HCOOH)_0 = 3.93 \times 10^{-4}$; $(HClO_4) = 0.104$ *M*

No.	$(AcOH) \times 10^4$	t, min.	$(O_3)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	$\Delta B \times 10^4$	k_A	k_B	k_B'	k_B' (In) $\times 10^3$
1	4.0	48.0	14.17	0.87	1.62	4.05	1.87	3.37	1.35
2	8.0	53.0	13.28	.76	1.11	3.35	1.17	1.54	1.23
3	8.0	58.0	16.68	1.03	1.72	3.45	1.10	1.49	1.19
4	16.0	58.8	15.31	0.90	1.05	3.10	0.65	0.77	1.23
5	30.0	60.5	14.21	.94	0.38	3.23			
6	100.0	67.0	15.87	1.05	.38	3.02			

pared as described in ref. 1. A large stock supply of C. P. perchloric acid was set aside for the experiments.

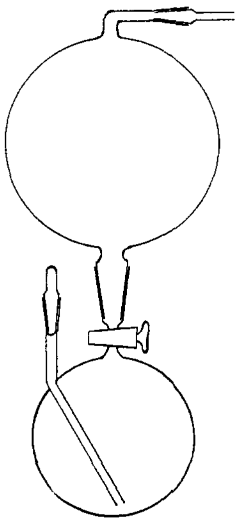

Fig. 1.—Diagram of reaction cell. Lower bulb is the reaction cell. The cell was filled through the side-arm up to the stopcock. The upper bulb prevents entrainment of liquid when air is drawn through.

The rate measurements were carried out in acid solution at 0°. A run consisted of a single experiment in which the initial and final concentrations of ozone and formic acid were determined and the time of reaction measured.

The required volume of the formic acid solution of known concentration, together with the inhibitor, was placed in a calibrated (*ca.* 100-cc.) cell of the type shown in Fig. 1 and cooled in an ice-bath. Then the cell was filled rapidly to the stopcock with the ozone solution, the exact concentration of which had been determined. After leaving the cell in the ice-bath for the desired length of time (usually over forty minutes), a tube was substituted for the stopper on the side-tube and air was rapidly drawn through the solution. The ozone was absorbed from the air by a series of three tubes containing acidified potassium bromide, neutral potassium iodide, and alkaline potassium iodide solution in this order. It was found that the ozone concentration dropped to about one-half its initial value after air had been drawn through for a minute.[5] At the end of the aspirating period (twelve minutes), the contents of the absorption tubes were poured together and the liberated iodine determined. The formic acid was left in the reaction cell and was determined as follows. The solution was made basic with sodium carbonate solution and standard potassium permanganate solution in excess was added. To effect rapid oxidation the solution was boiled for several minutes. After cooling, the excess oxidizing agent was determined by adding I^- and titrating the liberated iodine. The determinations of formic acid yielded values of $\Delta(HCOOH)$ which are most accurate in the intermediate range of concentrations. At very low concentrations, less than 10^{-4} *M*, the results were erratic.

Results and Discussion

Both reactions A and B are inhibited by chloride ion and acetic acid. Table I presents a series of results on the variation of k_A and k_B with the concentration of sodium chloride; Table II presents a similar series for the inhibitor acetic acid. k_B' is defined below; (In) denotes the concentration of the added inhibitor.

The results of Tables I and II show that, with increasing concentration of the inhibitor, ΔB decreases and reaches a limiting value greater than zero, at high inhibitor concentration. This limit is quite small for chloride ion, but is appreciable for acetic acid. The analogy with the peroxide–ozone system is striking, and a similar explanation is offered for the limit at high inhibitor concentration. For example, the decomposition of ozone at high concentration of the acetic acid inhibitor is assumed to be due to a chain reaction of the

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[5] To allow for reaction during the removal of ozone, 0.8 min. was added to the recorded time, t, in calculating k_B and 1.2 min. in calculating k_A.

ozone with the radicals AcO_2 and AcO (cf. reactions 2h and 3h, pages 3361–2, ref. 1).

In order to determine the rate of decomposition of ozone due only to the radicals HO and HO_2 (reactions (3) and (2) below), a correction ΔB_i was subtracted from the tabulated values of ΔB when the limiting value of ΔB was large, and this corrected value was used in calculating k_B. In Table II, 0.11, 0.16, 0.22 and 0.25 were subtracted from the tabulated values of ΔB in Expts. 1, 2, 3 and 4, respectively. The correction is small in comparison to the ΔB values, except at high inhibitor concentration. It was calculated by assuming ΔB_i to be proportional to the fraction of chains broken by the inhibitor, to the time of reaction and to $(O_3)^{3/2}$. Experiment 6, Table II, gives the value when all the chains are broken by AcOH, for particular values of time and ozone concentration. The assumed law for the variation of ΔB_i with (O_3) was indicated by some experiments; a first or second order variation would not materially affect the results.

The limiting value of k_A is nearly the same for the two inhibitors; it is independent of (O_3) but increases slightly as (HCOOH) is raised. If all the chains are destroyed by the inhibitors, and if there is no alternative non-radical path for reaction of formic acid and ozone, this limiting value will be the specific rate of production of free radicals in a mixture of O_3 and HCOOH. In any case, it gives an upper limit for this specific rate.

TABLE III

VARIATION OF $(k_A)_{\text{limit}}$ AT HIGH CHLORIDE ION CONCENTRATIONS

$(Cl^-) = 3 \times 10^{-3}$ *M*; $(HClO_4) = 0.104$ *M*

No.	*t*, min.	$(O_3)_0 \times 10^4$	$(HCOOH)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	$\Delta B \times 10^4$	k_A
1	69.5	13.77	3.97	1.03	0.02	3.18
2	107.0	6.51	3.97	0.74	.03	3.13
3	25.5	8.96	15.88	1.16	.00	3.40
4	92.7	16.48	2.05	0.67	.14	2.71
5	109.5	15.42	1.02	.34	.14	2.40

The results of Table III also show clearly that ΔB at high chloride does not become zero and that the limiting value increases as $(HCOOH)_0$ decreases.

Tables I and II give values of k_B'—the values of k_B corrected for the effect of the substances which break the chains when no inhibitor is added.[6] If one assumes the chain breaking steps

$$\mathrm{HO} + \mathrm{In} \longrightarrow \mathrm{R} \qquad (5i)$$
$$\mathrm{R} = \text{Products}$$

then $k_B' = C/k_{5i}(\mathrm{In})$. When the inhibitor and its concentration are the only variables, C is a true constant, and $k_B'(\mathrm{In})$ is a constant specific for each inhibitor. Examination of the last columns in Tables I and II shows that $k_B'(\mathrm{In})$ is constant as (In) is varied. A comparison of the mean values of $k_B'(\mathrm{In})$ for AcOH and Cl^- permits the relative specific rate of reaction of HO with AcOH and Cl^- to be calculated, and yields the result that in 0.104 *M* H^+ at $\mu = 0.104$, HO reacts 102 times more rapidly with Cl^- than with AcOH.

In order to compare these relative specific rates with those obtained in the H_2O_2–O_3 reactions, the ionic strength was increased to 0.2 by the addition of sodium perchlorate. Table IV contains these results. From the mean values for $k_B'(\mathrm{In})$, it is calculated that at 0.104 *M* H^+ and $\mu = 0.2$, HO reacts 72 times as rapidly with Cl^- as with AcOH. The result from the H_2O_2–O_3 work for these conditions is 68.[7] This agreement is considered proof that the same intermediate is present in both reactions. The value of the ratio of specific reaction rates in the H_2O_2–O_3 system was obtained by the analysis of very complex results. The fact that the same value is obtained in the present simple system is strong support for the interpretation there given.

Comparison of the values of $k_B'(\mathrm{In})$ at $\mu = 0.20$ with the corresponding ones at lower ionic strength shows that an increase in μ has a slight accelerating effect on the reaction

$$\mathrm{AcOH} + \mathrm{HO} \longrightarrow \mathrm{H_2O} + \mathrm{AcO} \qquad (5h)$$

and a marked retarding effect on

$$\mathrm{H^+} + \mathrm{Cl^-} + \mathrm{HO} \longrightarrow \mathrm{H_2O} + \mathrm{Cl} \qquad (5)$$

The 25% change in

$$\frac{k_5(\mathrm{H^+})}{k_{5h}} = \left(\frac{k_B'(\mathrm{AcOH})}{k_B'(\mathrm{Cl^-})}\right)$$

is about that expected for the ionic type represented by reaction 5.

The mechanism for the decomposition of ozone by the radicals HO and HO_2, in the presence of moderate amounts of the inhibitor acetic acid, may be represented by the reactions

$$\mathrm{HCOOH} \rightleftarrows \mathrm{HCO_2^-} + \mathrm{H^+}$$
$$\mathrm{HCO_2^-} + \mathrm{O_3} \xrightarrow{k_1} \mathrm{HO} + \mathrm{CO_2^-} + \mathrm{H_2O} \qquad (1)$$
$$\mathrm{HO} + \mathrm{O_3} \xrightarrow{k_3} \mathrm{HO_2} + \mathrm{O_2} \qquad (3)$$
$$\mathrm{HO_2} + \mathrm{O_3} \xrightarrow{k_2} \mathrm{HO} + 2\mathrm{O_2} \qquad (2)$$

and the chain breaking step 5h.

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[6] Ref. 1, footnote 19, p. 3361.

[7] This assumes that the rate of reaction of HO with Cl^- is proportional to (H^+), with AcOH is independent of (H^+). This assumption is proved to be correct below (*cf.* Tables V, VI, VII).

TABLE IV

COMPARISON OF EFFECT OF Cl^- AND AcOH AS INHIBITORS AT HIGHER IONIC STRENGTH

$(HCOOH)_0 = 4.10 \times 10^{-4}$ *M*, $(HClO_4) = 0.104$ *M*, $\mu = 0.20$

In	(In) $\times 10^4$	*t*, min.	$(O_3)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	k_A	k_B	$k_B'(In)$
None	...	22.5	15.37	0.79	6.4	4.00	
Cl^-	5	49.2	15.63	.89	3.4	1.82	
Cl^-	5	42.2	14.09	.88	4.3	1.81	1.63×10^{-5}
Cl^-	5	53.0	11.53	.83	4.2	1.77	
AcOH	400	47.0	14.22	1.04	5.0	1.62	1.17×10^{-3}
AcOH	400	42.0	15.75	0.98	4.4	1.76	

TABLE V

k_A AND k_B AT 0.0296 *M* $HClO_4$ AND $\mu = 0.104$

$(HCOOH)_0 = 2.93 \times 10^{-4}$ *M;* Expts. 2–4, Cl^- inhibitor; 5–9, AcOH inhibitor

No.	(In) $\times 10^5$	*t*, min.	$(O_3)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	$\Delta B \times 10^4$	k_A	k_B	k_B'	$k_B'(In)$
1	None	8.0	18.37	0.77	3.25	20.3	14.0	..	.....
2	1.8	10.1	19.85	.67	1.34	12.2	3.30	4.32	7.80×10^{-5}
3	3.6	13.5	18.87	.81	0.99	11.9	1.87	2.18	7.86×10^{-5}
4	300	20.8	19.43	1.03	.13	10.5	..	..	.....
5	40	10.8	20.38	0.75	1.97	12.9	4.2	5.9	2.36×10^{-3}
6	40	12.1	15.61	.63	1.33	12.4	4.2	5.9	2.36×10^{-3}
7	40	18.6	10.38	.65	0.84	13.1	3.9	5.4[a]	2.16×10^{-3}
8	80	12.7	18.24	.70	1.15	11.3	2.4	2.9	2.32×10^{-3}
9	1000	20.6	15.45	.79	0.43	9.7	..	..	

[a] $(O_3)_0(O_3)_t$ differed by a factor of 4 from that in Expt. 5. A small uncertainty is introduced because the exact variation of $(\Delta B)_i$ with (O_3) is not known.

TABLE VI

k_A AND k_B AT 0.0102 *M* $HClO_4$, $\mu = 0.104$

Expts. 1–3, chloride inhibitor; 4–6 AcOH inhibitor.

No.	(In)	*t*, min.	$(O_3)_0 \times 10^4$	$(HCOOH)_0 \times 10^4$	$\Delta(HCOOH) \times 10^4$	$\Delta B \times 10^4$	k_A	k_B	$k_B'(In)$[a]
1	10^{-4}	8.8	17.40	2.10	0.93	1.17	32	4.0	4.4×10^{-4}
2	3×10^{-3}	9.2	16.30	4.20	1.79	0.09	34		
3	3×10^{-3}	9.1	17.54	4.20	1.78	.06	32		
4	8×10^{-4}	10.0	16.40	2.10	0.88	1.82	32	5.8	5.36×10^{-3}
5	4×10^{-3}	12.2	10.04	4.20	1.13	0.15	27		
6	10^{-2}	10.0	15.72	4.20	1.50	.43	27		

[a] The value of k_B in the absence of added inhibitor was taken as ten times the value in the corresponding experiments at 0.104 *M* $HClO_4$; a small variation in this figure will not produce an appreciable change in $k_B'(AcOH)/k_B'(Cl^-)$.

TABLE VII

SUMMARY OF RESULTS ON VARIATION OF (H^+)

k_{Al} is the limiting value of k_A at high (Cl^-)

Data from table	(H^+)	$\frac{k_B'(AcOH)}{k_B'(Cl^-)}$	$\frac{k_B'(AcOH)}{k_B'(Cl^-)(H^+)} = \frac{k_5}{k_{5h}}$	k_{Al}	$k_{Al}(H^+)$	$\frac{k_B'(AcOH)(H^+)}{(HCOOH)}$
1 and II	0.104	102	980	3.15	0.327	0.35
V	.0296	30	1000	10.5	.312	.28
VI	.0102	12	1170	32	.327	.34

Evidence that ozone reacts with formate ion rather than formic acid is presented later. Other oxidizing agents (I_2,[8a] Br_2[8b] and $KMnO_4$[8c]) show a similar behavior. The mechanism of reaction 1 may be more complex than is indicated above; the interpretation of the results requires only that the rate of production of HO $\propto$ $(HCO_2^-)(O_3)$.

The above mechanism gives the result that

$$k_B' = \frac{2k_1Kk_3(HCOOH)}{k_{5h}\,(AcOH)(H^+)}$$

Since k_1 is not known, k_3/k_{5h} cannot be calculated from the present work. However, the published value[1] of *ca.* 6.0 for this ratio may be used to estimate $k_1K/(H^+)$. Substituting this value, and $k_B'(AcOH) = 1.25 \times 10^{-3}$ (Table II), and 3.45×10^{-4} *M* for the average concentration of HCOOH in these experiments, $k_1k/(H^+)$ is found to be 0.30.

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[8] (a) Kiss and Urmanczy, *Z. anorg. allgem. Chem.*, **214**, 348–56 (1934); (b) Josefowicz, *Rocz. Chem.*, **9**, 309–24 (1929); (c) Mann and Tompkins, *Trans. Faraday Soc.*, **37**, 201–209 (1941) (each of these gives references to earlier work).

TABLE VIII

VARIATION OF k_A AND k_B WITH (HCOOH) AND (O_3) IN THE ABSENCE OF ADDED INHIBITORS

$(HClO_4) = 0.104\ M$

No.	t, min.	$(O_3)_0 \times 10^4$	$(HCOOH)_0 \times 10^4$	$\Delta B \times 10^4$	$\Delta(HCOOH) \times 10^4$	k_B	k_A
1	9.2	16.33	25.63	1.44	2.77	7.3	7.9
2	10.8	14.45	16.54	1.27	2.00	6.7	8.4
3	11.9	12.92	11.90	1.10	1.38	6.5	8.2
4	15.1	14.03	8.02	1.61	1.12	6.4	7.2
5	37.5	5.56	8.20	0.54	1.04	6.3	7.3
6	26.0	15.24	3.97	2.14	0.75	4.2	5.6
7	35.8	14.40	2.05	2.14	.47	3.5	5.4
8	55.0	6.87	1.95	0.88	.35	4.1	5.7
9	46.5	16.34	0.99	2.80	.20	2.7	3.2
10	53.5	18.09	.50	3.55	.13	2.5	3.4
11	47.8	17.35	.25	2.32	(.06)	1.8	...
12	67.5	15.96	.10	1.72	(.03)	1.1	...
13	76.0	15.70	.05	1.47	(.02)	.86	...
14	70.5	14.30	.025	0.75	(.01)	.54	...

This is about one-tenth of the observed limiting value of k_A at high inhibitor concentration. This discrepancy is explained most simply by assuming an alternative non-radical path for reaction A, which accounts for about 90% of the reaction at high inhibitor concentrations, *e. g.*, to produce bicarbonate ion: $HCO_2^- + O_3 \rightarrow HOCO_2^- + O_2$. Another explanation is that certain radicals not affected by the inhibitors are producing reaction A by a chain process. A decision between these alternative interpretations is not possible at present.

Tables V and VI present the results of experiments at lower concentrations of hydrogen ion and constant ionic strength. These results together with those of Tables I and II are summarized in Table VII.

The results in Table VII show that k_5/k_{5h} is nearly constant over the ten-fold range of hydrogen-ion concentration investigated. However, the rate of reaction of HO with Cl^- probably becomes independent of (H^+) at very low values of this factor. This is suggested by the drift of the ratios in Table VII, and by the results of an independent experiment in which it was shown that Cl^- is a fairly efficient inhibitor for the spontaneous decomposition of ozone in a phosphate buffer (*p*H about 7).

Column 7, Table VII shows that

$$\frac{k_B'(H^+)(AcOH)}{(HCOOH)} \left(= \frac{2k_1K\ k_3}{k_{5h}} \right)$$

is nearly constant as the concentration of hydrogen ion is varied. This equation was derived from a mechanism in which O_3 reacts with HCO_2^- rather than with HCOOH; the results show that this assumption is correct The observation that the limiting value of k_A at high chloride ion varies inversely with the concentration of hydrogen ion ($k_{A1}(H^+)$ is constant, Table VII, column 6) is also consistent with this mechanism.

At low (H^+), k_{A1} for acetic acid is less than that for Cl^-. This suggests that the inhibitor acetic acid is not completely regenerated at low (H^+), but is partially oxidized to a substance which reduces MnO_4^- (*e. g.*, methyl alcohol). This is supported by results obtained in the course of another study: a solution containing O_3, $Na_2C_2O_4$, AcOH and AcONa was allowed to react for some time, and the residual ozone was removed; the resulting solution was found to reduce more MnO_4^- than corresponded to the oxalate initially present.

To determine the nature of the chain breaking steps in the absence of added inhibitors, a series of experiments with solutions containing O_3, HCOOH and $HClO_4$ alone was carried out. Most of the experiments were checked by duplicates which, except at the lowest concentrations of formic acid, gave values of k_B agreeing within about 5%.

These results show that at high values of (HCOOH), k_B approaches a limit of about 6.8. The values of k_B are nearly the same in Expts. 4 and 5, although (O_3) $(O_3)_t$ varies by a factor of 7.5. In this region of concentration, at constant (H^+) k_B defined by

$$-\left[\frac{d(O_3)}{dt} - \frac{d(HCOOH)}{dt}\right] = k_B(O_3)^2$$

is independent of both (HCOOH) and (O_3).

This rate law follows from a mechanism consisting of reactions (1), (2), and (3) together with the chain breaking steps

$$HO + HCOOH \longrightarrow HCO_2 + H_2O \qquad (5f)$$
$$HCO_2 \longrightarrow \text{Products}$$

(the last step may involve additional reactions of HCOOH and O_3 and contribute to reaction A) and

$$k_B = \frac{2k_1K}{(H^+)}\frac{k_3}{k_{5f}}$$

Using the value of $k_1K/(H^+)$ calculated above, $k_3/k_{5f} = 6.8/0.60 = 11.1$; *i. e.*, HO reacts 11.1 as rapidly with O_3 as with HCOOH in 0.104 *M* H^+ at 0°. The relative specific rates of reaction of HO with O_3, H_2O_2, AcOH, and HCOOH, and Cl^- in 0.104 *M* H^+ and $\mu = 0.104$ are 1, 0.32, 0.17, 0.09, 17.3. The first three figures are taken from ref. 1. It is assumed that the ionic strength will not affect the ratios appreciably.

Although the results at lower concentrations of (HCOOH) are fairly reproducible, they are very complex and only a qualitative discussion of these limited data is attempted. At concentrations of HCOOH below 8×10^{-4} *M*, k_B decreases. This may be interpreted by assuming that the chain breaking step $HO + HCO_2 \rightarrow CO_2 + H_2O$ becomes important. With this as the only chain breaking step, the rate law for reaction B becomes

$$\text{rate of B} = k(O_3)^{3/2}(HCOOH)^{1/2}$$

(This derivation requires also the assumption that the stationary concentration of HO greatly exceeds that of HO_2.) k_B, however, does not decrease continually with HCOOH as would be predicted by this law but levels off at 10^{-4} *M* HCOOH and begins to fall off again at 2.5×10^{-5} *M* HCOOH and lower.

It is suggested that at the very low concentrations of HCOOH, organic free radicals also contribute to reaction B

$$CO_2^- \text{ (or } HCO_2) + O_3 \longrightarrow CO_3^- + O_2$$
$$\left.\begin{array}{l} CO_3^- + O_3 \longrightarrow CO_4^- + O_2 \\ CO_4^- + O_3 \longrightarrow CO_3^- + O_2 \end{array}\right\} \begin{array}{c}\text{Chains analogous to HO–} \\ HO_2 \text{ chains}\end{array}$$

CO_3^- and CO_4^- are expected to be powerful oxidizing agents and their concentration would be suppressed as HCOOH is increased. Thus, at values above 10^{-4} *M* HCOOH, the HO, HO_2 chains only are important.

In some respects the present system proved to be simpler than the peroxide–ozone system. For example, the action of the Cl^- inhibitor is less complex because the reaction of atomic chlorine (produced in 5) with formic acid gives an organic radical which does not contribute appreciably to reaction B. Thus, the complication of the $Cl + Cl^- = Cl_2^-$ equilibrium is absent. However, it was not possible experimentally to determine the specific rate of the chain initiating reaction in the present work, and this makes the interpretation less complete. Furthermore, the mechanism of reaction A is not completely understood.

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Summary

The rate of reduction of O_3 by HCOOH (reaction A) and the rate of the accompanying decomposition of O_3 (reaction B) have been measured at varying concentrations of O_3, HCOOH, $HClO_4$ and of the inhibitors Cl^- and AcOH. Both reactions are shown to be chain reactions.

The experimental data are consistent with the following conclusions: HO–HO_2 chains are responsible for the decomposition of ozone. The relative specific rate of reaction of HO with Cl^- and AcOH, calculated from the present work, agreed closely with that obtained in the peroxide–ozone reaction. Over the ten-fold range of (H^+), the rate of reaction of HO with AcOH was found to be independent of (H^+) while that with Cl^- was found to vary nearly linearly with (H^+).

In the absence of added inhibitor, at high formic acid, the chains are broken by reaction of HO with formic acid. The relative specific rate of reaction of HO with O_3 and formic acid in 0.104 *M* (H^+) is 11.

The chain initiating step is a reaction of O_3 with HCO_2^-. The observed limiting value for the specific rate of reaction A at high inhibitor concentration is not equal to the specific rate of chain initiation but includes the specific rate of some additional path for reaction A.

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