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Ozonization of Organic Compounds. VII. Carboxylic Acids, Alcohols, and Carbonyl Compounds

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The rate and products of the ozonization of carboxylic acids, alcohols, and ketones have been studied in water at 30 °C. The ozonization of alcohols gave corresponding carbonyl compounds as major product. The ozonization of ketones brought about primarily the carbon-carbon bond cleavage and gave carboxylic acids. Saturated carboxylic acids such as acetic acid, propionic acid, and isobutyric acid were ozonized only slowly in neutral water, but they were ozonized faster in alkaline aqueous solution. On the other hand, α-hydroxy carboxylic acids such as glycolic acid and lactic acid were ozonized even in pure water. The mechanism of ozonization of these compounds and the effect of pH are discussed.

The ozonization of organic compounds has been studied extensively for many years[1–4] and it has been applied for the preparation and identification of organic compounds. Water treatment by ozone has received much attention recently because of its advantages over currently employed methods such as chlorine treatment.[5–7] In order to establish the validity and limit of water treatment by ozone, it is of fundamental importance to know the rate and products of the ozonization of various compounds in water. In the course of our study on the ozonization of organic compounds, we have undertaken the study on the ozonization of carboxylic acids, alcohols, and ketones in water. The ozonization of carboxylic acids is especially important since the ozonization of aromatic hydrocarbons,[8–10] phenol,[11–16] and alkylbenzenesulfonic acids[17,18] gives carboxylic acids and they are known as the typical refractory compounds in water.

Experimental

Materials and Procedures. Commercial alcohols, ketones, and carboxylic acids were used as received. Water was purified by passing through an ion exchange resin followed by distillation. Following buffer solutions were used (1 M=1 mol dm^{-3}).

pH 1.1 : 0.2 M KCl (50 ml)+0.2 M HCl (97 ml)+ H_2O (53 ml)
pH 5.3 : 1/30 M KH_2PO_4 (32 ml)+1/30 M Na_2HPO_4 (1 ml)
pH 7.1 : 0.2 M KH_2PO_4 (50 ml)+0.2 M NaOH (29.6 ml)+H_2O (120.4 ml)
pH 9.9 : 0.1 M Na_2CO_3 (5 ml)+0.1 M $NaHCO_3$ (5 ml)
pH 12.1: 0.1 M Na_2HPO_4 (50 ml)+0.1 M NaOH (43.2 ml)+H_2O (6.8 ml)

Ozone was produced by a standard ozone generator, Nippon Ozone Co. Ltd., Model O-3-2, by charging pure oxygen dried beforehand by silica gel.

The ozonization was carried out by bubbling ozone-oxygen gas through the reaction mixture at 30 °C. The gas was introduced at a speed of 100—200 ml/min and the rate of ozone supply was 0.12—0.20 mmol/min.

Analytical Methods. The amounts of substrate reacted and products formed were measured by a gas liquid chromatography (GLC, Shimadzu Model GC-4BPTH, with Porapak Q column and FID detector), a high pressure liquid chromatography (HPLC, JASCO, GP-A30, Shodex Ionpak C-811 column and 0.1% H_3PO_4 eluent), and an isotachophoretic analyzer (IP, Shimadzu Model IP-1B).[9,11] Total amount of peroxides was determined by iodometric titration. Hydrogen peroxide was measured separately from the difference between the titers before and after the treatment with catalase as described previously.[11]

Total yield of carbonyl compounds was measured as follows. Product solution was treated with 2,4-dinitrophenylhydrazine saturated in 2 M aqueous hydrochloric acid, allowed to stand overnight at room temperature, and filtered to remove 2,4-dinitrophenylhydrazone. The filtrate was analyzed spectrometrically to measure the consumption of 2,4-dinitrophenylhydrazine, $\lambda_{max}=322$ nm and $\varepsilon=1.1\times10^4$ M^{-1} cm^{-1}. In some cases, 2,4-dinitrophenylhydrazone was dried and weighed. Carbon dioxide was analyzed as previously.[11]

Results

Ozonization of Alcohols. The results of ozonization of 2-butanol are shown in Table 1. It was found that appreciable amount of 2-butanol was carried away out of the reaction vessel with ozone-oxygen gas; for example, about 2 mmol of 2-butanol was removed in 2 h when only oxygen was introduced under the similar conditions as in Table 1. Therefore, the amount of disappeared 2-butanol shown in Table 1 is larger than that actually reacted. The poor material balance in Table 1 is apparently due to this disappearance of 2-butanol as well as the formation of carbon dioxide.

However, it is clear that ozonization of 2-butanol in water gave 2-butanone as a major product. For example, ozonization for 30 min gave 2-butanone with 83% selectivity. Small amounts of formic, acetic, and propionic acids and hydrogen peroxide were also found. These products are similar to those in the ozonization of 2-butanol in organic solvent.[19]

The ozonization of 1-butanol gave butanal as a major product with smaller amount of butyric acid.

As shown in Table 1, the rate of ozonization was not much affected by the pH of the solution.

Ozonization of 2-Butanone. The results are shown in Table 2. The major product was acetic acid, and smaller amounts of methylglyoxal, pyruvic acid, formic acid, methanol, and acetaldehyde were also observed. Neither ethyl acetate nor methyl propionate was found.

Ozonization of 3-Pentanone. The results are included in Table 2. Formic, acetic, and propionic acids were observed. At high pH, the amount of formic

TABLE 1. OZONIZATION OF 2-BUTANOL (BOH) IN 100 ml AQUEOUS SOLUTION AT 30 °C, 2 h

Run No.	1	2	3	4	5	6
Initial pH	1.1	5.3	5.8	6	9.9	12.1
Initial BOH(mmol)	10.90	10.69	10.69	11.91	10.90	10.69
BOH after 1 h[a]	7.3	8.94	9.03		8.23	8.03
BOH after 2 h[a]	6.73	7.63	6.66	9.17	6.85	6.10
BOH reacted in 2 h[a]	4.17	3.06	4.03	2.74	4.05	4.59
Products in mmol						
H_2O_2	0.14	0.14	0.19	0.07	0	0
ROOH	0	0	0	Trace	0	0
HCOOH	0.09	0.06	0.09	0.05	0.09	0.33
CH_3COOH	0.06	0.11	0.14	0.06	0.09	0.96
C_2H_5COOH	0.15	0.20	0.24	0.04	0.55	0.73
$CH_3COCOOH$		Trace	0			0.01
$(COOH)_2$			0			Trace
Carbonyls[b]		1.33				
2-Butanone[c]	0.93[d]	1.13[e]	1.34	1.00	1.61	1.05[f]
Acetaldehyde	0.02	0.03	0.02	0.02		0.06
Methanol	Trace	Trace	0.3			Trace

a) Appreciable amount of 2-butanol was brought away out of the reaction vessel with oxygen-ozone gas, see text. b) Total carbonyls measured from the disappearance of 2,4-dinitrophenylhydrazine, see Experimental. c) By HPLC. d) 0.83 mmol by GLC. e) 1.13 mmol by GLC. f) 1.26 mmol by GLC.

TABLE 2. OZONIZATION OF 2-BUTANONE (BON), 3-PENTANONE (PON), AND METHYLGLYOXAL (MG) IN 100 ml WATER AT 30 °C

Run No.	7	8	9	10	11	12	13
Substrate S	BON	BON	BON	PON	PON	PON	MG
Initial S(mmol)	10.32	10.05	1.04	10.2	50.1	50.1	2.94
Final S(mmol)	5.81	6.45	0.54	6	35	30	1.87
S reacted(mmol)	4.51	3.60	0.50	4	15	20	1.07
Time/h	4	2	2	2	3	3	2
Initial pH				6	6	9.9	
Products in mmol							
H_2O_2							0.02
Peroxide	Trace	Trace	Trace	0.04	0.02	0	Trace
Acids[a]				0.11	0.48		
HCOOH[b]	0.11	0.05	Trace	0.02 (0.03)	0.01 (0.01)	0.32	
CH_3COOH[b]	2.17	0.91	0.26	0.07 (0.06)	0.20 (0.22)	0.61	0.18
C_2H_5COOH[b]	Trace	Trace	0	0.08 (0.06)	0.24 (0.25)	0.88	
$(COOH)_2$							0.04
$CH_3COCOOH$	0.09	0.05	0.01				0.55
CH_3OH	0.05	0.09	0.02				Small
CH_3CHO	0.02	0.04	0.01				
CH_3COCHO	0.15	0.08	0.05				
$CH_3COOC_2H_5$			0				
$C_2H_5COOCH_3$			0				

a) By titration. b) By HPLC, numbers in parentheses are by isotachophoretic analysis.

acid increased appreciably. The formation of acetic acid and propionic acid in the ozonization of 3-pentanone has been reported previously.[1]

Some unknown products were observed by HPLC. Although it was not identified conclusively, one of the unknown products may be 2,3-pentanedione. The formation of 2,3-butanedione in the ozonization of 2-butanone has been reported.[20]

Ozonization of Methylglyoxal. The results included in Table 2 show that the major reaction is the oxidation of formyl group to carboxyl group. Smaller amounts of acetic acid and oxalic acid may have been formed through pyruvic acid.

Ozonization of Glycolic Acid and Lactic Acid. The results of ozonization of glycolic acid gave glyoxylic acid as primary and major product, which was further ozonized to oxalic acid (Table 3). Smaller amount of formic acid was also found. The ozonization of

TABLE 3. OZONIZATION OF GLYCOLIC ACID (GA) AND LACTIC ACID (LA) IN WATER AT 30 °C, 2 h

Run No.	14	15	16	17	18	19
Substrate S	GA	GA	LA	LA	LA	LA
Initial S(mmol)	1.17	3.13	1.10	3.31	1.05	1.00
Final S(mmol)	0.40	1.91	0.29	2.44	0.72	0.20
S reacted(mmol)	0.77	1.22	0.81	0.87	0.33	0.80
Initial pH					1.1	9.9
Products in mmol						
H_2O_2	0.01	0.02	0.05	0.04	Trace	0
CO_2		0.78				
HCOOH	0.03	0.09	0.03	0.09	Trace	0
CH_3COOH			0	Trace	0.08	0.07
$CH_3COCOOH$			0.52	0.78	0.22	0.76
OHCCOOH	0.12	0.67				
$(COOH)_2$	0.17	0.31	0.04	0.04	Trace	0.05

TABLE 4. OZONIZATION OF ACETIC ACID (AA) IN WATER AT 30 °C, 1.5 h

Run No.	20	21
Initial AA(mmol)	5.01[a)]	5.07
Final AA(mmol)	4.95	3.02
AA reacted(mmol)	0.06	2.05
Initial pH	7.0	13.0
Final pH	7.0	9.4
Products in mmol		
HCOOH	0	Trace
$HOCH_2COOH$	0	0.00_4
OHCCOOH	0.02	0.03
$(COOH)_2$	0.02	0.50

a) Sodium acetate.

TABLE 5. OZONIZATION OF PROPIONIC ACID (PA) IN WATER IN 30 °C, 1.5 h

Run No.	22	23	24	25	26
Initial PA(mmol)	4.97	5.07	5.05	2.24	4.97
Final PA(mmol)	4.92	4.99	4.79	1.76	2.44
PA reacted(mmol)	0.05	0.08	0.26	0.48	2.53
Initial pH	1.3	2.8	4.9	8.0	12.6
Final pH	1.3	2.7	4.9	7.6	9.2
Products in mmol					
H_2O_2	0.03	0.01	0.02	0	0
HCOOH	0.03	0.01	0	0	0.02
CH_3COOH	0.02	0.03	0.01	0.10	0.54
$(COOH)_2$	Trace	Trace	0.01	0.03	0.14
$CH_3CH(OH)COOH$				0.01	0.05
$CH_3COCOOH$	0.00_4	Trace	0.05	0.06	0.15

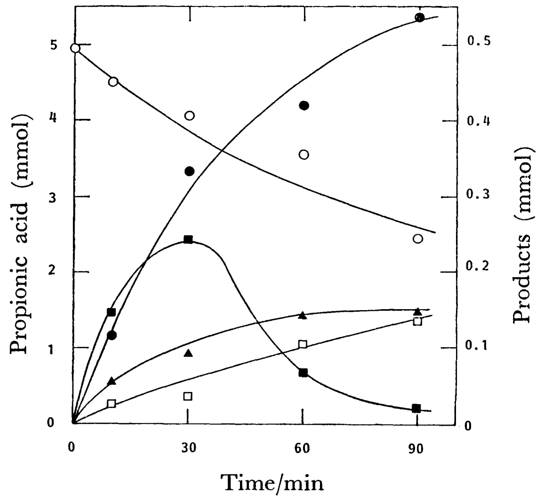


Fig. 1. Ozonization of propionic acid in NaOH–H_2O at 30 °C, initial pH 12.6 (Run 26).
○: Propionic acid; ●: acetic acid; ■: formic acid; ▲: pyruvic acid; □: oxalic acid.

lactic acid gave pyruvic acid as major product with about 90% selectivity. Small amounts of formic acid and oxalic acid were also observed. The formation of hydrogen peroxide was observed from both glycolic acid and lactic acid, but no organic peroxide was found.

Table 3 also shows the effect of pH in the ozonization of lactic acid. The conversion of lactic acid was higher at higher pH. Pyruvic acid was always formed as a major product.

Ozonization of Pyruvic Acid. Acetic and oxalic acids were formed as major products in the ozonization of pyruvic acid.

Ozonization of Acetic, Propionic, Isobutyric, and Pivalic Acids. Saturated carboxylic acids such as acetic, propionic, isobutyric, and oxalic acids were stable toward ozone at 30 °C. However, they were ozonized at appreciable rate at higher pH. Table 4 shows the results of ozonization of acetic acid and its sodium salt. Acetic acid has been accepted as an inactive solvent in the ozonization, but it is ozonized in alkaline medium. The products were formic acid, glycolic acid, glyoxylic acid, and oxalic acid. These acids, except oxalic acid, were further ozonized to give eventually oxalic acid and carbon dioxide. Succinic acid was not observed. Sodium acetate was ozonized only slowly at pH 7.

The results of ozonization of propionic acid are shown in Table 5. The change in the product distribution with time is shown in Fig. 1. Again, the rate of ozonization increased with increasing pH of the medium. The products observed were formic acid, acetic acid, lactic acid, pyruvic acid, and oxalic acid. Figure 1 shows that acetic acid and oxalic acid are

TABLE 6. OZONIZATION OF ISOBUTYRIC ACID (BA) IN WATER AT 30 °C, 1.5 h

Run No.	27	28	29	30	31	32
Initial BA(mmol)	4.96	5.05	4.97	5.00	5.03	5.08
Final BA(mmol)	4.91	5.00	4.61	4.34	4.41	3.19
BA reacted(mmol)	0.05	0.05	0.36	0.66	0.62	1.89
Initial pH	1.3	2.7	4.9	7.2	10.1	12.7
Final pH	1.3	2.7	4.9	7.4	8.4	9.4
Products in mmol						
CO_2				0.88	0.51	
Carbonyls				0.19	0.14	
CH_3COCH_3	0.03	0	0.14	0.11	0.15	0.35
HCOOH	0.05	0	0.01	0.02	0.02	0.06
CH_3COOH	0.02		0.13	0.17	0.16	0.58
$(COOH)_2$	0		Trace	0	0	0.03
$CH_3COCOOH$	0.01		0.03	0.07	0.08	0.21
$(CH_3)_2C(OH)COOH$	0.02		0.11	0.03	0.02	0.04

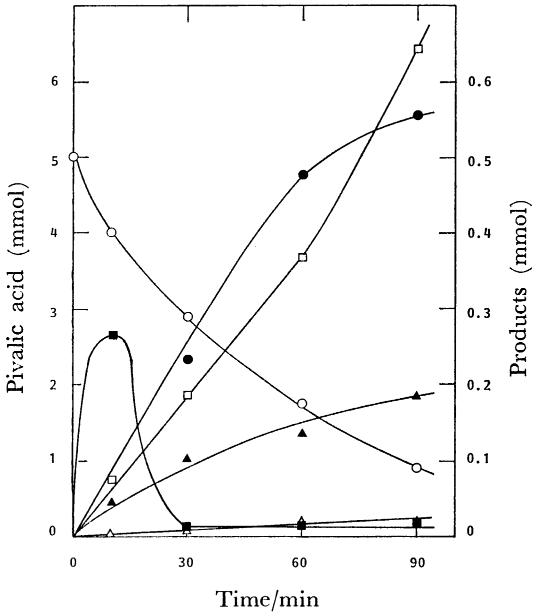


Fig. 2. Ozonization of pivalic acid in water at 30 °C, initial pH 13.0.
○: Pivalic acid; □: acetic acid; ●: acetone ▲: pyruvic acid; ■: formic acid; △: oxalic acid.

stable final products, whereas formic acid is further ozonized to carbon dioxide and water.[11]

The results of ozonization of isobutyric acid are shown in Table 6. Isobutyric acid was virtually resistent toward ozone in water, but the rate of ozonization increased markedly with increasing pH of the solution as observed for propionic acid. The major products were formic acid, acetic acid, pyruvic acid, acetone, and carbon dioxide. Smaller amounts of oxalic acid and α-hydroxyisobutyric acid were also observed. Little peroxide was found.

Pivalic acid was found to be ozonized, although slowly, even in pure water. The rate of ozonization increased similarly at higher pH. Figure 2 shows the results of ozonization of pivalic acid at initial pH 12.97. Acetic acid, acetone, and pyruvic acid were obtained as major products. Acetone and pyruvic acid accounted for 85% of total carbonyls estimated spectrometrically using 2,4-dinitrophenylhydrazine. Formic acid was observed in considerable amount at the initial stage, but it was further ozonized to carbon dioxide and water. Small amount of oxalic acid was also observed.

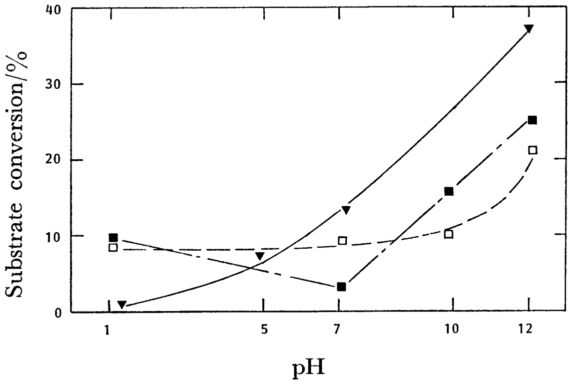


Fig. 3. Effect of pH on the rate of ozonization of isobutyric acid (▼, 5 mmol, 90 min), cyclohexanone (■, 10 mmol, 60 min), and cyclohexanol (□, 10 mmol, 60 min) in 100 ml water at 30 °C.

The effect of pH on the rate of ozonization of isobutyric acid, cyclohexanone, and cyclohexanol is shown in Fig. 3.

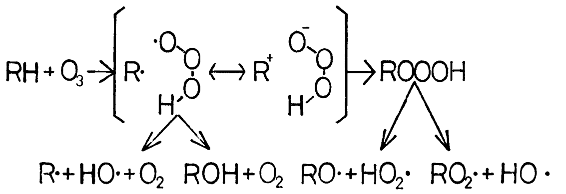
Discussion

Ozone can behave as a 1,3-dipole, an electrophile or a nucleophile.[4] It reacts quite rapidly with carbon-carbon double bonds, but its electrophilic attack on carbon-hydrogen bonds is usually slow. This accounts for the well known fact that the rate of removal of carboxylic acids from water by ozone is slow.

In alkaline medium, it has been reported that ozone is unstable and gives hydroxyl radical[21–25] and oxygen atom,[26] both of which are more reactive than ozone toward C–H bond. The p*K* of the hydroxyl radical is 11.85,[26] and hence at pH above 11.85 the oxygen ion O^- must act as the most important attacking species. Furthermore, since the decomposition of ozone is initiated by OH^- ions and accelerated by a free radical chain reaction, the rate of ozone destruction and that of active hydroxyl radical formation depend on experimental variables such as pH and solutes present in water. Some solutes accelerate the chain reaction, but some inhibit the chain reaction by scavenging hydroxyl radical.[23] It should be noted, therefore, that the relative importance of various active species also varies with experimental variables.

At pH below 9, ozone molecule must be the sole active species.

The detailed mechanisms of the initial attack of ozone toward carbon-hydrogen bonds has not yet been conclusively established. It appears that the ozonization of carbon-hydrogen bonds can proceed both by radical and ionic processes.[27-30] The formation of 1-chloro- and 1-bromoadamantane in the ozonization of adamantane in the presence of bromotrichloromethane[31] suggests the presence of carbon radical. On the other hand, the high ratio of retention of configuration in the ozonization of saturated hydrocarbons[31,32] implies that this radical is not entirely free. The hydrotrioxide,[30,31] whether it is formed by radical or ionic process, should decompose to give eventually alkoxyl and peroxyl radicals under the present reaction conditions. Murray *et al.*[33] have observed a low temperature NMR that indicated the existence of hydrotrioxide.



The mechanism of ozonization of alcohols, ketones, and carboxylic acids will be discussed below taking the above discussion into consideration.

A probable reaction pathway for the ozonization of 2-butanol is shown in Fig. 4. The relative importance of these reactions in Fig. 4 depends, as discussed above, on the experimental variables. The compounds in the boxes were found experimentally. Ozone must attack hydrogen α to hydroxyl group to give hydrotrioxide.[31,33] It decomposes to give 2-butanone, the major product observed experimentally. The radical decomposition can yield alkyl, alkoxyl, and peroxyl radicals. The alkoxyl radical must undergo β-scission or hydrogen atom abstraction to give acetic acid, propionic acid, and 2-butanone. The ethyl and methyl radicals formed simultaneously in the β-scission should react with oxygen and give eventually ethanol, acetaldehyde, acetic acid, methanol, and formic acid. Alkyl and peroxyl radicals should give 2-butanone.

As discussed above, the attack on the α-hydrogen by hydroxyl radical and/or oxygen ion formed from ozone becomes more important at higher pH.

In any event, 2-butanone is formed from 2-butanol as a major product. It has been observed that the ozonization of alcohols gives corresponding carbonyl compounds both in water and in organic solvents.[19,31,34,35]

As shown in Table 2, the ozonization of 2-butanone gave acetic acid as a major product and that of 3-pentanone gave acetic acid and propionic acid. Three processes have been considered for the ozonization of ketone;[1] that is, (1) ozonolysis of double bond of the enol form of ketone, (2) nucleophilic attack of ozone to give ester, followed by oxidation of ester, and (3) ozone-initiated oxidation by molecular oxygen. The absence of ethyl acetate and methyl propionate in the ozonization of 2-butanone (Table 2) and also the absence of ethyl propionate in the ozonization of 3-pentanone (Table 2) indicate that the second process does not play an important role under the present reaction conditions. It was found that these esters were not ozonized at appreciable rate.

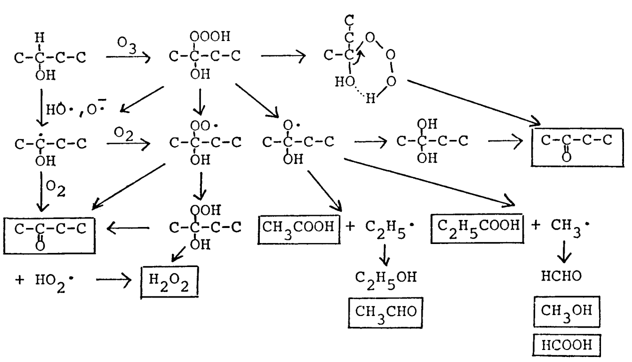
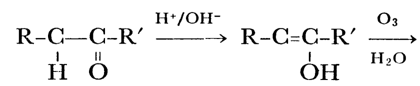


Fig. 4. Major reaction pathway in the ozonization of 2-butanol in water.

Thus, the ozonization of ketones must proceed by the processes both (1) and (3), the relative importance depending on pH and the substrate. The rate of ozonization of ketone is accelerated by both acid and alkaline due to a preferred formation of the enol form; for example,



$$\mathrm{R{-}\underset{H}{C}{-}\underset{O}{\overset{\|}{C}}{-}R'} \xrightarrow{\mathrm{H^+/OH^-}} \mathrm{R{-}C{=}\underset{OH}{C}{-}R'} \xrightarrow[\mathrm{H_2O}]{\mathrm{O_3}}$$

$$\mathrm{RCHO} + \mathrm{H_2O_2} + \mathrm{R'COOH}.$$

We have previously reported the ozonolysis of unsaturated carboxylic acids.[11,36] Saturated carboxylic acids are in general stable toward ozone. As described above, acetic acid, propionic acid, isobutyric acid, and oxalic acid were not ozonized easily in pure water. However, α-hydroxy carboxylic acids such as glycolic acid and lactic acid were ozonized even in neutral water. The hydroxy group must have some accelerating effect and the ozonization must proceed as that of 2-butanol, giving corresponding carbonyl compounds as the primary and major product.

The probable major reaction pathway in the ozonization of isobutyric acid is shown as an example in Fig. 5. The ozonization of other saturated carboxylic acids should proceed similary. As shown in Fig. 5, the attack of ozone and/or hydroxyl radical on tertiary C–H bond gives 1-carboxy-1-methylethyl radical and its oxygenated radicals, which eventually yield the observed products, *i.e.*, α-hydroxyisobutyric acid, pyruvic acid, acetic acid, formic acid, acetone, and carbon dioxide.

The products formed from the 2-carboxypropyl radical were not found, although small amounts of un-

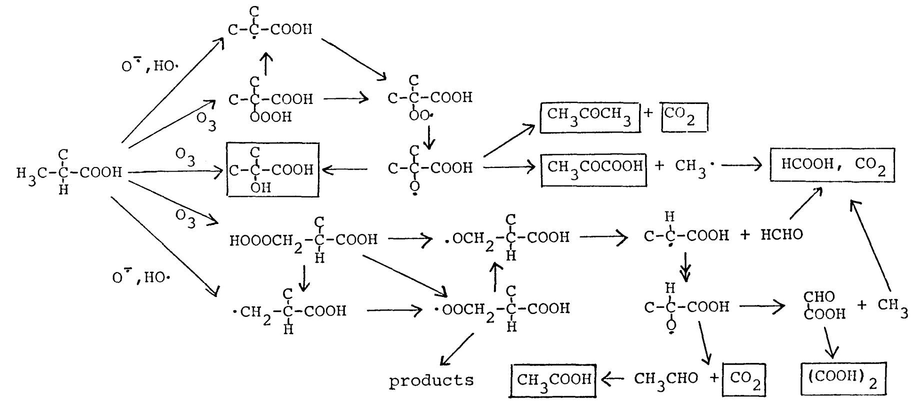


Fig. 5. Probable major reaction pathway in the ozonization of isobutyric acid in water.

identified products were observed.

The increase in the rate of ozonization of carboxylic acids at higher pH must be ascribed to the increase in the reactivities of substrate and to the formation of active attacking species. It has been reported[37] that carboxylate anion has higher reactivity than parent carboxylic acid toward the hydroxyl radical which is also an electron seeking reagent like ozone.

The products observed in the ozonization of carboxylic acids at higher pH are similar with those observed in the oxidation of carboxylic acids induced by hydroxyl radical generated by Fenton reagent and photolysis of hydrogen peroxide.[38]

From the viewpoint of water treatment, it may well be concluded that, as generally accepted, ozone is a powerful oxidizing reagent, especially for aromatic ring, but the complete destruction of saturated carboxylic acids in not practical.

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