Photolytic Oxidation of Aliphatic Acids by Aqueous Sodium Hypochlorite

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Photolytic oxidation of acetic and propionic acids by aqueous sodium hypochlorite has been studied. In the presence of excess of sodium hypochlorite, these acids were photo-oxidised effectively to CO_2 and H_2O, but the reaction did not occur in the dark. By contrast, irradiation of an equimolar mixture of propionic acid and sodium hypochlorite gave the oxygenated products $CH_3CH(OH)CO_2H$, $HOCH_2CH_2CO_2H$, $CH_2(CO_2H)_2$, CH_3COCO_2H, CH_3CO_2H, $HOCH_2CO_2H$, and CO_2 together with small amounts of the chlorinated products $CH_3CHClCO_2H$, $ClCH_2CH_2CO_2H$, and $ClCH_2CO_2H$. The chlorination products were favoured at lower wavelength (*e.g.* >300 nm). Secondary photo-oxidation of these products was also studied and the reactivities are discussed.

THE removal of organic contaminants in waste water has generally been achieved by biochemical and physical methods. But these methods are often insufficient for some kinds of organic materials, such as the lower fatty acids, which remain after ordinary oxidation.

The metal-ion-catalysed H_2O_2 oxidation of acetic acid,[1] for which u.v. irradiation accelerates the oxidation,[2] has been reported, as has the auto-oxidation of esters.[3] The only products from H_2O_2 oxidation of acetic acid and sodium acetate [1,2] were CO_2 and H_2O, while CO_2 and CO were produced from the auto-oxidation of esters.[3] Glycolic, glyoxalic, and oxalic acids were formed by α-irradiated auto-oxidation of acetic acid.[4] Recently, an effective industrial process was developed for the photo-oxidative removal of organic material in waste water by treatment with alkaline aqueous hypochlorite,[5] most material completely decomposing to CO_2, HCl, and H_2O.

In our previous reports, photo-oxidations of alkylbenzenesulphonic acids [6] and polyethers [7] by NaOCl were shown to lead effectively to CO_2 and H_2O, by a mechanism involving atomic oxygen. The present paper reports an extension of this photo-oxidation to acetic and propionic acids. We have examined the mechanism and probable intermediates as well as the products, especially with propionic acid.

RESULTS AND DISCUSSION

Photo-oxidation of Propionic Acid.—Irradiation of 0.1M-$CH_3CH_2CO_2Na$ by excess (0.72M) of NaOCl in aqueous alkaline solution (pH >12) gave complete oxidation (*i.e.* CO_2 and H_2O were formed), no important intermediate being observed. However, propionic acid is fairly resistant to this oxidation, so that *ca.* 26% NaOCl in aqueous $CH_3CH_2CO_2Na$ gave only gaseous O_2 with no appreciable amount of organic product. The formation of CO_2 almost corresponds to the consumption of $CH_3CH_2CO_2Na$ (Figure 1).

When 0.5M-$CH_3CH_2CO_2Na$ was photolysed with a nearly equimolar amount of NaOCl there were observed a number of intermediates, $CH_3CH(OH)CO_2H$, $HOCH_2CH_2CO_2H$, $CH_2(CO_2H)_2$, CH_3COCO_2H, CH_3CO_2H, and $HOCH_2CO_2H$ along with small amounts of chlorinated products, $CH_3CH(Cl)CO_2H$, $ClCH_2CH_2CO_2H$, and $ClCH_2CO_2H$, and only small amounts of CO_2 and O_2 were evolved (Table 1). α-Chloropropionic acid tended to accumulate as the reaction progressed, but only a small amount of β-chloropropionic acid was detected (Figure 2).

$$ClCH_2CH_2CO_2^- \xrightarrow{OH^-} \begin{cases} CH_2{=}CHCO_2^- + HCl & \text{(1a)} \\ CH_2{=}CH_2 + CO_2 + Cl^- & \text{(1b)} \end{cases}$$

This may be due to the ready dehydrochlorination of β-chloropropionic acid in alkaline solution.[8] Indeed, products derived from $CH_2{=}CHCO_2H$, *i.e.* $HOCH_2CH(Cl)CO_2H$, $ClCH_2CH(OH)CO_2H$ (HOCl addition), $ClCH_2CH(Cl)CO_2H$ (Cl_2 addition), and $CH_3CCl_2CO_2H$ were detected by g.l.c.–mass spectrometry.

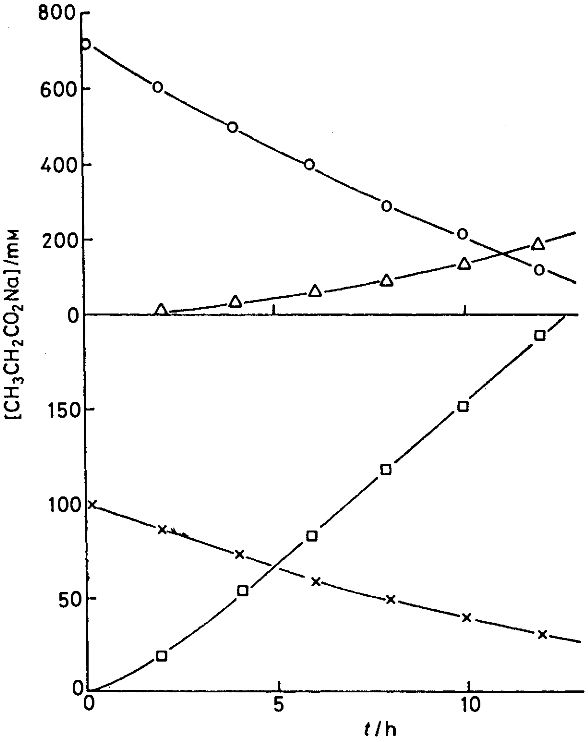


FIGURE 1 Photo-oxidation of $CH_3CH_2CO_2Na$ by excess of aqueous NaOCl at 20°: ○, NaOCl; △, NaOCl decomposed to give O_2; ×, $CH_3CH_2CO_2Na$; □, CO_2. $[NaOCl]_0$ 720 mM; $[CH_3CH_2CO_2Na]_0$ 100 mM; pH >12

When a Pyrex cell was used instead of a quartz cell, the yield of α- and β-chloropropionic acids decreased from 19 to 11% based on substrate consumed, showing

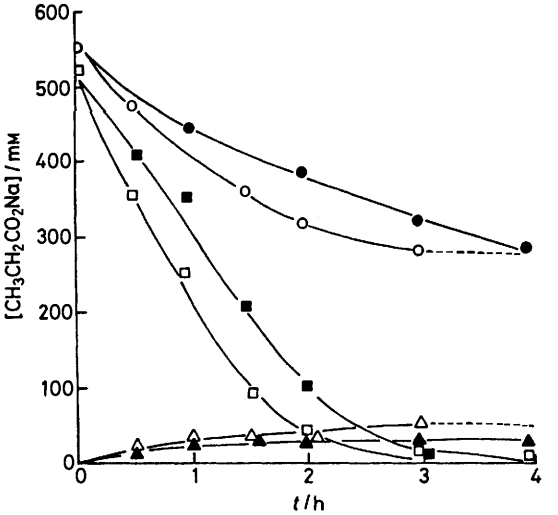


FIGURE 2 Effect of wavelength on the yield of $CH_3CH(Cl)CO_2Na$ in the photo-oxidation of $CH_3CH_2CO_2Na$ by aqueous NaOCl at 20°: ○, NaOCl; □, $CH_3CH_2CO_2Na$; △, $CH_3CH(Cl)CO_2Na$ at >230 nm; ●, NaOCl; ■, $CH_3CH_2CO_2Na$; ▲, $CH_3CH(Cl)CO_2Na$ at >300 nm. $[NaOCl]_0$ 520 mM, $[CH_3CH_2CO_2Na]_0$ 500 mM. Conversion: NaOCl 97.2%, $CH_3CH_2CO_2Na$ 48.0% after 3 h at >230 nm; NaOCl 96.2%, 47.3% after 4 h at >300 nm; pH >12

that the chlorination products are favoured at lower wavelength (< *ca.* 300 nm).

The probable intermediates, α- and β-hydroxy- and α- and β-chloro-propionic acids, were photolysed with an equimolar amount of NaOCl, and their reactivities were compared (Tables 2 and 3 and Figure 3). In the oxidation of α-hydroxypropionic acid, the rate of consumption of NaOCl was much greater than that for propionic acid, and the products (CH_3CO_2H and CO_2) show the primary oxidation of the α-carbon atom. For β-hydroxypropionic acid, β-hydrogen was abstracted *ca.* 3.3 times faster than α-hydrogen, from the yields of $CH_2(CO_2H)_2$ and $HOCH_2CO_2H$. On the other hand, α-chloropropionic acid shows less consumption of NaOCl than propionic acid, giving mainly $CH_3CH(OH)CO_2H$; hence the consumption of NaOCl is accelerated with increasing reactivity of the substrates as observed for the photo-oxidation of ethers.[7] Thus the presence of a hydroxy group increases the reactivity, while a chlorine atom retards the oxidation. These observations agree with the η values (a measure of reactivity for the reaction $RH + \cdot OH \longrightarrow R\cdot + H_2O$ of substituted meth-

TABLE 1

Yields of photo-oxidation products from $CH_3CH_2CO_2H$ by aqueous NaOCl at 20° [a,b]

Products	Yield (mM)	Selectivity [c] (%)
$CH_3CH(OH)CO_2H$	42.0	21.9
$HOCH_2CH_2CO_2H$	8.6	4.5
$CH_2(CO_2H)_2$	Trace	
CH_3COCO_2H	Trace	
CH_3CO_2H	10.1	5.3
$HOCH_2CO_2H$	Trace	
CO_2	20.3	10.0
$CH_3CH(Cl)CO_2H$	27.6	14.4
$ClCH_2CH_2CO_2H$	9.5	5.0
$ClCH_2CO_2H$	Trace	

[a] $[NaOCl]_0$ 443 mM, $[CH_3CH_2CO_2H]_0$ 530 mM. Conversion; NaOCl 100%, $CH_3CH_2CO_2H$ 36.0% after 5 h. [b] pH >12. [c] Based on substrate consumed.

TABLE 2

Yields of photo-oxidation products from α- and β-hydroxypropionic acids by aqueous NaOCl at 20° [a]

Substrates	Products	Yield (mM)	Selectivity [b] (%)
$CH_3CH(OH)CO_2H$ [c]	CH_3CO_2H	66.0	83.4
	CH_3COCO_2H	Trace	
	CO_2	67.5	85.7
$HOCH_2CH_2CO_2H$ [d]	$CH_2(CO_2H)_2$	105	77.2
	$HOCH_2CO_2H$	32.0	23.5
	CO_2	38.3	28.5

[a] pH >12. [b] Based on substrate consumed. [c] $[NaOCl]_0$ 469 mM, $[CH_3CH(OH)CO_2H]_0$ 515 mM. Conversion: NaOCl 100% $CH_3CH(OH)CO_2H$ 13.6% after 3 h. [b] $[NaOCl]_0$ 456 mM, $[HOCH_2CH_2CO_2H]_0$ 505 mM. Conversion: NaOCl 100% $HOCH_2CH_2CO_2H$ 36.0% after 4 h.

TABLE 3

Yields of photo-oxidation products from α- and β-chloropropionic acids by aqueous NaOCl at 20° [a]

Substrates	Products	Yield (mM)	Selectivity [b] (%)
$CH_3CH(Cl)CO_2H$ [c]	$CH_3CH(OH)CO_2H$	43.0	58.4
	CH_3CO_2H	Trace	
	CH_3COCO_2H	Trace	
	CO_2	~0	~0
$ClCH_2CH_2CO_2H$ [d]	$HOCH_2CH(Cl)CO_2H$	46.8	28.8
	$ClCH_2CH(OH)CO_2H$	57.5	35.4
	$ClCH_2CH(Cl)CO_2H$	7.8	4.5
	$CH_3CCl_2CO_2H$	15.5	9.5
	$HOCH_2CH_2CO_2H$	1.5	0.9
	$HOCH_2CO_2H$	16.1	9.9
	$ClCH_2CO_2H$	2.9	1.8
	$(CO_2H)_2$	Trace	

[a] pH >12. [b] Based on substrate consumed. [c] $[NaOCl]_0$ 458 mM, $[CH_3CH(Cl)CO_2H]_0$ 515 mM. Conversion: NaOCl 100% $CH_3CH(Cl)CO_2H$ 14.3% after 6.5 h. Gaseous O_2 was evolved in this case, but was not estimated. [d] $[NaOCl]_0$ 451 mM, $[ClCH_2CH_2CO_2H]_0$ 508 mM. Conversion: NaOCl 100% $ClCH_2CH_2CO_2H$ 36.0% after 2.5 h.

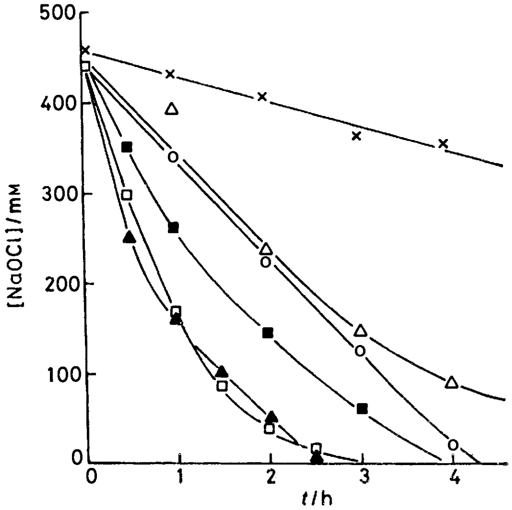
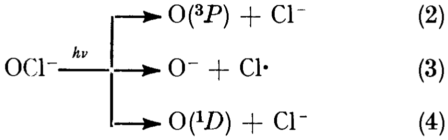


FIGURE 3 Decomposition of aqueous NaOCl in the presence of substituted propionic acids at 20°: ×, NaOCl alone; ○, $CH_3CH_2CO_2Na$; □, $CH_3CH(OH)CO_2Na$; ■, $HOCH_2CH_2CO_2Na$; △, $CH_3CH(Cl)CO_2Na$; ▲, $ClCH_2CH_2CO_2Na$. Conditions are as shown in Tables 1—3; $[NaOCl]_0$ 460 mM for NaOCl alone

anes);[9] η is *ca.* 0.7 for OH and *ca.* −0.7 for Cl. In contrast to α-chloropropionic acid, β-chloropropionic acid was dehydrochlorinated easily as shown above [equations (1a and b)]; hence it was oxidised rapidly even in the dark.

The reaction is initiated by excitation and decomposition of NaOCl [$\lambda_{\max.}$ 292 nm (ε 400 l mol^{-1} cm^{-1})],[10] because the light absorption of the substrates [$\lambda_{\max.}$ 204 nm (ε 60 l mol^{-1} cm^{-1}) for CH_3CO_2H and 207 nm (65) for $CH_3CH_2CO_2H$ in water] is negligible under the present conditions on account of the transparency of the reaction system over 230 nm.



$$\mathrm{OCl^-} \xrightarrow{h\nu} \begin{cases} \mathrm{O(^3\mathit{P}) + Cl^-} & (2) \\ \mathrm{O^- + Cl\cdot} & (3) \\ \mathrm{O(^1\mathit{D}) + Cl^-} & (4) \end{cases}$$

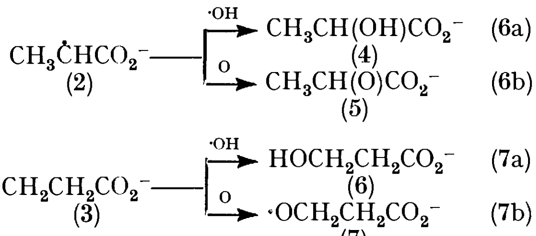
NaOCl is photolysed chiefly *via* reaction (2) at over 320 nm, while reactions (3) and (4) were favoured at lower wavelength (<320 nm).[11] Hydroxyl radical is then formed by reaction (5) (pK_a of •OH is 11.9).[12]

$$\mathrm{O(^1\mathit{D}) + H_2O \longrightarrow 2\,{\cdot}OH} \qquad (5a)$$

$$\mathrm{O^- + H_2O \longrightarrow {\cdot}OH + OH^-} \qquad (5b)$$

The reaction is initiated by α- and β-hydrogen atom abstraction from propionate ion (1) by the odd-electron species •OH, O$^-$, O(^3P), O(^1D), and Cl•. A reaction leading to $CH_3CH_2CO_2\cdot$ followed by decarboxylation ($CH_3CH_2CO_2\cdot \xrightarrow{-CO_2} CH_3CH_2\cdot$) is unimportant, since neither C_2H_6 nor C_4H_{10} was detected in the products.

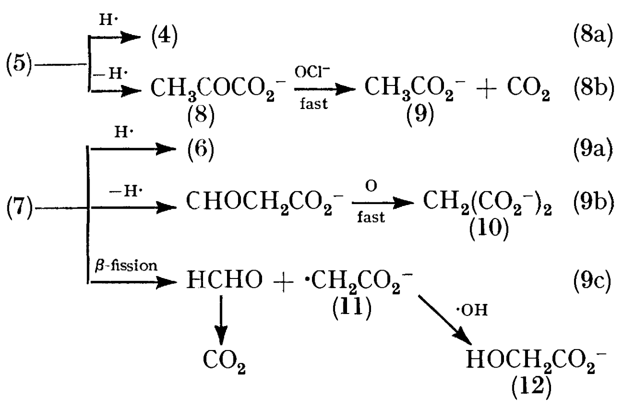
Radicals thus formed by hydrogen abstraction undergo further oxidation by •OH and O [equations (6) and (7)].



$$\underset{(2)}{\mathrm{CH_3\dot{C}HCO_2^-}} \begin{cases} \xrightarrow{\cdot\mathrm{OH}} \underset{(4)}{\mathrm{CH_3CH(OH)CO_2^-}} & (6a) \\ \xrightarrow{\mathrm{O}} \underset{(5)}{\mathrm{CH_3CH(O)CO_2^-}} & (6b) \end{cases}$$

$$\underset{(3)}{\mathrm{{\cdot}CH_2CH_2CO_2^-}} \begin{cases} \xrightarrow{\cdot\mathrm{OH}} \underset{(6)}{\mathrm{HOCH_2CH_2CO_2^-}} & (7a) \\ \xrightarrow{\mathrm{O}} \underset{(7)}{\mathrm{{\cdot}OCH_2CH_2CO_2^-}} & (7b) \end{cases}$$

Intermediates (5) and (7) suffer further reactions to give fairly stable products [equations (8) and (9)]. Products (4), (6), (8)—(10), (12), and CO_2 were identified (Table 1).



$$(5) \begin{cases} \xrightarrow{\mathrm{H}\cdot} (4) & (8a) \\ \xrightarrow{-\mathrm{H}\cdot} \underset{(8)}{\mathrm{CH_3COCO_2^-}} \xrightarrow[\text{fast}]{\mathrm{OCl^-}} \underset{(9)}{\mathrm{CH_3CO_2^-}} + \mathrm{CO_2} & (8b) \end{cases}$$

$$(7) \begin{cases} \xrightarrow{\mathrm{H}\cdot} (6) & (9a) \\ \xrightarrow{-\mathrm{H}\cdot} \mathrm{CHOCH_2CO_2^-} \xrightarrow[\text{fast}]{\mathrm{O}} \underset{(10)}{\mathrm{CH_2(CO_2^-)_2}} & (9b) \\ \xrightarrow{\beta\text{-fission}} \mathrm{HCHO} + \underset{(11)}{\mathrm{{\cdot}CH_2CO_2^-}} & (9c) \end{cases}$$

$$\mathrm{HCHO} \longrightarrow \mathrm{CO_2} \qquad \mathrm{{\cdot}CH_2CO_2^-} \xrightarrow{\cdot\mathrm{OH}} \underset{(12)}{\mathrm{HOCH_2CO_2^-}}$$

Another possibility is the coupling of atomic chlorine with these radicals (2), (3), and (11), since chlorinated products were detected as shown in Table 1. Since irradiation at >300 nm lowers the yield of the chlorinated products compared with >320 nm light, undissociated molecular chlorine would not participate to any degree in chlorination. This observation is consistent with the fact that the decomposition of NaOCl to produce Cl• [equation (3)] is preferred at the lower wavelength[9] (<320 nm). The exact chlorination process is difficult to ascertain because of the strong basicity of the solution which is necessary to stabilise NaOCl, and which at the same time accelerates the hydrolysis of the chloro compounds.

When photo-oxidation was carried out with a less reactive substrate or a lower concentration of substrate, the effect of molecular oxygen produced by the decomposition of NaOCl became significant, the solution becoming saturated with oxygen even at the initial stage. Molecular oxygen may attack radicals to form the peroxyl radicals $CH_3CH(O\dot{O})CO_2^-$ and $\dot{O}OCH_2CH_2CO_2^-$.[13] Since this oxygenation is very fast, little chlorination is observed, and hence the species OH, O$^-$, O, and Cl abstract hydrogen only. This is the case for the photo-oxidation of 0.1M-$CH_3CH_2CO_2Na$ by 0.72M-NaOCl and for the photo-oxidation of the less reactive CH_3CO_2Na by NaOCl, where no chloro compound is produced.

Photo-oxidation of Acetic Acid.—The reaction of 0.105M-CH_3CO_2Na and 0.47M-NaOCl gave complete oxidation (*i.e.* CO_2 and H_2O are formed). A small amount of glycolic acid which formed disappeared during the reaction. However, acetic acid is less reactive than propionic acid, so that *ca.* 30% NaOCl in aqueous CH_3CO_2Na evolved as gaseous O_2. The formation of CO_2 almost corresponds to the consumption of CH_3CO_2Na (Figure 4).

There is little difference in effectiveness between the photo-oxidation of ethers by NaOCl[7] and by H_2O_2.[14] However, the situation is different with acetic acid. The rate of hydrogen atom abstraction by electrophilic radicals such as •OH and Cl• was greatly decreased by the presence of an electron-withdrawing group (CO_2H), while the less electron-withdrawing CO_2^- group shows the opposite[15] or less[16] effect, so that the oxidation proceeds in the presence of carboxylate ion. The molar ratio of CO_2 *versus* O_2 produced, which indicates the effectiveness of photo-oxidation is as follows: 1.1, CH_3CO_2H by H_2O_2; 2.1, CH_3CO_2Na by NaOCl; 7.1, CH_3CO_2Na by H_2O_2. In other words, the complete oxidation of acetic acid is best achieved by alkaline H_2O_2.

An attempt to detect the intermediates from the photo-oxidation of CH_3CO_2Na by equimolar NaOCl gave the same results as observed for CH_3CO_2Na with excess of NaOCl (Table 4). *Ca.* 28% of NaOCl decomposed to give O_2, the only product being CO_2.

TABLE 4

Yields of photo-oxidation products from CH_3CO_2Na by aqueous NaOCl at 20° [a-c]

Products	Yield mM	Yield % [d]
$HOCH_2CO_2H$	Trace	
$ClCH_2CO_2H$	Trace	
CO_2	102	89.0

[a] pH >12. [b] $[NaOCl]_0$ 430 mM, $[CH_3CO_2Na]_0$ 570 mM. Conversion; NaOCl 100%, CH_3CO_2Na 10.1% after 6 h. [c] 28.1% of NaOCl decomposed only to give O_2. [d] Carbon yield based on the consumed substrate

The mechanism for the photo-oxidation of acetic acid with alkaline aqueous NaOCl may be analogous to that of propionic acid involving hydrogen abstraction by radical species. Radical (11) may undergo further reactions giving $HOCH_2CO_2H$, $ClCH_2CO_2H$, and CO_2 which were identified (Table 4).

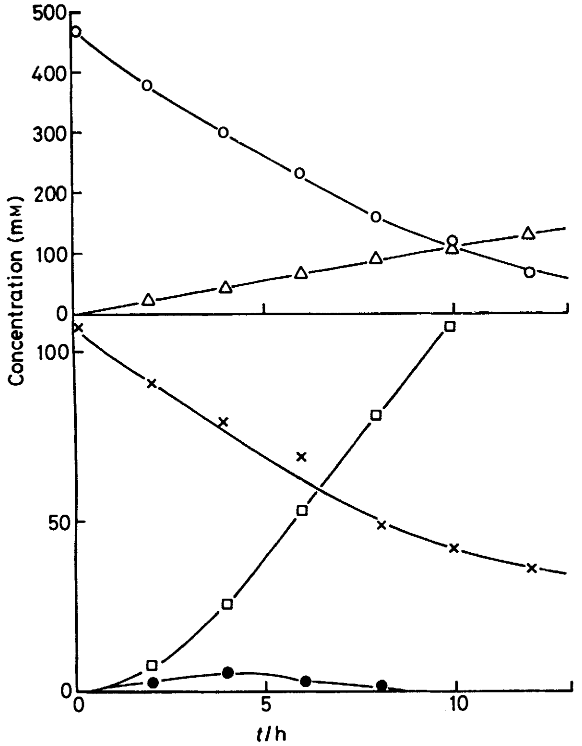


FIGURE 4 Photo-oxidation of CH_3CO_2Na by excess of aqueous NaOCl at 20°; ○, NaOCl; △, NaOCl decomposed to give O_2; ×, CH_3CO_2Na; □, CO_2 in form of Na_2C_3; ●, $HOCH_2CO_2Na$. $[NaOCl]_0$ 474 mM, $[CH_3CO_3Na]_0$ 106 mM; pH >12.

$$(9) \xrightarrow{-H\cdot} (11) \qquad (10)$$

Dark Reactions and Conclusions.—Control experiments in the dark showed practically no reaction of $CH_3CH_2CO_2Na$ and CH_3CO_2Na with either equimolar or excess of NaOCl over 6 days. Although >90% of NaOCl was used up in the oxidation of equimolar hydroxy- or chloro-substituted propionic acids, complete oxidation to CO_2 and H_2O did not take place. Hence, u.v. irradiation is essential for fast and complete oxidation of aliphatic acids with NaOCl.

In practice, waste water usually contains only low concentrations of unreactive organic contaminants[5] which cannot be removed by biochemical and physical methods; hence oxidation by molecular oxygen may be significant. However, there is the possibility of chlorination as pointed out previously; *e.g.* $CHCl_3$ is formed from polyethers and chlorinated phenols from benzenesulphonic acids, and this may present problems of secondary pollution.

EXPERIMENTAL

Materials.—Aqueous sodium hypochlorite was prepared by bubbling Cl_2 into ice-cooled aqueous NaOH in the dark, the precipitate of NaCl being filtered off. The solution can be stored for several weeks in a refrigerator. The concentration of NaOCl was determined by iodometry before use. Propionic and acetic acids were of first grade, and used after distillation; no impurities were detected by g.l.c. after esterification by CH_2N_2: $CH_3CH_2CO_2H$, b.p. 141—142°; CH_3CO_2H, b.p. 118—119°.

Photo-oxidation.—The irradiation was carried out in a cylindrical 8 × 200 mm quartz vessel or a 8 × 200 mm Pyrex vessel using a 300-W high-pressure mercury lamp. Aqueous *ca.* 1M-$CH_3CH_2CO_2Na$, *ca.* 1M-CH_3CO_2Na, and *ca.* 1M-NaOCl were prepared, and they were mixed and diluted, if necessary, before irradiation. *Ca.* 30—40 ml of this solution was introduced into the cell and irradiated at 20° using a merry-go-round apparatus. The solution was acidified after irradiation to prevent hydrolysis of the chlorinated products. Excess of NaOCl was removed by suitable reagents such as $(CO_2H)_2$, HCHO, and $Na_2S_2O_3$.

Analysis.—The irradiated solution, after acidification by HCl, was extracted with ether or $CHCl_3$. The aqueous layer was condensed by evaporation and the residue was extracted with methanol. The two extracts were combined, condensed, and esterified by CH_2N_2 in ether. The analysis of methyl esters was mainly done by g.l.c. using a Yanagimoto GCG 180 gas chromatograph. Two columns, PEG 20M (1.2 m) and Porapak QS (0.7 m), were used. The esters were identified by comparison of g.l.c. peaks with those of authentic samples in both columns and the yield was also estimated by g.l.c. using both columns with $CH_3[CH_2]_5CO_2CH_3$ and biphenyl as internal standards.

Products were also identified by g.l.c.–m.s. using a Schimadsu GCMS-7000 mass spectrometer with a 2.0-m copper column packed with PEG 20M.

The gaseous products evolved were collected in a gas burette, and O_2 was determined by alkaline pyrogallol after absorption of CO_2 by aqueous $Ba(OH)_2$. After absorption of CO_2 and O_2, no gaseous organic compounds were detected by g.l.c. using a 1.5-m copper column packed with Porapak T. Carbon dioxide was present in the form of Na_2CO_3 in the alkaline reaction mixture, so that CO_2 was expelled from the mixture by N_2 after acidification of the solution with H_2SO_4, absorbed by aqueous 0.1N-$Ba(OH)_2$, and estimated by acidimetry.

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REFERENCES

[1] D. F. Bishop, G. Stern, M. Fleishman, and L. S. Marshall, *Ind. Eng. Chem., Process Res. Development*, **1968**, **7**, 110.

[2] P. Sims and P. Grover, *Ind. Eng. Chem. Process Res. Development*, **1975**, **14**, 348.

[3] (*a*) B. I. Parsons and C. J. Danby, *J. Chem. Soc.*, 1956, 1795; (*b*) B. I. Parsons and C. Hinshelwood, *ibid.*, p. 1799; (*c*) B. I. Parsons, *ibid.*, p. 1804.

[4] W. M. Garrison, H. R. Haymond, W. Bennett, and S. Cole, *J. Chem. Phys.*, 1956, **25**, 1287.

[5] Y. Kojima, *PPM*, 1973, 42.

[6] N. Nakamura and Y. Ogata, *Bull. Chem. Soc. Japan*, 1977, **50**, 1287.

[7] Y. Ogata, K. Takagi, and T. Suzuki, *J.C.S. Perkin II*, 1978, 562.

[8] (*a*) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 841; (*b*) N. L. Wendler, *ibid.*, 1949, **71**, 375; (*c*) CIBA Ltd., Swiss Pat., 280,474/1952 (*Chem. Abs.*, 1953, **47**, 6977b); (*d*) E. Grovenstein and D. E. Lee, *J. Amer. Chem. Soc.*, 1953, **75**, 2639.

[9] M. Anber, D. Meyerstein, and P. Neta, *J. Chem. Soc.* (*B*), 1966, 742.

[10] G. V. Buxton and M. S. Subhani, *J.C.S. Faraday I*, 1972, 958.

[11] R. J. Cvetanovic, *Adv. Photochem.*, 1963, **1**, 115.

[12] J. Rabani and M. S. Matheson, *J. Phys. Chem.*, 1966, **70**, 761.

[13] J. Hund and H. Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 5999.

[14] Y. Ogata, K. Tomizawa, and K. Fujii, *Bull. Chem. Soc. Japan*, 1978, **51**, 2628.

[15] J. M. Tedder, *Quart. Rev.*, 1960, **14**, 340.

[16] H. Paul and H. Fischer, *Z. Naturforsch.*, 1970, **25**, 443.