BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 642—645 (1970)

Kinetics of Alkaline Hydrolysis of Esters. II.[*1] Unsaturated Esters and Oxalic Esters

R. C. SHARMA and M. M. SHARMA

Department of Chemical Technology, University of Bombay, Matunga Road, Bombay-19, India

(Received July 14, 1969)

The kinetics of alkaline hydrolysis of some typical esters, with unsaturation in the alkyl and the acyl portions, was studied. It was found that, in general, unsaturation results in enhancing the rate as compared to that of the corresponding saturated esters, provided that there is no conjugation between the double bond and the carboxyl carbonyl group. Oxalic esters hydrolyze relatively very fast due to the close proximity of the two ester groups. Rate constants for the alkaline hydrolysis of di-*n*-propyl-, di-isopropyl-, di-*n*-butyl-, di-*s*-butyl-, dicyclohexyl- and di-*β*-chloroethyl oxalates were obtained by using the theory of mass transfer accompanied by fast pseudo first-order reaction (diffusion method).

There is limited information in literature concerning the effect of unsaturation, present either on the alkyl or the acyl portion of the ester, on the kinetics of alkaline hydrolysis of esters.[2,3] It was therefore thought desirable to study some typical esters.

In the case of oxalic esters also only limited information is available. The first step of the alkaline hydrolysis of these esters is known to be an extremely fast reaction. Skrabal and coworkers[4-6] have studied the kinetics of this reaction using a phosphate buffer ($HPO_4^{2-}/H_2PO_4^-$) solution. The values of rate constant for the first step of the alkaline hydrolysis of dimethyl and diethyl oxalates obtained by them at 25°C were approximately 20000 and 6300 *l*/g mol sec. Tommila and Stenberg[7] studied the kinetics of alkaline hydrolysis of diethyl oxalate in a flow reactor similar to that used by Hartridge and Roughton.[8] The value of the rate constant was 3900 *l*/g mol sec in water at 30°C. Homan[9] found the value of the rate constant for the alkaline hydrolysis of di-*t*-butyl oxalate in 66.7 per cent (v/v) aqueous dioxane at 25°C to be 21.7 *l*/g mol sec. Sharma and Sharma[1] employed the theory of mass transfer with chemical reaction to obtain the value of the rate constant for the alkaline hydrolysis of di-*n*-butyl oxalate. They reported a value of 1780 *l*/g mol sec in water at 30°C. It was thought desirable to cover a more representative range of oxalic esters.

Experimental

Materials. Vinyl and isopropenyl acetates, methyl-, ethyl- and *n*-butyl acrylates and methyl methacrylate were purified by distillation at reduced pressure. Allyl acetate was synthesized by the reaction of allyl alcohol and acetic anhydride in the presence of one per cent sulphuric acid, and subsequently purified by distillation.

Oxalic diesters of *n*-propyl-, isopropyl-, *n*-butyl-, *s*-butyl, cyclohexyl and *β*-chloroethyl alcohols were synthesized by refluxing anhydrous oxalic acid with appropriate alcohol, taken as two to three times the stoichiometric requirement, in the presence of about three per cent sulphuric acid. The esters were purified by distillation at reduced pressure (10 to 50 mmHg). The physical properties for all the esters are reported in literature. The properties of purified esters agreed with those reported in literature.

Kinetic Measurements. The kinetics of alkaline hydrolysis of esters was studied in the aqueous medium. The rate constants for unsaturated esters were determined by the conventional method. The experimental procedure for this method was reported in a previous paper.[1] In some cases studies were made at lower temperatures (0.2 to 15°C). A constant temperature bath was used, where the temperature could be controlled to within ±0.05°C.

The theory of mass transfer accompanied by fast pseudo first-order reaction was used to study the kinetics of alkaline hydrolysis of oxalic esters. Details of the

---

[*1] The previous paper by the authors[1] may be treated as Part I.

1) R. C. Sharma and M. M. Sharma, *J. Appl. Chem.*, **19**, 162 (1969).

2) E. A. Haloiven, *Acta Chem. Scand.*, **10**, 485 (1956).

3) R. T. Myers, A. R. Collett and C. L. Lazzell, *J. Phys. Chem.*, **56**, 461 (1952).

4) A. Skrabal, *Monatsh.*, **38**, 29 (1917).

5) A. Skrabal and A. Matievie, *ibid.*, **39**, 765 (1918).

6) A. Skrabal and E. Singer, *ibid.*, **41**, 339 (1920).

7) E. Tommila and H. Stenberg, *Suomen Kemistilahiti*, **19B**, 19 (1946).

8) H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc., Ser. A*, **104**, 376 (1923).

9) J. D. H. Homan, *Rec. Trav. Chim.*, **63**, 181 (1944); *Chem. Abstr.*, **39**, 1587 (1945).

method for the determination of rate constants have already been reported.[1,10–12)]

Analysis. Methods of analysis have already been reported[1)] except in the case of solid oxalic esters (dicyclohexyl and di-β-chloroethyl). In these cases about 20 m*l* of 8 N H_2SO_4 solution was added to 25 m*l* of an aqueous solution containing disodium oxalate. The solution was heated to about 70°C and titrated against standard $KMnO_4$ solution. Under these conditions disodium oxalate is oxidized quantitatively.[13)]

Results and Discussion

1) Unsaturated Esters. An unsaturated carbon to carbon linkage near the carbonyl carbon in a carboxylic ester should speed up the rate of alkaline hydrolysis compared to that of the corresponding saturated ester due to the electronegative nature of unsaturation.[14,15)] However, if there is conjugation of the unsaturation with the carboxyl $(-\underset{\substack{| \\ O^-}}{C}=O)$ group then this retards the rate of the alkaline hydrolysis of the ester. Esters considered in this work could be divided in two groups: (i) unsaturation present in the alkyl group, (ii) unsaturation present in the acyl part.

(i) Unsaturation in the Alkyl Group. The presence of unsaturation on the alkyl portion of an ester accelerates the rate of alkaline hydrolysis. The effect decreases when the unsaturation moves away from the reaction centre. The results are given in Table 1.

TABLE 1. RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF UNSATURATED ESTERS IN AQUEOUS MEDIUM

Ester	Temperature °C	k_2 *l*/g mol sec
Vinyl acetate	0.3	0.392
	5	0.594
	10	0.854
	15	1.17
Isopropenyl acetate	10	0.145
	20	0.285
	30	0.512
Allyl acetate	30	0.23
Ethyl propionate	30	0.119
Methyl acrylate	30	0.198
Ethyl acrylate	30	0.102
n-Butyl acrylate	30	0.074
Methyl methacrylate	30	0.083

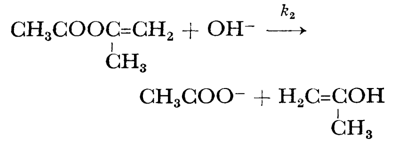
Only a limited amount of information is available in literature concerning the kinetics of alkaline hydrolysis of vinyl acetate.

$$CH_3COOCH{=}CH_2 + OH^- \xrightarrow{k_2} CH_3COO^- + H_2C{=}CHOH \qquad (1)$$

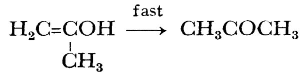
$$H_2C{=}CHOH \xrightarrow{\text{fast}} CH_3CHO \qquad (2)$$

The value of the rate constant for alkaline hydrolysis of vinyl acetate has been reported as 10.3 *l*/g mol sec by Skrabal and Zahorke.[16)] They used a borate buffer solution for kinetic studies. The accuracy of the rate constant will be dependent on a precise knowledge of the hydroxyl ion concentration in the borate buffer solution. The value reported in this work is very different from that given by Skrabal and Zahorke.[16)] The kinetics of alkaline hydrolysis of vinyl acetate was studied in the homogeneous phase by the conventional method[17)] at lower temperatures (0.2 to 15°C) and data were extrapolated to room temperature. The extrapolated value of 2.6 *l*/g mol sec at 27°C is in good agreement with that obtained by the "diffusion method" (2.34 *l*/g mol sec at 27°C).

In the case of isopropenyl acetate, it would be expected that the steric hindrance due to the methyl group at the α-carbon atom of the alkyl portion would considerably decrease the rate of alkaline hydrolysis:



$$CH_3COO\underset{\substack{| \\ CH_3}}{C}{=}CH_2 + OH^- \xrightarrow{k_2} CH_3COO^- + H_2C{=}\underset{\substack{| \\ CH_3}}{C}OH \qquad (3)$$



$$H_2C{=}\underset{\substack{| \\ CH_3}}{C}OH \xrightarrow{\text{fast}} CH_3COCH_3 \qquad (4)$$

The rate constant for this ester is about one sixth of that for vinyl acetate. The ratio of the rate constants for vinyl and isopropenyl acetates may be compared with the ratio for ethyl and isopropyl acetates (0.145 and 0.032 *l*/g mol sec at 30°C, respectively).

The value of the rate constant for the alkaline hydrolysis of phenyl acetate is about 12 times that of ethyl acetate.[18)] The value of the rate constant for phenyl acetate should be obviously higher than that of isopropenyl acetate as there are two more unsaturation linkages present between 2,3- and 4,5-carbon atoms in the phenyl group. Further-

---

[10)] M. M. Sharma and A. K. Nanda, *Trans. Instn. Chem. Engrs.*, **46**, T44 (1968).

[11)] A. K. Nanda and M. M. Sharma, *Chem. Eng. Sci.*, **21**, 707 (1966).

[12)] A. K. Nanda, M. M. Sharma, *ibid.*, **22**, 769 (1967).

[13)] A. I. Vogel, "Quantitative Inorganic Analysis," 3rd Ed., Longmans Green & Co., N. Y. (1962), p. 301.

[14)] H. Olsson, *Z. Phys. Chemie*, **133**, 233 (1928).

[15)] J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

[16)] A. Skrabal and A. Zahorke, *Monatsh.*, **48**, 459 (1927).

[17)] R. C. Sharma and M. M. Sharma (Paper to be published).

[18)] A. Skrabal and M. A. Hugetz, *Monatsh.*, **47**, 17 (1926).

more, the rate constant for phenyl acetate should be expected to be less than that of vinyl acetate as the latter is sterically less hindered.

The rate constant for allyl acetate was found to be 0.23 *l*/g mol sec in water at 30°C, which is about one twelfth of that for vinyl acetate. In the case of allyl acetate the double bond is further away from the reaction center. Moreover it is well known that when an electronegative group or atom moves away from the reaction center the rate decreases. For instance, the value of the rate constant for the alkaline hydrolysis of chloromethyl acetate is about twenty times higher than that for β-chloroethyl acetate.[19,20]

(ii) Unsaturation in the Acyl Part. Unsaturation between α-, β-carbon atoms of the acyl portion results in conjugation with the carboxyl carbonyl group $(-\underset{|}{C}=O)$ of the ester. The effect of conjugation is not very marked in acrylic acid.[21] (The dissociation constants (K_a) of propionic and acrylic acids are 1.33×10^{-5} and 5.56×10^{-5}, respectively). However, the effect is much greater in acrylates, since here the conjugation energy of carbonyl group is approximately 4000 cal lower than that of carbonyl group in the acid.[22]

The values of the rate constant for the alkaline hydrolysis of ethyl propionate, methyl-, ethyl- and *n*-butyl acrylates and methyl methacrylate were obtained in water at 30°C by the conventional method and are given in Table 1.

The value of the rate constant decreases with the increase in the size of the alkyl group of acrylates. The relative decrease was found to be of the same magnitude as that in the case of acetic ester.

The effect of methyl substitution on the acyl portion, near the reaction center, was also investigated. The retardation of the alkaline hydrolysis of methyl methacrylate as compared to that of methyl acrylate was observed. The decrease in the rate constant when a hydrogen atom of the α-carbon atom of the acyl portion is replaced by a methyl group is comparable in the case of methyl acrylate and methyl methacrylate, and ethyl propionate and ethyl isobutyrate.[2] The ratio of the rate constants in these two cases is about 2.5 to 3.

2. Oxalic Esters. In order to obtain the values of the rate constant by the diffusion method, it is necessary to know the values of solubility and diffusivity of the ester in water. Solubilities of oxalic esters in water and aqueous solutions of sodium chloride were determined. The results were correlated by the methods reported in literature[23-25] and are given in Table 2. Diffusivities of esters were estimated by the method of Wilke and Chang[26] and are given in Table 3. The rate constants determined by the diffusion method are also given in Table 3.

In oxalic esters, the two ester groups are in close proximity to each other. The ester group (-COOR′) is a strong electron-attracting group and it is well known that such groups enhance the rate of alkaline hydrolysis. Hence the values of rate constants for alkaline hydrolysis of oxalic esters are relatively very high.

The kinetics of alkaline hydrolysis of dimethyl- and diethyl oxalates could not be studied in this work because of their higher solubilities. However, in the case of di-*n*-propyl oxalate the necessary conditions were satisfied. Extraction of this ester in the stirred cell was carried out only for five minutes to avoid the formation of disodium oxalate in excess of its saturation concentration. However, in the case of di-*n*-butyl oxalate, because of its very low solubility, experiments could be conducted even upto 30 min.

The values of the rate constant for di-*n*-propyl- and di-*n*-butyl oxalates are 2020 and 1780 *l*/g mol·sec, respectively. The ratio of rate constants of diethyl to di-*n*-propyl, and di-*n*-propyl to

TABLE 2. SOLUBILITIES OF OXALIC ESTERS IN WATER AND AQUEOUS SODIUM CHLORIDE SOLUTIONS (1 to 3M)

No.	Ester	Temperature °C	Solubility in water $[E]_w\times10^5$ g mol/cm³	K_s* *l*/g ion
1	Di-*n*-propyl oxalate	30	1.83	0.202
2	Di-isopropyl oxalate	30	4.6	0.164
3	Di-*n*-butyl oxalate[1]	30	0.23	0.264
4	Di-*s*-butyl oxalate	30	0.368	0.223
5	Di-β-chloroethyl oxalate	30	3.71	0.15
		5	1.56	0.15
6	Di-cyclohexyl oxalate	30	0.02	0.18

* $\log_{10}\frac{[E]_w}{[E]} = K_s I$ [1]

[E] = Solubility of the ester in aqueous sodium chloride solution, g mol/cm³

I = Ionic strength, g ion/*l*

---

[19] E. Tommila, S. Hietala and J. Nyrkoo, *Soumen Kemistilehti*, **28B**, 143 (1955).

[20] E. K. Euranto and R. A. Euranto, *ibid.*, **35B**, 96 (1962).

[21] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca (1953), p. 328.

[22] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York (1945), p. 202.

[23] F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

[24] D. W. Van Krevelen and P. J. Hoftizer, *Chem. Ind.*, **1948**, 168.

[25] P. J. Kothari and M. M. Sharma, *Chem. Engng. Sci.*, **21**, 391 (1966).

[26] C. R. Wilke and P. Chang, *A. I. Ch. E. Jl.*, **1**, 264 (1955).

TABLE 3. SPECIFIC RATES OF EXTRACTION, DIFFUSIVITIES AND RATE CONSTANTS FOR ALKALINE HYDROLYSIS OF OXALIC ESTERS IN AQUEOUS SOLUTION

No.	Ester	Concentration of electrolytes g mol/l		Temperature °C	Specific rate of extraction $\frac{\text{g}\cdot\text{mol}}{\text{cm}^2\cdot\text{sec}}$	Diffusivity $\times 10^6$ cm²/sec	Rate constant l/g mol sec
		NaCl	NaOH				
1	Di-*n*-propyl oxalate	1	0.56	30	6.0×10^{-7}	5.65	2020
2	Di-isopropyl oxalate	1	0.6	30	1.27×10^{-6}	5.65	890
3	Di-*n*-butyl oxalate[1)]	0	0.3	30	1.18×10^{-7}	6.37	1780
4	Di-*s*-butyl oxalate	1	0.5	30	8.2×10^{-8}	5.11	810
5	Di-β-chloroethyl oxalate	0	0.3	5	6.7×10^{-7}	3.56	2160
6	Dicyclohexyl oxalate	0	0.25	30	8.35×10^{-9}	6.43	1080

di-*n*-butyl oxalates are approximately 2 and 1.2, respectively. For the acetates of the corresponding alcohols the ratio of rate constants for alkaline hydrolysis are about 1.23 and 1.2, respectively. (The values of the rate constant for ethyl, *n*-propyl and *n*-butyl acetates are 0.41, 0.12 and 0.1 l/g mol·sec in water at 30°C, respectively). Oxalic esters, other than dimethyl and diethyl oxalates, seem to follow the normal trend of change in the rate constant due to inductive and steric factors.

The rate constant for di-β-chloroethyl oxalate would be expected to be higher than that of diethyl oxalate due to the electronegative nature of the chlorine atoms present at the β-carbon atoms of the alkyl portions.

It was observed that the solubility of di-β-chloroethyl oxalate (mp 45°C) in water increases with an increase in the temperature. It is so high at 30°C that the necessary conditions for the validity of pseudo first-order reaction mechanism are not satisfied. However, all the conditions were satisfied when the experiments were carried out at 5°C in a bubble column where the temperature was kept constant by circulating water at the desired temperature through the outer jacket. The rate constant was found to be 2160 l/g mol sec at 5°C. If the energy of activation for the alkaline hydrolysis of di-*n*-propyl ester is assumed to be the same as that for other related oxalic esters of about 7 kcal/mol,[7)] then the rate constant for di-*n*-propyl oxalate at 5°C works out to be about 700 l/g mol sec. This value is about one-third of that of di-β-chloroethyl oxalate. The rate constant of β-chloroethyl acetate is about 3.5 times higher than that of *n*-propyl acetate.

The steric effect was investigated by studying the kinetics of alkaline hydrolysis of di-isopropyl, di-*s*-butyl and dicyclohexyl oxalates. The value of the rate constant for the alkaline hydrolysis of di-isopropyl oxalate was found to be 890 l/g mol sec and that of di-*s*-butyl oxalate 810 l/g mol sec. These values are very close to each other, probably because of a similar steric effect offered by the isopropyl and *s*-butyl groups. The rate constants for isopropyl and *s*-butyl acetates and the corresponding formates are practically the same. However, the rate constant for dicyclohexyl oxalate is higher than the expected value. The discrepancy might be caused by the error involved in the determination of the solubility of this ester which is relatively very low. A 10 per cent error in the solubility results in about 20 per cent error in the rate constant.[1)]

One of the authors (R.C.S.) wishes to thank the University Grants Commission for an award of a scholarship which enabled this work to be carried out.