

Thermal and alkali-catalyzed hydrolysis study of *R,R',4,4'*-cyclohexylidenediphenyloxyacetic acids and their ethyl esters

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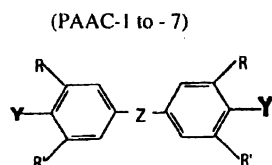
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R,R',4,4'-Cyclohexylidenediphenyloxyacetic acid (PAAC-1 to PAAC-7, R = H, CH₃, Cl, Br, NO₂ and R' = H, Cl, Br, NO₂) are thermally stable up to 226–320°. Kinetic parameters are interpreted in light of the nature of the substituents. A large and positive magnitudes of ΔS^\ddagger indicated less ordered transition state than individual phenoxy acid molecules. The endo- or exothermic DTA transitions supported some physical or chemical changes.

Various thermodynamic parameters of ethyl esters of the above acids in MeOH-H₂O (1 : 1, v/v) have been determined conductometrically from second order rate constants at 30, 35 and 40° and are interpreted in terms of the nature of substituents on the reaction rate. The experimental data are in accordance with the bimolecular acyl fission mechanism. A large and negative ΔS^\ddagger and small *A* indicate highly ordered transition state as compared to individual ester molecules and it is rate-determining step.

Phenoxy acids are widely helpful in the field of agriculture as herbicides as well as insecticides¹. A limited work has been reported on the alkali-catalyzed kinetic study of the diesters² especially by the method of conductance³. To our knowledge no work has been reported on thermal analysis of diphenyloxyacetic acids of bisphenol-C derivatives. The present work reports thermal and alkali-catalyzed hydrolysis study of *R,R',4,4'*-cyclohexylidenediphenyloxyacetic acids and their ethyl esters (DE-1 to -7).



Y = OCH₂COOH,

Z = Cyclohexyl

PAAC-1 : R = R' = H

PAAC-5 : R = R' = Br

PAAC-2 : R = CH₃, R' = H

PAAC-6 : R = R' = NO₂

PAAC-3 : R = R' = Cl

PAAC-7 : R = CH₃, R' = NO₂

PAAC-4 : R = CH₃, R' = Cl

Y = OCH₂COOC₂H₅,

Z = Cyclohexyl

DE-1 : R = R' = H

DE-5 : R = R' = Br

DE-2 : R = CH₃, R' = H

DE-6 : R = R' = NO₂

DE-3 : R = R' = Cl

DE-7 : R = CH₃, R' = NO₂

DE-4 : R = CH₃, R' = Cl

Results and Discussion

Thermal analysis of phenoxy acids :

The thermal analyses are based on the measurements of

some physical properties such as mass, heat of reaction, volume, etc.⁴. The shape of the curve depends on the kinetic parameters such as reaction order (*n*), frequency factor (*A*) and activation energy (E_a^\ddagger)⁵. The DTA-TG thermograms of PAAC-1 to -7 were obtained at the heating rate of 15°/min in an N₂ atmosphere. The DTA exo/endothemic transitions, initial decomposition temperature (IDT), decomposition temperature range, % weight loss involved for a given step and temperature of maximum degradation (T_{max}) are reported in Table 1. The results reveal that endo- or exothermic transitions are due to either some physical change or formation of new compounds as supported by no weight-loss over the corresponding temperature region in TG curves. Endo- and exothermic transitions also indicate rupture of the phenoxy acid molecules and it is confirmed by weight-loss in TG curves.

From Table 1, it is clear that PAAC-1 to -7 is thermally stable up to 226–320°. The observed thermal stability order is PAAC-5 > PAAC-6 > PAAC-7 > PAAC-4 > PAAC-3 > PAAC-2 > PAAC-1. PAAC-1 to -4 followed one-step degradation while PAAC-5 to -7 followed two-step degradation. It is interesting to note that the nature of substituents (CH₃, Cl, Br and NO₂) increases thermal stability as well as temperature of maximum weight-loss. The bromine and nitro groups have predominant effect on the said parameters. The residual weight (10–37%) at higher temperature might be due to formation of highly thermally stable products.

Table 1. TGA-DTA data of the phenoxy acids

Phenoxy acid	Transition	Temp. °C	IDT °C	Decom. range °C	% Wt. loss	T_{max} °C	E_a^\ddagger kJ mol ⁻¹	A s ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	n	γ
PAAC-1	Endo	159.0									
	Endo	241.5									
	Exo	627.7	226.2	226–249	19.6	235.8	241.1	1.58×10^{23}	194.7	2.29	0.994
	Endo	736.2									
PAAC-2	Endo	882.1									
	Endo	271.0									
	Exo	514.4	244.2	244–280	63.1	268.2	160.6	5.25×10^{13}	12.8	1.01	0.988
	Exo	668.9									
PAAC-3	Endo	204.3									
	Endo	276.1	250.9	251–287	63.0	275.6	197.3	1.20×10^{17}	77.0	1.15	0.998
PAAC-4	Exo	517.7									
	Endo	181.4									
PAAC-5	Endo	206.5	264.9	265–299	72.5	289.6	243.0	8.44×10^{20}	150.4	0.96	0.950
	Endo	289.6									
	Exo	535.1									
	Endo	127.8	319.5								
PAAC-6	Endo	343.6	488.2	320–350	80.3	342.8	225.9	2.59×10^{17}	82.4	0.81	0.966
	Exo	512.5		488–529	8.6	509.4	386.9	1.29×10^{24}	155.3	2.41	0.992
	Endo	110.2	277.9	278–317							
PAAC-7	Endo	349.1	485.2	485–608	42.2	304.7	280.1	5.38×10^{23}	203.9	1.44	0.988
	Endo	630.0			42.6	581.3	85.5	5.92×10^2	-200.8	0.72	0.995
	Exo	310.8	272.0	272–311	32.7	298.0	170.0	5.62×10^{13}	12.9	1.05	0.994
PAAC-7	Exo	658.8	581.1	581–670	41.8	644.9	786.3	1.58×10^{43}	572.7	4.03	0.910

The energy of activation (E_a^\ddagger) and order of the degradation (n) for PAAC-1 to -7 were determined according to the method of the Freeman-Anderson⁶ and the least-square values along with correlation coefficients (γ) are reported in Table 1. The frequency factor (A) and the entropy change (ΔS^\ddagger) determined at T_{max} are also reported. High magnitude of activation energy indicates rigid nature of the phenoxy acids. The high values of n indicate the complex nature of the degradation reaction especially for the second step (PAAC-7) as supported by fair correlation coefficient. Methyl and chlorine substituents caused lowering in E_a^\ddagger (PAAC-2 and -3) but the combined effect resulted in increase of E_a^\ddagger (PAAC-4), which is almost the same as for PAAC-1. Similarly, the presence of nitro group enhanced the value of E_a^\ddagger (PAAC-6) but the combined effect of nitro and methyl groups resulted in E_a^\ddagger to a greater extent. According to Arrhenius equation, the rate constant is governed by both A and E_a^\ddagger . A large and positive magnitudes of ΔS^\ddagger indicate less ordered transition state than the individual phenoxy acid molecules.

The ether linkage and side substituents (CH_3 , Cl, Br and NO_2) are weak points in phenoxy acid molecules, which degrade selectively and free radicals may form. These free radicals further recombine to form new products and degrade at higher temperature. The formation of new products is supported by either endo- or exothermic transitions in DTA thermograms. The degradation is a complex

process and involves a variety of reactions such as rearrangement, cross-linking, etc.

Alkali-catalyzed hydrolysis of phenoxy esters :

The second order rate constants (k) of alkali-catalyzed hydrolysis of DE-1 to -7 at three different temperatures (30, 35 and 40°) are reported in Table 2. The results reveal that k increases with temperature except DE-7, for which it decreases with temperature. The CH_3 , Cl and NO_2 substituents affected the rate constant to a lesser extent but bromine substituent influenced it to a considerable extent.

Self-association of methanol and water breaks down on mixing and new H-bonds is formed due to association of methanol and water molecules, which affects the solvation of both initial and transition states. The transition state is polar in nature due to the association of the catalyst (OH^-) with ester molecule. The bulky ester molecule in the initial state is likely to get solvated by MeOH due to dipole-dipole interaction. The OH^- ion is likely to be desolvated in MeOH- H_2O system, which will result in the lowering of activation energy and hence an increase in the rate constant. The energy of activation (E_a^\ddagger) and the frequency factor (A), determined according to Arrhenius equation, and other thermodynamic parameters are reported in Table 2. The rate constant is influenced by ΔG^\ddagger , which is dependent on the nature of the solvent, the nature of the ions and ionic strength of the solution. From Table 2, it is clear that ΔH^\ddagger and ΔS^\ddagger remained almost constant for a given ester but different for different esters at all temperatures, but ΔG^\ddagger slow-

Table 2. Kinetic parameters of the esters in MeOH-H₂O system at different temperatures

Ester	Temp. °C	k $\Omega^{-1} \text{ min}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔG^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{JK}^{-1} \text{ mol}^{-1}$	E_a^\ddagger kJ mol^{-1}	A s^{-1}
DE-1	30	178.82	5.52	66.45	-201.1	10.56	196.7
	35	193.16	5.44	67.44	-201.3		
	40	204.42	5.35	68.39	-201.4		
DE-2	30	179.02	3.28	66.43	-208.4	8.32	81.9
	35	193.46	3.20	67.42	-208.5		
	40	198.87	3.11	68.43	-208.7		
DE-3	30	177.45	5.62	66.55	-201.1	10.66	198.3
	35	180.42	5.54	67.51	-201.2		
	40	198.93	5.45	68.46	-201.3		
DE-4	30	174.45	-3.07	66.53	-229.7	1.97	6.35
	35	175.55	-3.15	67.63	-229.8		
	40	178.96	-3.23	68.73	-229.9		
DE-5	30	212.13	9.73	65.97	-185.6	14.77	1270.0
	35	248.46	9.65	66.88	-185.8		
	40	262.27	9.56	67.75	-185.9		
DE-6	30	170.17	10.36	66.57	-185.5	15.40	1281.7
	35	190.95	10.28	67.44	-185.6		
	40	207.88	10.19	68.35	-185.8		
DE-7	30	177.75	-9.71	66.28	250.8	-4.67	0.5
	35	172.93	-9.79	67.49	-250.9		
	40	167.54	-9.87	68.72	-251.1		

ly increased with temperature. The large and negative ΔS^\ddagger and small A suggest that the transition state is in highly ordered state than individual ester molecules and it is a rate-determining step.

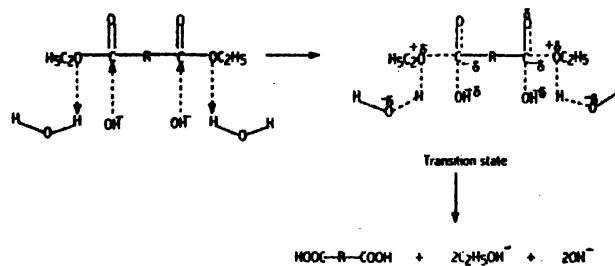
From Table 2, it is interesting to note that the combined effect of Me and Cl or NO₂ groups (DE-4 and DE-7) resulted in lowering of E_a^\ddagger and A , indicating solute polarity in favor of the formation of polar transition state. Thus, the presence of electropositive (CH₃) and electronegative (Cl or NO₂) groups in the ester molecules favors desolvation of OH⁻ ions in MeOH-H₂O system causing decrease of E_a^\ddagger . The cause of the decrease in k with temperature for DE-7 is not clear but probably it might be due to the formation of molecular clusters as a result of dipole-dipole interactions of the opposite type.

The mechanism of alkaline hydrolysis of the esters is presented in Scheme 1.

The experimental data are in accordance with the general mechanism proposed through acyl oxygen fission.

On the basis of experimental findings, it is concluded that phenoxy acids are thermally stable up to about 226–320°. The nature of substituents (CH₃, Cl, Br and NO₂) affects thermal stability and T_{max} to a considerable extent. The endo- or exothermic DTA transitions support some physical or chemical changes. Various kinetic parameters

of alkali-catalyzed hydrolysis of DE-1 to -7 have been interpreted in terms of nature of the substituents. The experimental data are found in accordance with the bimolecular acyl fission mechanism.



Scheme 1

Experimental

Phenoxyacetic acids of bisphenol-C derivatives (PAAC-1 to -7) were synthesized by condensing bisphenol-C derivatives with chloroacetic acid in the presence of sodium hydroxide at reflux temperature for 4 h. Ethyl esters (DE-1 to -7) were synthesized by condensing the respective PAAC with ethanol using sulfuric acid as a catalyst at reflux temperature for 4 h. All compounds were crystallized from MeOH-H₂O system prior to use.

DTA-TG thermograms were scanned on a Mettler TS System at the heating rate of 15° min⁻¹ in nitrogen atmos-

phere. Methanol was fractionally distilled and permanganate-treated double-distilled water was used for the preparation of 0.02 *M* sodium hydroxide solution. Ester solutions (0.01 *M*) were prepared in pure methanol. The kinetic measurements were carried out conductometrically (Equiptronics EQ-664) as a function of time. Equal volumes (25 ml) of the ester and alkali were thermostated at required temperature. The solutions were quickly mixed and change in conductance (C_t) was followed at the interval of 5 min. The initial conductance (C_0) was measured quickly after mixing two solutions and the final conductance (C_∞) of each mixture at infinite time was measured after 24 h. The second order kinetic equation in terms of conductance was employed for the determination of the specific rate constant,

$$k = [1/t(C_0 - C_\infty)] [C_0 - C_t] / (C_t - C_\infty)$$

The value of k for each ester was determined graphically at three different temperatures, 30, 35 and 40°.

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References

1. G. Subramaniam, R. Savithri and S. Thambipillai, *J. Indian Chem. Soc.*, 1989, **66**, 797; H. H. Garchar, S. H. Kalola and P. H. Parsania, *Asian J. Chem.*, 1993, **5**, 340.
2. H. H. Garchar and P. H. Parsania, *J. Indian Chem. Soc.*, 1996, **73**, 359; V. V. Srivastava, R. I. Singh, S. B. Singh, P. Prasad and L. Singh, *J. Indian Chem. Soc.*, 1990, **67**, 619.
3. L. N. Singh, D. N. Singh, D. K. Verma, Manjula and K. P. Singh, *J. Indian Chem. Soc.*, 1990, **67**, 463.
4. W. W. Wendlandt, "Thermal Methods of Analysis". 2nd. ed., Wiley, New York, 1974; T. Meisel and K. Seytold, *Crit. Rev. Anal. Chem.*, 1981, **12**, 267.
5. D. W. Levi, L. Reich and H. T. Lee, *Polym. Eng. Sci.*, 1965, **5**, 135; L. Reich and D. W. Levi, *Macromol. Chem.*, 1963, **66**, 102.
6. E. S. Freeman and D. A. Anderson, *J. Polym. Sci.*, 1961, **54**, 253.