J. Org. Chem. 1980, 45, 1162-1164

Kinetics and Mechanism of Chlorine Addition to Acrylic Acid and Its Derivatives with Special Reference to the Nature of the Transition State

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Received August 16, 1979

The nature of the carbocationic intermediate involved in electrophilic halogen addition to a carbon-carbon double bond is an unsettled matter for many olefin-halogen reactions. The structure of this intermediate depends on several factors such as the structure of the olefin, the halogen, the solvent, and the added electrolytes, if any.[1] The mechanism of electrophilic chlorine addition to cinnamic acid and its derivatives has been studied in great detail.[2,3] Johnson, on the basis of studies of product stereochemistry,[2] has proposed a mixed mechanism involving a carbonium ion and an ion pair for chlorine addition to these olefins. From a study of the effect of added salt on product stereochemistry, de la Mare[3] has postulated that the addition products of these olefins come predominantly from zwitterionic intermediates. However, not much work has been done on chlorine addition to acrylic acid and its derivatives. In this paper we report a kinetic study of chlorination of acrylic acid and its derivatives in acetic acid medium. The emphasis is to elucidate the nature of the transition state in this reaction.

Recently, Schmid[4] has shown by comparing the structure-reactivity profiles for addition of a proton, bromine, and arenesulfenyl chloride to alkenes that the variation in the effect of substituting a methyl group for an olefinic hydrogen on the rate of addition can be used to probe the nature of the rate-determining transition state. A similar analysis of the structure-reactivity correlation for the addition of chlorine to acrylic acid and its derivatives has been carried out in this work.

Results and Discussion

Chlorine addition to acrylic acid and its derivatives is second order overall. The rate constants determined from the slopes of plots of log $[b(a-x)/a(b-x)]$ against time (where a and b are the initial concentrations of olefin and chlorine, and x is the amount of chlorine reacted in time t) are presented in Table I. The individual orders with respect to a typical olefin (acrylamide) and chlorine were established by a differential plot (Table II and Figure 1).

Table I. Rate Constants and Ratios of k_{CH_3}/k_H for Chlorine and Bromine Addition to Acrylic Acid and Its Derivatives

	Cl_2 addition in HOAc		Br_2 addition in 60% aqueous HOAc	
olefin	10^2k_2 (26 °C),[a] $M^{-1}\ s^{-1}$	k_{CH_3}/k_H	10^2k_2 (30 °C), $M^{-1}\ s^{-1}$	k_{CH_3}/k_H
acrylic acid	0.0362	29.5		
trans-crotonic acid	1.06			
methyl acrylate	0.045	34.7	0.41	6.2
trans-methyl crotonate	1.56		2.53	
methyl acrylate	0.045	124.7	0.41	11.7
methyl methacrylate	5.61		4.79	
butyl acrylate	0.0671	126.1	0.51	12.7
butyl methacrylate	8.46		6.46	
acrylamide	0.54	80.2	2.92	9.3
methacrylamide	43.3		27.27	

[a] Average of three kinetic runs.

Table II. Rate Data for Chlorine Addition to Acrylamide in Acetic Acid at 26 °C

10^2[acrylamide], M	$10^2[Cl_2]$, M	$-10^6\ d[Cl_2]/dt$,[a] $M\ s^{-1}$	order
5	0.5	1.36	0.90
10	0.5	2.48	
15	0.5	3.43	
20	0.5	5.21	
10	0.35	1.51	1.02
10	0.46	2.07	
10	0.59	2.63	
10	0.97	4.65	

[a] Initial rate determined from a plot of chlorine concentration against time.

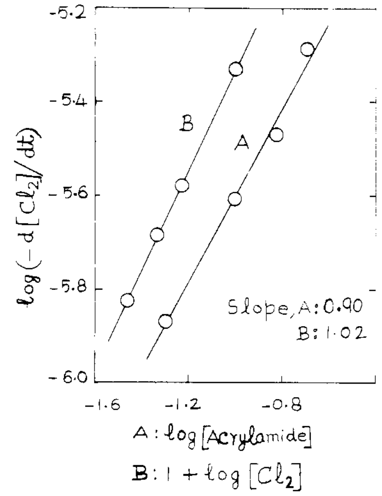

Figure 1. Plots to determine the orders in olefin and halogen for the chlorination of acrylamide in acetic acid at 26 °C.

The magnitude of variation of the effect of introducing a methyl group for an olefinic hydrogen in a series of vinyl compounds on the rates of addition depends on the nature of the rate-determining transition state. If the reaction involves an open-ion-like rate-determining transition state, the change in the ratio k_{CH_3}/k_H over a range of olefins will be large, and it will be small if the transition state resembles a bridged ion[4] (k_{CH_3} and k_H denote the rate constants for the methyl-substituted and unsubstituted vinyl compounds). The ratios k_{CH_3}/k_H for chlorination, determined from the rates of chlorine addition to acrylic acid, crotonic acid, methyl acrylate, methyl crotonate, methyl methacrylate, butyl acrylate, butyl methacrylate, acrylamide, and methacrylamide, are given in Table I. The table also contains k_{CH_3}/k_H values for bromine addition to derivatives of acrylic acid evaluated from the kinetic work of Viswanathan and Ganesan.[5] Inspection of Table I shows that the variation of k_{CH_3}/k_H for both chlorine and bromine addition to acrylic acid and its derivatives is small. This

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[1] P. B. D. de la Mare, "Electrophilic Halogenation", Cambridge University Press, Cambridge, 1976.

[2] M. D. Johnson and E. N Trachtenberg, *J. Chem. Soc. B*, 1018 (1968).

[3] P. B. D. de la Mare, M. A. Wilson, and M. J. Rosser, *J. Chem. Soc., Perkin Trans. 2*, 1480 (1973).

[4] G. H. Schmid, *J. Org. Chem.*, **43**, 777 (1978).

[5] S. Viswanathan and R. Ganesan, *Indian J. Chem.*, **9**, 674 (1971).

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Table III. Rate Constants for Chlorine Addition to Methyl Acrylate in Acetic Acid-Water Mixtures at 26 °C

% water content (v/v)	dielectric const,[a] D	$10^2 k_2$, $M^{-1} s^{-1}$
2	8.9	0.0921
3	10.2	0.149
5	12.4	0.231
8	15.8	0.393
9	17.0	0.437
10	18.2	0.498

[a] Dielectric constants are the values determined by Campbell and Gieskes.[10]

indicates that addition to these olefins probably involves a bridged-ion-like transition state. If we compare k_{CH_3}/k_H for bromination and chlorination for any one of the pairs of olefins, the ratio is greater for chlorine addition than for bromine addition. The greater sensitivity of chlorination to substituent effect indicates increased charge development in the transition state, and the bridging in the chloronium ion is probably weaker than that in bromination. This is also consistent with the lower bridging ability of chlorine.

The effect of a methyl substituent in the α and β positions has also been determined from the rates of addition to methyl methacrylate and methyl crotonate. This ratio, $k_{\alpha\text{-}CH_3}/k_{\beta\text{-}CH_3}$, is 3.6 for chlorine addition and 1.9 for bromine addition. These low values are also characteristic of a bridged-ion-like transition state (for addition of arenesulfenyl chloride involving a bridged transition state, this ratio is 1.3, and for hydration of alkenes involving an open-ion-like transition state, it has been found to be as high as 10^3–10^4).[6] Thus the above results indicate that chlorination of acrylic acid and its derivatives most probably involves a weakly bridged rate-determining transition state.

The effect of solvent dielectric constant on the rate of chlorine addition to a typical olefin (methyl acrylate) was investigated to obtain an estimate of the polarity of the rate-determining transition state. For this, rate constants in different acetic acid–water mixtures were determined. As suggested by Kwart,[7] the Laidler–Eyring equation

$$\ln k = \ln k_0 - \frac{1}{kT}\frac{D-1}{2D+1}\left(\frac{\mu_A^2}{\gamma_A^3}+\frac{\mu_B^2}{\gamma_B^3}-\frac{\mu_\ddagger^2}{\gamma_\ddagger^3}\right)$$

for the influence of solvent dielectric constant on the rate of a dipole–dipole reaction was made use of. In this equation D is the dielectric constant of the medium, k is the rate constant at a given D, and k_0 is that at $D = 1$; μ_A, μ_B, and $\mu_\ddagger$ are the dipole moments of the reactants (A and B) and activated complex, respectively, and γ_A, γ_B, and $\gamma_\ddagger$ are the radii of the reactants and activated complex.

The dipole moment of methyl acrylate[8] is 1.77 D and that of chlorine is zero. The values used for the radii of chlorine[9] and methyl acrylate were 1.85 and 3.18 Å, respectively. The molecular radius of methyl acrylate was calculated from its molar volume (the liquid phase density of 0.95 for methyl acrylate was used to calculate the molar volume). The packing density for this system[7] was taken as 0.9. The radius of the activated complex is assumed to be the sum of the radii of the reacting molecules. The dipole moment of the transition state complex ($\mu_\ddagger$) can be estimated from the plot of log k_2 against $(D - 1)/(2D + 1)$ (Table III and Figure 2). The slope is found to be 17.9, and $\mu_\ddagger$ is 15.12 D. The activated complex is thus found to be much more polar than the reactants. This conclusion is in accord with qualitative expectations, since it is well-known that, for a reaction in which the activated complex is more polar than the reactants, the rate increases with increasing polarity or dielectric constant of the medium.[11]

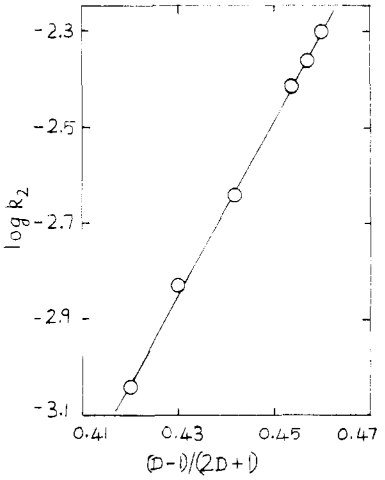

Figure 2. Plot of log k_2 against $(D - 1)/(2D + 1)$ for chlorine addition to methyl acrylate in acetic acid–water mixtures at 26 °C.

Experimental Section

Commercial samples of acrylamide (American Cyanamide Co.), methacrylamide (Rohm and Haas), and crotonic acid (BDH) were recrystallized and used. Methyl crotonate was prepared from crotonic acid by a standard method[12] (bp 118–120 °C). Esters of acrylic acid (British Drug House, laboratory reagent) were washed with sodium hydroxide, dried over anhydrous sodium sulfate, and distilled twice in an atmosphere of pure dry nitrogen. Acrylic acid (BDH, laboratory reagent) was distilled under reduced pressure in an atmosphere of nitrogen and used. Acetic acid (BDH, laboratory reagent) was purified by the method of Orton and Bradfield.[13] A chlorine solution in acetic acid was prepared by bubbling pure chlorine gas into the solvent.

The kinetics was followed by measuring chlorine concentration iodometrically. Since a solution of chlorine in acetic acid is very volatile it is very difficult to get accurate rate data for chlorine addition. In fact all the kinetic results reported so far by using solutions of chlorine, mixing in the usual way, and pipetting out aliquots for estimation (the conventional kinetic procedure) are subject to error. A simple and accurate experimental method has been devised in our laboratory by Ganesan and Kalachandra[14] to study the kinetics of chlorination of aromatic compounds. The same procedure was adopted in the present study. In this method the measured rate constants are accurate within an error limit of ±3%.

Registry No. Acrylic acid, 79-10-7; *trans*-crotonic acid, 107-93-7; methyl acrylate, 96-33-3; *trans*-methyl crotonate, 623-43-8; methyl methacrylate, 80-62-6; butyl acrylate, 141-32-2; butyl methacrylate, 97-88-1; acrylamide, 79-06-1; methacrylamide, 79-39-0; 2,3-dichloropropanoic acid, 565-64-0; 2,3-dichlorobutanoic acid, 600-32-8; methyl

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(6) G. H. Schmid and D. G. Garratt, "The Chemistry of Double Bonded Functional Groups, Supplement", A. A. Patai, Ed., Wiley, London, 1977, p 725.

(7) H. Kwart and T. H. Lilley, *J. Org. Chem.*, **43**, 2374 (1978).

(8) A. L. McClellan, "Tables of Experimental Dipole Moments", Rabara Enterprises, New York, 1974.

(9) W. J. Moore, "Physical Chemistry", 5th ed., Longman, London, 1972, p 157.

(10) N. Campbell and J. M. T. M. Gieskes, *Can. J. Chem.*, **42**, 1379 (1964).

(11) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

(12) A. I. Vogel, "Practical Organic Chemistry", 3rd ed., Longman, London, 1956, p 927.

(13) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

(14) R. Ganesan and S. Kalachandra, *Z. Physik. Chem. (Frankfurt am Main)*, 72, 269 (1970).

2,3-dichloropropanoate, 3674-09-7; methyl 2,3-dibromopropanoate, 1729-67-5; methyl 2,3-dichlorobutanoate, 54460-97-8; methyl 2,3-dibromobutanoate, 5469-24-9; methyl 2,3-dichloro-2-methylpropanoate, 918-78-5; methyl 2,3-dibromo-2-methylpropanoate, 3673-79-8; butyl 2,3-dichloropropanoate, 72726-18-2; butyl 2,3-dibromopropanoate, 21179-48-6; butyl 2,3-dichloro-2-methylpropanoate, 72726-19-3; butyl 2,3-dibromo-2-methylpropanoate, 72726-20-6; 2,3-dichloroacrylamide, 19433-84-2; 2,3-dibromoacrylamide, 15102-42-8; 2,3-dichloro-2-methylpropanamide, 7017-20-1; 2,3-dibromo-2-methylpropanamide, 72726-21-7.

Steric Effects. 4.[1] Multiparameter Correlation Models. Geometrical and Proximity Site Effects for Carboxylic Acid Esterification and Related Reactions

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Received July 12, 1979

A recent article[3] concerning the validity and importance of Hancock-type steric parameters[4] (E_s^c) prompts us to report our own results and observations in this area. This is a subject currently under controversy,[5a,b] and we feel that a careful analysis of the factors involved is necessary in order to reach conclusions that will stand the test of time. After a summary and analysis of the arguments of this article, we set forth our own approach to the problem of steric hindrance and its use in comparing the reactivities of methyl carboxylates and alkyl acetates.

In the article in question the authors, from Hancock's school, have attempted to revive interest in the use of Hancock's E_s^c parameter. They base their argument, in part, on an analysis of the rate data for the alkaline hydrolysis of methyl carboxylates and alkyl acetates. It is worth noting that the alkaline hydrolysis of methyl carboxylates (RCO_2Me) was originally used by Hancock to justify the development of the E_s^c scale.[4] This recent work considers that the data are adequately represented in terms of Taft's E_s parameters, thus sweeping aside one of the original arguments.

The situation is somewhat different in the case of alkyl acetates (CH_3CO_2R). Here the R group is in the nonacyl portion of the molecule, and its steric effect is not adequately reflected by the E_s parameter which was defined with respect to the acyl portion of an ester.

Correlations in terms of $E_s(R)$ and $E_s^c(R)$ were found to be unsatisfactory, with the latter more successful than the former. However, a correlation in terms of $E_s^c(RCH_2)$ was found to be excellent ($r = 0.9925$, $\psi = 0.141$); surprisingly enough a correlation in terms of $E_s(RCH_2)$ is not considered. Correlations in terms of $E_s^c(RCH_2)$ are taken as evidence for the validity and importance of this kind of parameter. Such an interpretation has to be treated with caution. It must be remembered that E_s^c is defined with respect to Taft's E_s as $E_s^c = E_s + 0.306(n_H - 3)$. When the groups used in a correlation are all of the form RCH_2, then E_s^c and E_s differ by a constant term (i.e., $E_s^c = E_s - 0.306$). This means, of course, that modifying E_s to give E_s^c produces no change in the validity of the correlation and provides no positive evidence in favor of E_s^c.

These remarks apply equally well to acid- and base-catalyzed hydrolysis. We agree with these authors when they question the necessity of developing sets of steric parameters from a variety of defining basis sets. This remark might well apply to Hancock-type parameters.

In our own work we have developed a scale of steric parameters[5a] (E_s') based on the Taft–Ingold hypothesis and a single reference reaction, i.e., the acid-catalyzed esterification of carboxylic acids in methanol at 40 °C, rather than average data for a variety of similar reactions. This revised Taft steric scale combines literature data with new rate-constant measurements to cover a range of greater than eight powers of ten in rate constant. Table I gives the appropriate E_s' values for a set of 13 alkyl groups which have been found by molecular-mechanics calculations to exist in predominantly eclipsed conformations in the presence of a carbonyl function.[7] Our strategy here is to correlate the *overall* steric effect of a group $R_1R_2R_3C$ as a function of a linear combination of the steric effects of the subgroups R_1, R_2, and R_3, taking into account the orientation of these subgroups with respect to the carbonyl. This may be carried out in a variety of ways, depending on the model chosen.

As a first approach we correlate $E_s'(R_1R_2R_3C)$ as a linear combination of $E_s'(R_iCH_2)$, the *equidistant site model*, where the atoms of R_i on both sides of eq 1 are the same

$$E_s'(R_1R_2R_3C) = \sum_i a_iE_s'(R_iCH_2) + a_0 \tag{1}$$

distance from the carbonyl group. But for $CHEt_2$ [which presents a large deviation (0.67)] this correlation is surprisingly good, considering the simplicity and weakness of the equidistance approximation.

Another approach is to consider a correlation in terms of $E_s'(R_i)$, the *subgroup additivity model*, as in eq 2. The

$$E_s'(R_1R_2R_3C) = \sum_i a_iE_s'(R_i) + a_0 \tag{2}$$

correlation is seen to be mediocre. The reason for this may be that the model is unsuitable or that some essential element is missing from eq 2. The key lies in the idea of six-number first proposed by Newman[8] in a qualitative way and later used quantitatively by Hancock.[9] This idea is based on the topology of groups since certain sites (i.e., position six) are singled out as having an effect different from that of the others. Equation 2 may be expanded to incorporate the six-number, eq 3. This *hybrid* equation,

$$E_s'(R_1R_2R_3C) = \sum_i (a_iE_s'(R_i) + b_i\Delta x_i) + a_0 \tag{3}$$

made up from the contribution of subgroups and six-number (*subgroup additivity plus topology model*), gives an excellent correlation. The a_i terms weight the individual contributions of the subgroups R_i whose orientations with respect to the carbonyl group have been determined by molecular mechanics, the b_i terms represent the supple-

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(1) Part 3: Dubois, J. E.; MacPhee, J. A.; Panaye, A. *Tetrahedron*, in press.

(2) (a) MacPhee J. A., Chargé de Recherche, Centre National de la Recherche Scientifique, France. (b) Panaye A., Maitre-Assistant â l'Université Paris VII.

(3) Idoux, J. P.; Schreck, J. O. *J. Org. Chem.* **1978**, *43*, 4002.

(4) Hancock, C. K.; Meyers, E. A.; Yager, B. J. *J. Am. Chem. Soc.* **1961**, *83*, 4211.

(5) (a) MacPhee, J. A.; Panaye, A.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 3553. (b) Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552.

(6) Taft, R. W., Jr. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 3.

(7) Dubois, J. E.; MacPhee, J. A.; Panaye, A. *Tetrahedron Lett.* **1978**, 4099.

(8) Newman, M. S. *J. Am. Chem. Soc.* **1950**, *72*, 4783.

(9) Hancock, C. K.; Yager, B. J.; Falls, C. P.; Schreck, J. O. *J. Am. Chem. Soc.* **1963**, *85*, 1297.

0022-3263/80/1945-1164$01.00/0