

Pressure Effect and Mechanism in the Acid-Catalyzed Hydration of Acrylic Acid

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Abstract: The effect of pressure up to 1700 atm on the rate of acid-catalyzed reversible hydration of acrylic acid has been studied at different temperatures. The activation parameters, *i.e.*, volume, entropy, and energy of activation have been calculated and found to be $-15.8 \pm \sim 1.2 \text{ cm}^3 \text{ mole}^{-1}$, $-31.9 \pm \sim 3.8 \text{ cal deg}^{-1} \text{ mole}^{-1}$, and $18.8 \pm \sim 1.4 \text{ kcal mole}^{-1}$, respectively, for the forward reaction and $-11.1 \pm \sim 2.5 \text{ cm}^3 \text{ mole}^{-1}$, $-26.5 \pm \sim 5.0 \text{ cal deg}^{-1} \text{ mole}^{-1}$, and $22.4 \pm \sim 2.0 \text{ kcal mole}^{-1}$, respectively, for the reverse reaction at atmospheric pressure and at 90° . The reaction has also been studied at different concentrations (1–3 *M*) of mineral acid and the rate has been found to be more nearly proportional to the hydrogen ion concentration rather than the Hammett acidity function. The data have been treated on the basis of Bunnett's modification (w and w^* factors) of the Zucker–Hammett theory and Bunnett's linear free energy relationship (ϕ factor). The activation parameters as well as the acidity dependence of the rate indicate the presence of at least one molecule of water in the activated complex. On the basis of the above findings, the probable mechanisms for the reaction have been discussed.

The acid-catalyzed hydration of acrylic acid was first studied by Lucas, *et al.*,¹ at 110 – 130° and 1 atm. However, these authors did not throw any light on the mechanism of the reaction. Later Taft,² on the basis of Zucker–Hammett theory³ and from a study of the entropy of activation, suggested that the hydration of olefins (the rates of which follow the h_0 function and ΔS^* is less negative) proceeds *via* a π -complex intermediate followed by slow decomposition (A1), whereas the hydration of crotonaldehyde and $\beta\beta$ -dimethylacrolein⁴ (the rates are proportional to hydrogen ion concentration and ΔS^* is more negative) involves a bimolecular slow step (A2). In a number of cases⁵ it has been observed that the Zucker–Hammett hypothesis does not provide a valid method for distinguishing between A1 and A2 mechanisms. Later Whalley⁶ showed that the pressure coefficient of the reaction rate can help to elucidate the reaction mechanism.

The present paper reports the results of our studies on the effect of pressure on the acid-catalyzed reversible hydration of acrylic acid, and discussion of probable mechanisms for such reaction.

Experimental Section

Materials. Acrylic acid was distilled under vacuum in an atmosphere of nitrogen. The distilled product on analysis showed one double bond per molecule. A solution of the acid, prepared by dissolving the requisite amount in boiled-out distilled water, was found to be very stable and could be stored for a long time.

A stock solution of perchloric acid was prepared by diluting 60% perchloric acid (G. R., E. Merck) and assayed by titration with standard alkali. All other chemicals used were either of E. Merck, G. R. grade or B. D. H. analar quality.

Analysis. The hydration of acrylic acid was followed by estimating the residual unsaturation at any instant by the bromine–bromide method as suggested by Critchfield.⁷

(1) H. J. Lucas and D. P. Pressman, *J. Am. Chem. Soc.*, **64**, 1953 (1942).
(2) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952).

(3) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(4) (a) H. J. Lucas, W. T. Stewart, and D. P. Pressman, *J. Am. Chem. Soc.*, **66**, 1818 (1944); (b) S. Winstein and H. J. Lucas, *ibid.*, **59**, 1461 (1937).

(5) J. Koskikallio, D. Pouli, and E. Whalley, *Can. J. Chem.*, **37**, 1360 (1959).

(6) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 798, 815 (1959).

(7) F. E. Critchfield, "Organic Functional Group Analysis," Pergamon Press, Ltd., Oxford, 1963, pp 107.

Apparatus and Procedure. The high-pressure reactor was designed to work up to a maximum pressure of 3000 atm. A sketch of the reactor is shown in Figure 1. A special type of gasket made of nitrile rubber was used for sealing the head of the pressure vessel. The pressure of the system was measured with an accuracy of $\pm 1\%$ by means of a Bourdon gauge connected at the bottom of the reactor. The reactor was kept fixed in a thermostat, the temperature of which was controlled within $\pm 0.01^\circ$.

In a typical run the required amounts of acrylic acid and perchloric acid were mixed. The mixture was taken into a sealed tube for studies at atmospheric pressure. For studies at high pressure, the reaction mixture was transferred to a specially designed glass reaction tube (Figure 1) containing mercury at the bottom. The reaction tube was closed by a stopper and placed in the pressure vessel maintained at the required temperature. Pressure was raised to the required level by an electrically operated booster pump. The stop watch was started when the pressure was half the desired value. Light paraffin was used as the pressure-transmitting fluid.

The reaction was allowed to proceed for some time after which the pressure was released, the reaction tube was taken out, and its contents were analyzed for the unsaturation. The process was repeated for about six time intervals for each run. The equilibrium reading was determined after keeping the reaction mixture for at least nine half-lives. As the reaction is very slow, the method of trial and error⁸ in some cases (particularly at 80°) was adopted to save time, for the determination of equilibrium constants. The values obtained agree well with the experimentally determined values. The kinetic measurements were taken at six different pressures (1–1700 atm) and the rate constants were calculated in each case.

No hydration was found to occur at room temperature ($\approx 30^\circ$) and pressure. There was no spontaneous uncatalyzed hydration under the experimental conditions.

The plot of $\log x_e/(x_e - x)$ (where x_e and x denote the unsaturation at equilibrium and at any time t , respectively) against time " t " was found to be linear (Figures 2 and 3). Thus the reaction shows the characteristics of a reversible first-order reaction. The rate constants were calculated from the slope of the above plots and the equilibrium constant (K)

$$k_1 + k_{-1} = 2.303(\text{slope}) \quad (i)$$

where k_1 and k_{-1} represent the rate constants for the forward and reverse reaction and $K = k_1/k_{-1}$.

Results and Discussion

The acid-catalyzed hydration of acrylic acid and its reverse reaction have been studied within the pressure range of 1–1700 atm at 80 , 85 , and 90° . The results are

(8) D. P. Pressman and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 2271 (1939).

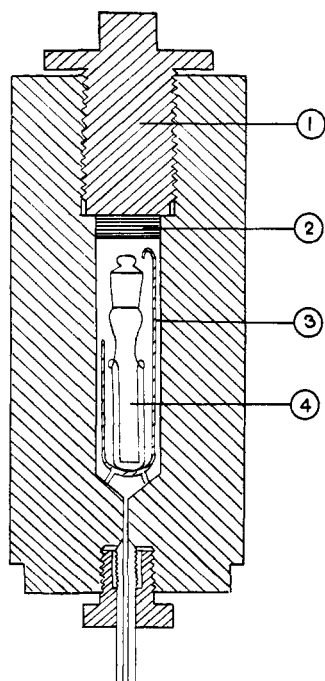


Figure 1. Schematic diagram of the high pressure reactor: 1, top closure; 2, rubber gasket; 3, reactor tube holder; 4, reaction tube.

summarized in Table I. The plot of $\log x_e/(x_e - x)$ against t was found to be linear (Figures 2 and 3) in each case when the reaction was studied at different conditions of temperature, pressure, and acid concentration showing that the hydration is first order with respect to the unsaturated compound and the dehydration is first order with respect to the hydrated compound.

Table I. Effect of Pressure on the Rate of Acid-Catalyzed Hydration of Acrylic Acid and Its Reverse Reaction^a

Temp, °C	Pressure, atm	$k_1 \times 10^6$, sec ⁻¹	$k_{-1} \times 10^6$, sec ⁻¹	K	$k_1' \times 10^6$, l. mole ⁻¹ sec ⁻¹	$k_{-1}' \times 10^6$, l. mole ⁻¹ sec ⁻¹
80.0	1	8.32	0.79	10.5	4.83	0.46
	680.2	11.21	0.95	11.7	6.32	0.53
	1020.3	14.10	1.13	12.5	7.83	0.63
	1360.4	16.58	1.28	12.9	9.10	0.71
85.0	1	12.49	1.24	10.1	7.26	0.72
	680.2	18.26	1.63	11.2	10.32	0.92
	1020.3	21.30	1.79	11.9	11.87	1.00
	1360.4	26.28	2.15	12.2	14.48	1.18
90.0	1700.5	30.38	2.35	12.9	16.56	1.28
	1	17.35	1.90	9.1	10.13	1.11
	340.1	21.68	2.26	9.6	12.47	1.30
	680.2	25.38	2.45	10.4	14.38	1.39
	1020.3	30.58	2.88	10.6	17.20	1.61
1360.4	37.14	3.31	11.2	20.54	1.83	

^a Concentration of acrylic acid = 0.03 M; concentration of perchloric acid = 1.767 M (at room temperature and pressure).

Our values of the equilibrium constant at atmospheric pressure differ slightly from that reported in the literature. Lucas and Pressman¹ obtained the value 11.40 at 110.6° and at atmospheric pressure and showed that the value should increase with the decrease in temperature as the reaction is exothermic. Our repeated ex-

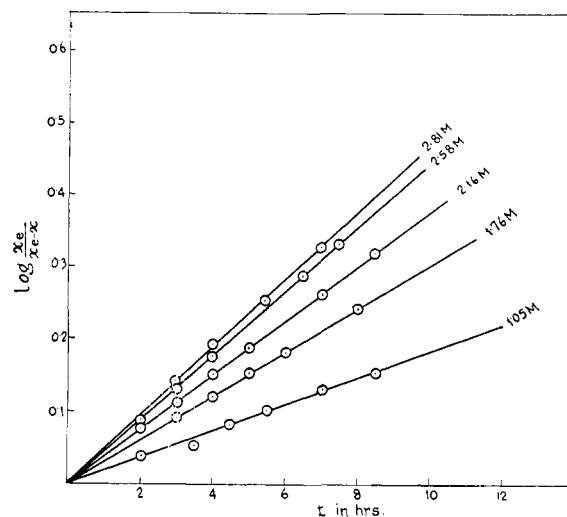


Figure 2. Effect of perchloric acid concentration on the hydration of acrylic acid at 90° and at 1 atm.

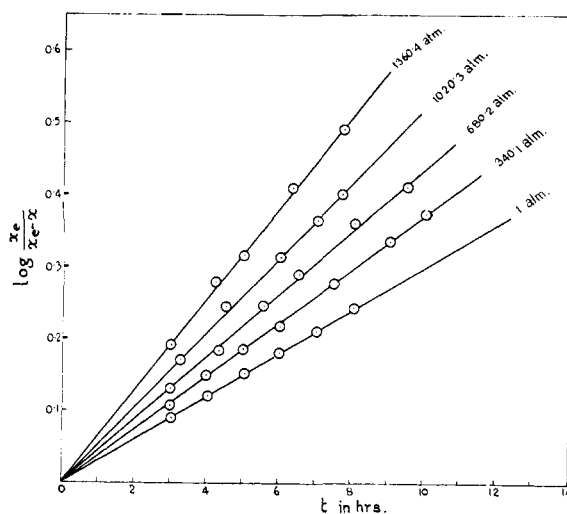


Figure 3. Effect of pressure on the hydration of acrylic acid at 90°.

perimental findings at 80, 85, and 90° showed that equilibrium constant does not exceed 11.0. However Critchfield⁷ has suggested that the bromate-bromide method as used by Lucas, *et al.*,¹ for the estimation of $\alpha\beta$ -unsaturated acids is unsuitable. Substitution of bromine instead of addition may be the cause of the higher values observed by the earlier workers. As appreciable amount of β -hydroxypropionic acid does not exist at equilibrium, some difficulties were encountered in measuring the equilibrium constant. In the present case, the values of rate constants, k_1 are more accurate than the values of k_{-1} , since the former is less sensitive to the changes in the value of x_e . The mean deviations of the duplicate measurements of equilibrium constants (K), k_1 , and k_{-1} were 5, 1, and 1%, respectively. The variation in the values of the equilibrium constant introduces an uncertainty of 1 and 2% in the values of k_1 and k_{-1} , respectively.

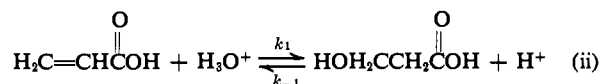
In order to study the effect of acid concentration, the reaction was carried out in 1.06, 1.77, 2.17, 2.58, and 2.81 M perchloric acid solutions at 90° and 1 atm. The results are presented in the Table II. The second-order rate constants (k_1' and k_{-1}'), obtained by dividing the

Table II. Effect of Perchloric Acid Concentration on the Rate and Equilibrium Constants of the Acid-Catalyzed Hydration of Acrylic Acid and Its Reverse Reaction^a

Perchloric acid concn, M	$k_1 \times 10^6$, sec ⁻¹	$k_{-1} \times 10^6$, sec ⁻¹	K	$k_1' \times 10^6$, l. mole ⁻¹ sec ⁻¹	$k_{-1}' \times 10^6$, l. mole ⁻¹ sec ⁻¹
1.058	10.94	1.05	10.4	10.33	1.00
1.767	17.35	1.90	9.1	9.81	1.07
2.168	21.25	2.33	9.1	9.79	1.07
2.583	25.45	2.86	8.9	9.84	1.11
2.811	26.89	3.02	8.9	9.56	1.07

^a Temperature = 90°, pressure = 1 atm, concentration of acrylic acid = 0.03 M.

first-order rate constants by hydrogen ion concentration, were found to be almost constant which indicates a first-order dependence of both hydration and the reverse reaction upon the hydrogen ion concentration. Therefore, the over-all reaction may be written as



The energy and entropy of activation have been determined from the study of the effect of temperature on the reaction rate. The energy of activation for the forward reaction has been found to be 18.8 ± 1.4 kcal mole⁻¹. The frequency factor was of the order of 10^6 . The entropy of activation has been calculated from the equation

$$k = \epsilon e \frac{kT}{h} e^{\Delta S^*/R} e^{-E/RT} \quad (\text{iii})$$

(the symbols have their usual meaning) and was found to be highly negative for both hydration and dehydration reaction. The results are presented in Table III. High negative value of ΔS^* indicates association of one or more molecules of water in the activated complex.

Table III. Activation Parameters for the Acid-Catalyzed Hydration of Acrylic Acid and Its Reverse Reaction^a

Temp, °C	Pressure, atm	Energy of activation, kcal mole ⁻¹		Entropy of activation, cal deg ⁻¹ mole ⁻¹		Frequency factor, l. mole ⁻¹ sec ⁻¹		Volume of activation, cm ³ mole ⁻¹	
		E_1	E_{-1}	ΔS_1^*	ΔS_{-1}^*	Log A_1	Log A_{-1}	ΔV_1^*	ΔV_{-1}^*
80.0	1	18.8	22.4	-31.9	-26.5	6.3	7.5	-14.0	-9.6
	680.2	20.6	24.2						
	1020.3	19.5	23.6						
	1360.4	20.5	23.8						
85.0	1			-31.9	-26.5	6.3	7.5	-14.4	-10.4
90.0	1			-31.9	-26.5	6.3	7.5	-15.8	-11.1
	340.1								
	680.2			-26.2	-21.0	7.6	8.7		
	1020.3			-29.1	-22.3	6.9	8.4		
	1360.4			-26.0	-21.7	7.6	8.6		

^aThe accuracy of the data has been mentioned earlier.

In order to get a better physical concept of the activated complex, the effect of pressure on the rate has been studied. The rates of both forward and reverse reaction were greatly influenced by pressure. The volume of activation was determined from the slope of the plot of $\log k$ (where k' is the second-order rate constant, *i.e.*, k/C_{HClO_4} , C_{HClO_4} is the concentration of perchloric acid at the temperature and pressure of the

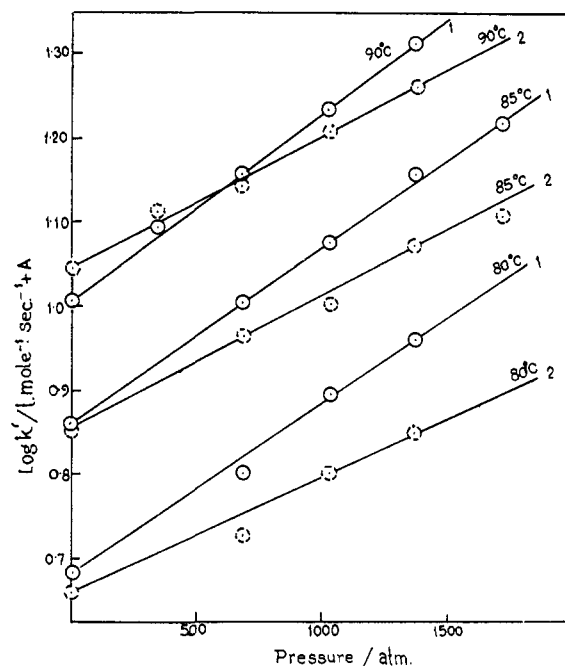


Figure 4. Effect of pressure on the reaction rates at 80, 85, and 90°: 1, hydration of acrylic acid, $A = 6$; 2, dehydration of β -hydroxypropionic acid, $A = 7$.

experiment),⁹ against pressure (Figure 4). In a similar way ΔV^0 , the total volume change of the reaction, may be determined by studying the effect of pressure on equilibrium constant. The volume of activation for the forward and reverse reaction were found to be $-15.8 \pm \sim 1.2$ cm³ mole⁻¹ and $-11.1 \pm \sim 2.5$ cm³ mole⁻¹, respectively. The large contraction indicates that the transition state contains at least one firmly bound molecule of water and so can be represented as (substrate \cdot $\text{H}^+ \cdot \text{H}_2\text{O}$)^{*}. It rules out a mechanism in which a π -protonated substrate isomerizes unimolecularly to a carbonium ion.

The Acidity Dependence of the Reaction. A linear plot with a slope 1.0 was obtained for both hydration and the reverse reaction when the logarithm of the rate constant was plotted against the logarithm of hydrogen

(9) (a) P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.*, **66**, 185 (1931); (b) G. C. Kennedy, W. L. Knight, and W. T. Holser, *Am. J. Sci.*, **256**, 590 (1958); (c) R. J. Withey and E. Whalley, *Can. J. Chem.*, **41**, 546 (1963).

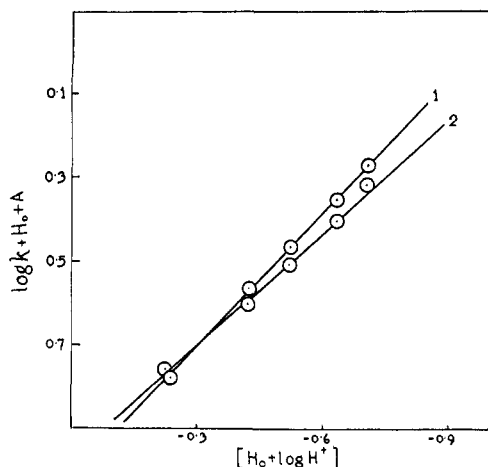


Figure 5. Bunnett's linear free energy plot for ϕ : 1, hydration of acrylic acid, $A = 6$; 2, dehydration of β -hydroxypropionic acid, $A = 7$.

ion concentration, whereas a slightly curved plot was obtained when $\log k_{-1}$ and $\log k_1$ were plotted against $-H_0$. According to the Zucker-Hammett hypothesis³ (though this has been much criticized by several workers⁵) the reaction follows an A2 mechanism, *i.e.*, the reaction proceeds through an activated complex which is formed from the reactants by addition of a proton and at least one molecule of water.

The present data have also been analyzed in the light of Bunnett's modifications¹⁰ of Zucker-Hammett hypothesis. Though this modification removes the disagreement for many reactions it does not do so in every case as pointed out by Whalley.¹¹

The parameter "w" was calculated from the slope of the plot between $(\log k + H_0)$ against $\log a_{\text{H}_2\text{O}}$. The value of "w" obtained was quite high (about +8.4) for the forward reaction and +7.7 for the reverse reaction.

An attempt was also made to determine w^* , plotting $(\log k - \log \text{HClO}_4)$ against $\log a_{\text{H}_2\text{O}}$. The values of w^* were found to be -1.2 and +0.9 for the forward and the reverse reactions, respectively. The values of w and w^* for both direct and reverse reactions suggest that the activated complex is highly solvated and also indicate that a water molecule acts as a proton transfer agent in the rate-determining step.¹⁰

Bunnett and Olsen,¹² from studies of equilibrium and the kinetics of a large number of reactions, found that linear relationships exist between $(\log k + H_0)$ (for reactions of weakly basic substrates) or $\log k$ (for strongly basic substrates) and $[H_0 + \log(H^+)]$. The slopes of these plots are taken as a parameter ϕ which characterizes the response of the reaction rate to changing acid concentration. Bunnett and Olsen from the comparison of earlier w plots¹⁰ and their linear free energy plots observed that the latter parameter is much superior than the former. On the basis of the ϕ values the three categories of reaction mechanisms are categorized as follows: water is not involved in the rate-determining step, $\phi < 0$; water acts as a nucleophile in the rate-limiting step, ϕ ranges from 0.22 to 0.56; and water

acts as a proton-transfer agent in the rate-limiting step, $\phi > 0.58$.

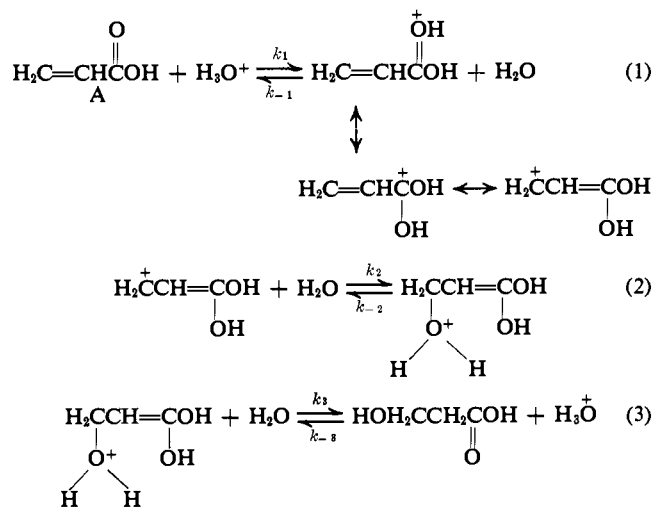
In the present case, the ϕ values as determined from the slopes of the plot of $(\log k + H_0)$ against $(H_0 + \log H^+)$ (Figure 5) were found to be +1.0 and +0.9 for the forward and the reverse reaction, respectively. This clearly indicates that the activated complex is highly solvated and water acts as a proton transfer agent in the rate-controlling step for both the reactions.

Mechanism

From studies of the effect of pressure on reaction rate, Whalley very recently has discussed the mechanism of the hydration of olefins.¹³ The volume and entropy of activation measured for these reactions were approximately $-10 \text{ cm}^3 \text{ mole}^{-1}$ and $-5 \text{ cal deg}^{-1} \text{ mole}^{-1}$, respectively. Though the hydration rates follow h_0 function and ΔS^* is much less negative, Whalley, from a consideration of the volume of activation alone, has strongly advocated an A2 mechanism for these reactions, thus rejecting the long-held unimolecular mechanism suggested by Taft. However, he could not provide a detailed mechanism for the reaction.

Compared to olefin hydration, the volume and the entropy of activation for the hydration of acrylic acid are highly negative and the acidity dependence of the rate shows that the hydration rate follows hydrogen ion concentration. The observed large negative values of ΔV^* and ΔS^* in the present case can be readily understood if at least one molecule of water is assumed to be bound in the transition state, the structure of which may be represented as $[\text{substrate} \cdot \text{H}^+ \cdot \text{H}_2\text{O}]^*$. Bunnett's modifications of the Zucker-Hammett theory and Bunnett's linear free energy relationship not only support this idea but also indicate that water acts as a proton-transfer agent in the rate-controlling step of the reaction. Keeping these ideas in view, several possible mechanisms for the acid-catalyzed hydration of acrylic acid and its reverse reaction have been discussed.

On the basis of Zucker-Hammett theory, Hine¹⁴ has discussed the mechanism of the acid-catalyzed hydration of crotonaldehyde. He has considered that the pre-equilibrium proton transfer on carbonyl oxygen is followed by slow nucleophilic attack of a water molecule



(10) J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960); **83**, 4956 (1961).

(11) (a) A. R. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 597 (1961);

(b) R. J. Withey and E. Whalley, *ibid.*, **41**, 546, 849 (1963).

(12) J. F. Bunnett and F. P. Olsen, *ibid.*, **44**, 1899, 1917 (1966).

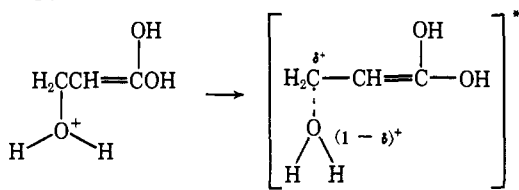
(13) E. Whalley, *ibid.*, **42**, 1019 (1964); **43**, 2453 (1965).

(14) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp 216.

which yields product after a rapid simultaneous proton transfer and uncatalyzed enol-keto transformation. A similar mechanism for the acid-catalyzed reversible hydration of acrylic acid is presented here for discussion. For the forward reaction, it yields a rate expression, $-\partial A/\partial t = k_1 k_2/k_{-1}(\text{H}_3\text{O}^+)(A)$, when k_3 and $k_{-1} \gg k_2$. The observed ΔV will be the sum of ΔV_1^0 and ΔV_2^* .⁶ The preequilibrium proton-transfer step neither involves a change in the number of molecules nor a change in the electronic charge. The volume change in such cases has been observed to be near zero and probably positive.⁶ A decrease in volume of about 12 cm³ mole⁻¹ is expected owing to the conversion of van der Waals forces to partial valence bonds when a water molecule approaches the protonated substrate during the formation of the activated complex. As a result a net negative value of ΔV^* may be realized.

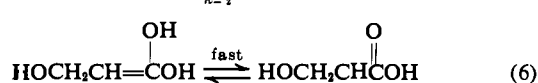
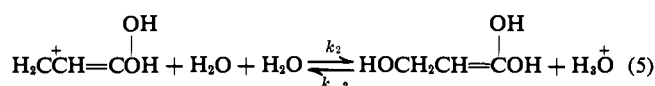
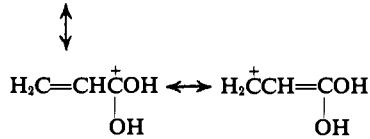
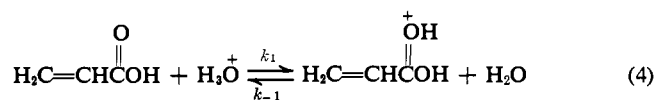
According to the principle of microscopic reversibility¹⁵ the dehydration should be the reverse of the mechanism for hydration. As a corollary, the rate-determining step must be the same for both the reactions.

For the reverse reaction, the volume of the hydroxy acid is little affected due to the protonation and the tautomeric transformation. The activated complex for the reverse reaction involves the stretching of C-O bond which will cause an increase in volume and an increase in entropy too.



So the above mechanism fails to explain the observed negative value of ΔV^* and ΔS^* for the reverse reaction. Moreover, the values of w , w^* , and ϕ indicate that water molecule acts as a proton-transfer agent rather than a nucleophilic agent in the rate-determining step. Hence the above mechanism based on Zucker-Hammett theory may be eliminated.

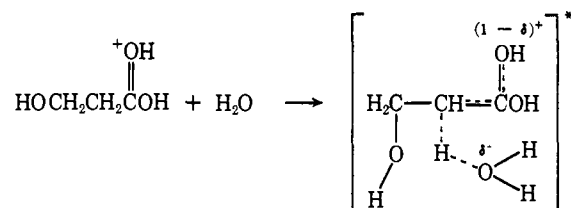
On the basis of Bunnett's linear free energy relationship we have suggested a mechanism which involves simultaneous nucleophilic attack and proton transfer (as in the case of N,N' -dimethylformamide¹⁶) by the water molecule, as the rate-determining step. The aspect of higher " w " and " ϕ " determine the over-all " w " and " ϕ " values.¹² The reaction scheme follows.



(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1953, pp 202.

(16) R. H. DeWolfe, *J. Am. Chem. Soc.*, **82**, 1585 (1960).

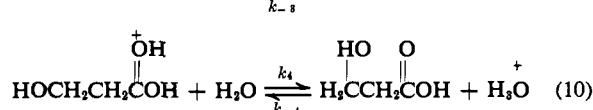
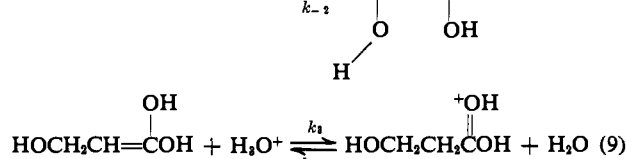
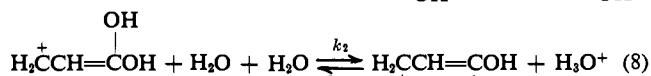
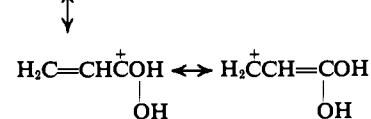
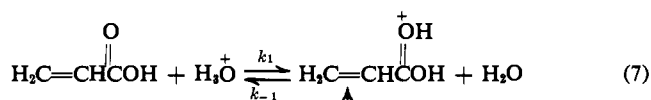
Here, again, ΔV^* for the forward reaction is a composite quantity being the sum of ΔV_1^0 and ΔV_2^* . The value of ΔV_1^0 has been discussed earlier. A large contraction may easily be visualized as two molecules of water are bound in the activated complex. The volume change due to the charge dispersion will be negligibly small compared to the structural contribution. The large negative value of ΔS^* may also be explained by the fact that partial immobilization of water molecules in



the activated complex causes lowering of entropy due to the loss of their translational and rotational degrees of freedom.

Considering the reverse reaction, the pressure has very little influence on the tautomeric transformation, as both the forms occupy almost the same volume in the absence of hydrogen bonds. In the slow proton transfer step, contraction may quite likely occur because of the approach of the hydronium ion. The ΔS^* will also assume a negative value because of the bound water molecule.

However Noyce and Reed,¹⁷ from studies of substituent effect on dehydration of a series of β -hydroxy β -phenyl ketones and acids, have suggested two alternate mechanisms for such reactions, one considering the catalytic enolization as the slow step and the other considering the carbonyl group to remain unaffected during the reaction, a mechanism very similar to olefin hydration.¹³ Bell¹⁸ has observed a general acid catalysis in the hydration of crotonaldehyde and mesityl oxide and has suggested that the catalytic enol-keto transformation is the slow step for these reactions. A similar mechanism for the hydration of acrylic acid with a slight modification follows.



In order to explain the observed volume change ΔV^* in the rate process in the forward direction, the rate

(17) D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5539 (1958).

(18) R. P. Bell, J. Preston, R. B. Whitney, *J. Chem. Soc.*, 1166 (1962).

equation may be used. Its final form may be represented as

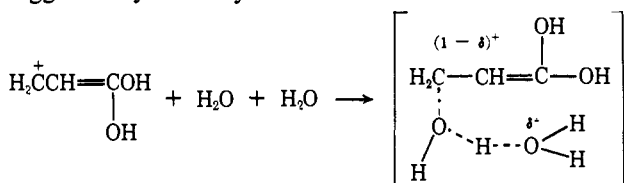
$$-\frac{\partial(A)}{\partial t} = k_3 K_1 K_2 (A) (H_3O^+)$$

when $k_3 \ll k_{-2}$ and k_4 . Here ΔV^* is a composite quantity and may be represented as¹⁹

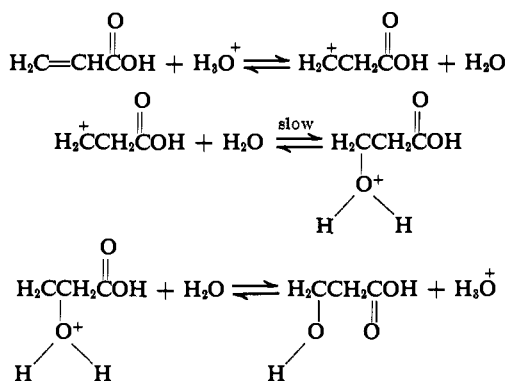
$$\Delta V_{\text{obsd}} = \Delta V_1^0 + \Delta V_2^0 + \Delta V_3^*$$

The contributions of ΔV_1^0 and ΔV_3^* are much less. A large contraction occurs in eq 8 owing to loss of a water molecule in the process. The sum of all these contributions results in a high negative value of ΔV^* for the forward reaction.

The estimation of ΔV^* for the reverse reaction is rather simple. A small but negative value of ΔV^* may be predicted since the above mechanism for the reverse reaction is very similar to that of the acid catalyzed enolization of ketones, the volume of activation of which has been recently determined to be -2 to -4 $\text{cm}^3 \text{mole}^{-1}$ by Whalley.²⁰ The structure of the activated complex in the present case resembling the one suggested by Whalley follows



Lastly, the following mechanism, originally suggested for the hydration of 4-(*p*-methoxyphenyl)-3-buten-2-one by Noyce and Reed,¹⁷ is presented here as to show how far it satisfies the experimental data. In this case



(19) D. W. Coillet and S. D. Hamann, *Trans. Faraday Soc.*, **57**, 2231 (1961).

(20) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1835 (1964).

the carboxyl group remains unaffected throughout the reaction.

By arguments similar to those discussed in the first mechanism, it may be shown that the above mechanism, although it explains the observed value of ΔV^* for the forward reaction, fails to do so for the reverse reaction. Moreover, it predicts a positive entropy of activation for the reverse reaction which is contrary to the observed finding.

Conclusion

On the basis of Bunnett's parameters (w and ϕ factors) and the volume as well as the entropy of activation several probable mechanisms for the acid-catalyzed hydration of acrylic acid and for its reverse reaction have been discussed. The observed negative values of ΔV^* and ΔS^* along with the high positive values of w and ϕ for the reverse reaction, eliminate mechanisms involving the nucleophilic attack of water molecule with the protonated substrate in the slow step. A mechanism involving the catalytic tautomeric change as the rate-controlling step which was originally suggested by Noyce and Reed and later supported by Bell explains the observed large negative values of ΔV^* and ΔS^* for the forward reaction and predicts a low negative value of ΔV^* for the reverse reaction. The mechanism proposed by us also satisfies the observed experimental findings for the forward reaction, but unfortunately, for the reverse reaction, no method is available to determine the extent of contraction, and thus no good estimate of the magnitude of ΔV^* could be made though a negative sign was evident. Further, the error involved in the determination of k_{-1} introduces an uncertainty of a few cubic centimeters per mole in the magnitude of ΔV^* for the reverse reaction which in no case alters the sign of the latter. Thus it is evident that the method of volume of activation definitely eliminates certain mechanisms in the present case, but because of these difficulties, fails to provide an unambiguous decision among the following possible mechanisms: (1) slow simultaneous nucleophilic attack and proton transfer followed by spontaneous tautomeric change, (2) slow simultaneous nucleophilic attack and proton transfer followed by acid-catalyzed tautomeric change, and (3) slow acid-catalyzed tautomeric change.

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