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Pressure Effects on the Reaction of Hydroxide Ion with Sodium 2-Bromoethanesulfonate

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Synopsis. Kinetic effect of pressure on the reaction of hydroxide ion with 2-bromoethanesulfonate was studied. The reaction was moderately accelerated by pressure and the activation volumes suggest that the presence of the negative charge on the sulfonato group does not produce any measurable solvation increase during activation.

Although kinetic effects of pressure have been studied for a variety of organic reactions,[1] little work has been done for reactions between anions or cations. This is rather surprising because activation volume is known to be sensitive to solvational changes, and the approach of two ionic species with the same sign is expected to produce an increase in solvation. For example, when we compare the following two reactions, we would expect more negative activation volume for the latter because of the concentration of the negative charges.

$$A + B^- \longrightarrow [A\cdots B^-]^* \longrightarrow P \qquad (1)$$

$$A^- + B^- \longrightarrow [A\cdots B^{2-}]^* \longrightarrow P \qquad (2)$$

In fact, this effect of charge concentration on volume change has been observed in the ionization equilibria of some dicarboxylic acids. According to Høiland,[2] and Delben and Crescenzi,[3] the second ionization is accompanied by much larger volume contraction than the first ionization when the two carboxyl groups are located in close spatial proximity to each other (Table 1). Therefore, it is an interesting question whether a similar effect of charge concentration on volume can be observed in kinetic processes.

In this communication, the kinetic effects of pressure on the following elimination reaction[4] is discussed.

TABLE 1. VOLUME CHANGES FOR THE FIRST AND SECOND IONIZATIONS OF SOME DICARBOXYLIC ACID[a,b)]

Compound	$\Delta \bar{V}_1^\circ$/mL mol^{-1}	$\Delta \bar{V}_2^\circ$/mL mol^{-1}
Oxalic acid	−6.72	−11.91
Malonic acid	−10.06	−18.55
Succinic acid	−12.86	−13.58
Glutaric acid	−13.17	−13.59
cis-1,2-Cyclohexane-dicarboxylic acid	−12.1	−22.9

a) From Refs. 2 and 3. b) At 25 °C in water.

$$BrCH_2CH_2SO_3^- + OH^- \longrightarrow CH_2{=}CHSO_3^- + Br^- + H_2O \qquad (3)$$

The second-order rate constants of the reaction at various pressures are given in Table 2 and illustrated in Fig. 1. It is clearly seen in Fig. 1 that the application of pressure causes a moderate increase in the rate constant, and the plot of ln k against pressure is linear in the pressure range studied. The activation volumes of the reaction estimated from the slopes of the plots are given in the last column of Table 2. When we consider the volume change accompanying the approach of an ion toward a neutral substrate, two factors should be taken into account, *i.e.*, volume decrease caused by the partial bond formation between the two species, and volume increase caused by charge delocalization from the attacking ion to the substrate. These factors counterbalance each other, and as a result, moderately negative activation volumes are observed. A case in point is the base-catalyzed hydrolysis of alkyl acetates. The activation volumes for the reaction are in the range of −5.6—7.6 mL mol^{-1}.[5,6)] On the other hand, if the substrate is electrically charged as in the present case, a stronger solute-solvent interaction in the transition state is con-

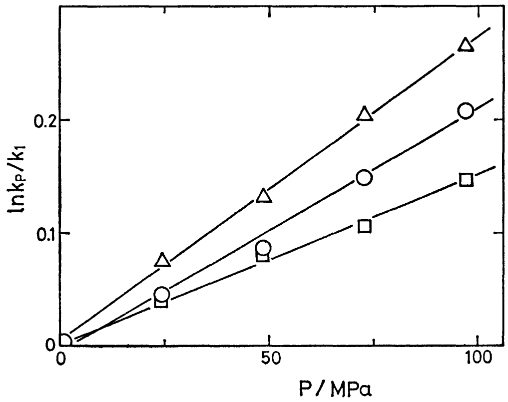

Fig. 1. Pressure dependence of the second-order rate constant for the reaction of hydroxide ion with 2-bromoethanesulfonate.
△: In H_2O at 10 °C, ○: in H_2O at 25 °C, □: in 60 wt% MeOH at 25 °C.

TABLE 2. SECOND-ORDER RATE CONSTANTS AND ACTIVATION VOLUMES FOR THE REACTION OF HYDROXIDE ION WITH 2-BROMOETHANESULFONATE ION

Solvent	T/°C	$k\times10^4$/M^{-1} s^{-1}					ΔV^*
		Pressure × 10^{-5}/Pa					mL mol^{-1}
		1	245	490	736	981	
H_2O	10	2.22	2.39	2.53	2.72	2.89	−6.3
H_2O	25	11.3	11.8	12.3	13.1	13.9	−5.3
60 wt% MeOH	25	4.32	4.49	4.68	4.80	5.00	−3.6

ceivable and it might result in much larger negative activation volume. However, the activation volumes in water for the present reaction are in the same range as the saponifications, suggesting strongly the absence of solvation reinforcement by the presence of the negative charge on the sulfonato group. The results in aqueous methanol support this argument. If the solvation increase occurs in the activation step, more negative activation volume could be expected in less polar solvents. The experiment shows, however, it is not the case. The value is slightly less negative in aqueous methanol.

The comparison of the present results with the ionization of dicarboxylic acids reveals an interesting point. Since the hydroxide ion attacks a hydrogen atom on the α-carbon which bears the sulfonato group, the distance between the two charge centers in the transition state may be comparable to the one in malonate ion if the delocalization of the negative charge from the hydroxide ion to the substrate is not extensive. Such a transition state formation is expected to be accompanied by solvation increase as in the second ionization of malonic acid, but the activation volumes reported here are not in accordance with this expectation as discussed above. Therefore, it can be safely stated that the extensive negative charge delocalization is realized in the transition state and, probably, the hydration sheath around the sulfonato group remains intact while desolvation occurs around the hydroxide ion.

The present results also indicate that care must be taken when we use reaction volume values in the estimation of activation volumes.

Experimental

Sodium 2-bromoethanesulfonate was prepared as described.[7] The total consumption of hydroxide ion agreed with the theoretical value.

The reactions under pressure were performed by means of a high pressure vessel shown in Fig. 2. The reaction mixture, c, contained in a 50 mL glass syringe was withdrawn through the stainless steel capillary tubing, b, by opening the sampling valve, a, while the pressure of the system was kept constant by sending in pressurizing fluid, hexane. The decrease of the hydroxide ion was followed by titration after quenching the mixture by an excess amount of hydrochloric acid.

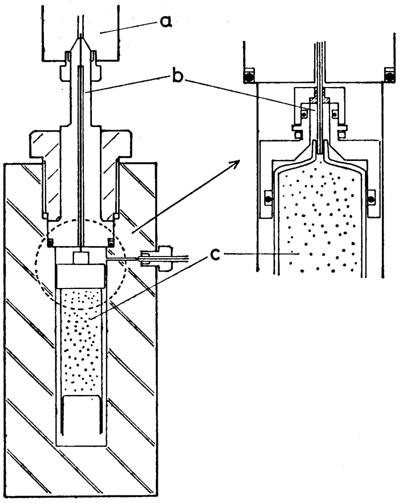

Fig. 2. High pressure reaction vessel with a sampling device.
a: Sampling valve, b: stainless steel capillary tubing, c: reaction mixture.

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