

The Solvolysis of Benzoyl Chloride in Water-Acetone Mixtures Under High Pressure

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By using a complete rate constant(k_c) which treats a solvent (water) as a reactant, and a conventional rate constant(k), which ignores the solvent in describing the rate, the parameters ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger were introduced. These quantities represent the volume change, the enthalpy change, and the entropy change accompanying the electrostriction which occurs when solvent molecules condense on the activated complex. The authors measured the rates of the solvolysis of benzoyl chloride in water-acetone mixtures at 15° to 30°C and 1 bar to 2500 bars. Applying the authors' theory to the experimental results, the parameters, ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger were evaluated, and it was found that they are all negative, indicating that water dipoles condense on the activated complex. They also proposed the following equations: $\Delta H_s^\ddagger = \Delta H_s^\ddagger + \Delta H_s^\ddagger$ and $\Delta S_s^\ddagger = \Delta S_s^\ddagger + \Delta S_s^\ddagger$, where ΔH_s^\ddagger and ΔS_s^\ddagger are the activation enthalpy change and the activation entropy change for the conventional reaction rate, respectively, and ΔH_s^\ddagger and ΔS_s^\ddagger are the corresponding quantities for the complete reaction rate. The authors proposed that for the SN_1 type, all the quantities, ΔH_s^\ddagger , ΔS_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger are comparatively large, and for the SN_2 type, these quantities are smaller than for the SN_1 type, and occasionally the case $\Delta S_s^\ddagger < 0$ occurs. Using these criteria, the authors concluded that at high temperature, high pressure and for a high water content solvent, the SN_1 type mechanism predominates whereas in the reversed case the SN_2 type predominates.

Introduction

Owing to the the advancement of high pressure chemistry during the last two decades, the electrochemistry for aqueous inorganic salt solutions has highly developed, this is partly due to the fact that the complete equilibrium constant(K^*), which includes solvent(H_2O) as a reactant, was exactly defined.¹⁻³ The conventional equilibrium constant(K), which does not include the solvent as a reactant, cannot describe the electrostriction effect between dissociated ions and solvent molecules, whereas K^* especially has the merit to treat this effect⁴⁻⁶.

Marshall et al have obtained various thermodynamic parameters derived from K^* in their papers^{2,3,6-8}. They found experimentally that the conventional molar volume change(ΔV) is proportional to the compressibility of the solvent, and have obtained a hydration number change(k , n in our paper) and complete thermodynamic parameters(ΔH_s , ΔS_s). They also introduced the complete rate constant⁹ (r_c , k_c in our paper). But they failed to define electrostriction parameters which have very important meaning in kinetics.

Therefore, in the present paper, the electrostriction parameters(ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger) are defined from the relation between the conventional rate constant(k) and the complete rate constant(k_c), which could be called the exact rate constant, thus the subscript, e is used in this paper. Using these definition for electrostriction parameters a theory of reaction kinetics for solvolysis was developed, and it was applied to the solvolysis of benzoyl chloride in water-acetone mixture solvent.

In this paper, we report our experimental results obtained by measuring the rates of the solvolysis under high pressure. From the rate constants k_c and k , obtained by experiment, the

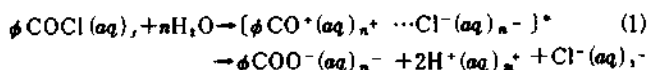
parameters ΔV_s^\ddagger , ΔH_s^\ddagger , and ΔS_s^\ddagger were evaluated by analysis. It was found that the new parameters ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger have all negative values indicating that water dipoles condense into the activated complex.

The variation of conventional thermodynamic parameters (ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger) with pressure, temperature and water content could be interpreted more concretely by using the change of ΔV_s^\ddagger , ΔH_s^\ddagger and ΔS_s^\ddagger with these variables. From the evaluation of all parameters entering in our theory, we were able to predict the degree of the critical bond elongation and the charge separation in the activated complex.

Many papers were reported for the solvolysis of benzoyl chloride, but the mechanism have not been clearly determined¹⁰⁻¹¹. In this paper, we shall consider the mechanism from our viewpoint, and decide to which of the SN_1 and SN_2 types the reaction of benzoyl chloride belongs from our criteria which were newly formulated.

Theory

The mechanism of the solvolysis of benzoyl chloride is considered to be as follows:



where the following relations hold:

$$j + n = n^+ + n^- \quad (2a)$$

$$n^+ + n^- < m^- + 2m^+ + 1^- \quad (2b)$$

The rate of Eq.(1) is expressed by

$$\text{Rate} = k_c [\text{H}_2\text{O}]^n (\phi\text{COCl}(aq)_j) \quad (3)$$

$$=k_c [\phi \text{COCl} (aq)], \quad (4)$$

where

$$k_c = k_e [\text{H}_2\text{O}]^n \quad (5)$$

In the above, k_c is so-called the conventional rate constant⁶; and k_e is called "the complete rate constant", after Marshall's nomenclature. One notes that in Eq.(4) the solvent H_2O is ignored in the rate expression according to the conventional method. From Eq.(5), one obtains

$$\ln k_c = \ln k_e + n \ln [\text{H}_2\text{O}] \quad (6)$$

Thus the plot of $\ln k_c$ vs. $\ln [\text{H}_2\text{O}]$ at various pressures yields a straight line, the slope of which is n , while the intercept gives $\ln k_e$. In our experiment, k_e and $[\text{H}_2\text{O}]$ in Eq.(6) are functions of pressure, thus n and k_e are not a function of pressure over the range studied in the present study.

From Eq.(6) one obtains the following equations:

$$\left(\frac{\partial \ln k_c}{\partial P}\right)_T - \left(\frac{\partial \ln k_e}{\partial P}\right)_T - n \left(\frac{\partial \ln [\text{H}_2\text{O}]}{\partial P}\right)_T = -n\beta \quad (7a)$$

and

$$\left(\frac{\partial \ln k_c}{\partial P}\right)_T = -n\beta \quad (7b)$$

where

$$\beta = \left(\frac{\partial \ln [\text{H}_2\text{O}]}{\partial P}\right)_T \quad (8)$$

and it is the compressibility of water. By multiplying both sides of Eq.(7a) by $-RT$, the following equation results:

$$\Delta V_c^\ddagger - \Delta V_e^\ddagger = -nRT\beta \quad (9a)$$

where

$$\Delta V_i^\ddagger = -RT \left(\frac{\partial \ln k_i}{\partial P}\right)_T \quad (i=c \text{ or } e, k_i = \text{rate const.}) \quad (9b)$$

In the above, ΔV_c^\ddagger is the conventional activation volume change, and ΔV_e^\ddagger is the complete activation volume change. We define $\Delta V_i^\ddagger = \Delta V_c^\ddagger - \Delta V_e^\ddagger$ which is called here the electrostriction volume change in the activated complex. Since in our experiment $\Delta V_i^\ddagger \approx 0$ because of the independency of k_e on P , one obtains from Eq.(9):

$$\Delta V_c^\ddagger \approx \Delta V_e^\ddagger = -nRT\beta \quad (10)$$

The following equation is also derived from Eq.(6):

$$\begin{aligned} \left(\frac{\partial \ln k_c}{\partial T}\right)_P - \left(\frac{\partial \ln k_e}{\partial T}\right)_P &= n \left(\frac{\partial \ln [\text{H}_2\text{O}]}{\partial T}\right)_P + \left(\frac{\partial n}{\partial T}\right)_P \ln [\text{H}_2\text{O}] \\ &= -n\alpha + \left(\frac{\partial n}{\partial T}\right)_P \ln [\text{H}_2\text{O}] \end{aligned} \quad (11)$$

where

$$\alpha = - \left(\frac{\partial \ln [\text{H}_2\text{O}]}{\partial T}\right)_P \quad (12)$$

and it is the thermal expansion coefficient of water. By multiplying both sides of Eq.(11) by RT^2 , we obtain the following equation:

$$\Delta H_c^\ddagger - \Delta H_e^\ddagger = RT^2 \left(-n\alpha + \left(\frac{\partial n}{\partial T}\right)_P \ln [\text{H}_2\text{O}]\right) \quad (13)$$

where ΔH_c^\ddagger and ΔH_e^\ddagger are the conventional activation enthalpy

change, and the complete activation enthalpy change, respectively.

We define $\Delta H_i^\ddagger = \Delta H_c^\ddagger - \Delta H_e^\ddagger$ which is called here the electrostriction enthalpy change in the activated complex. Thus Eq.(13) is expressed as

$$\Delta H_i^\ddagger = RT^2 \left(-n\alpha + \left(\frac{\partial n}{\partial T}\right)_P \ln [\text{H}_2\text{O}]\right) \quad (14)$$

The reason why ΔH_i^\ddagger is called as such is considered in the following. As the definition $\Delta H_i^\ddagger \equiv \Delta H_c^\ddagger - \Delta H_e^\ddagger$ shows, this quantity related to the difference of ΔH_c^\ddagger from k_e for Eq.(4) and ΔH_e^\ddagger from k_e for Eq.(3), i.e., it is due to n molecules of water participated in the formation of activated complex [see Eq.(1)], where the water dipoles are attracted to the activated complex in which a partial charge separation occurred. This fact is also substantiated by Eq.(14), since its right hand side includes only the quantities related to the n molecules of water. One may also note that during the condensation of n molecules of water, the redistribution of j water molecules occurs in the activated complex as one sees from eq.(2a). The quantity of $\Delta V_i^\ddagger \equiv \Delta V_c^\ddagger - \Delta V_e^\ddagger$ which was mentioned previously is similarly understood as in the case of ΔH_i^\ddagger .

We consider next, the activation entropy change. Since

$$\Delta G_i^\ddagger = -RT \ln \frac{h k_i}{kT} \quad (i=c \text{ or } e, k_i = \text{rate const.})$$

and since $\Delta S_i^\ddagger = -[\partial(\Delta G_i^\ddagger)/\partial T]_P$, we obtain

$$\Delta S_i^\ddagger = RT \left(\frac{\partial \ln k_i}{\partial T}\right)_P + R \left(\ln \frac{h k_i}{kT} - 1\right) \quad (15a)$$

and

$$\Delta S_c^\ddagger - \Delta S_e^\ddagger = RT \left[\left(\frac{\partial \ln k_c}{\partial T}\right)_P - \left(\frac{\partial \ln k_e}{\partial T}\right)_P\right] + R \ln \left(\frac{k_c}{k_e}\right) \quad (15b)$$

In Eq.(15b), ΔS_c^\ddagger and ΔS_e^\ddagger are the conventional activation entropy change and the complete activation entropy change, respectively.

Let us define $\Delta S_i^\ddagger = \Delta S_c^\ddagger - \Delta S_e^\ddagger$. By substituting Eqs. (6) and (11) to (15b), one obtain

$$\Delta S_i^\ddagger = RT \left(-n\alpha + \left(\frac{\partial n}{\partial T}\right)_P \ln [\text{H}_2\text{O}]\right) + nR \ln [\text{H}_2\text{O}] \quad (16)$$

The quantity ΔS_i^\ddagger is called here the electrostriction entropy change in the activated complex, i.e., it is the entropy change due to the condensation of n water molecules.

Experimental

A. Materials. Acetone was purified by drying over calcium chloride followed by fractional distillation, and benzoyl chloride was purified by vacuum distillation.

B. Conductance Bridge and Conductance Cell. The conductance bridge is composed of B.N. 532 capacitor, B.N. 332 resistor and B.N. 12 12/2 detector made by Rohde Schwarz Co., Germany. The conductance cell (Figure 1) is composed of two parts, a glass tube stopper of about 4 cm and a glass tube holder of electrolyte solution of 8 cm long, both being 1 cm in diameter. Two Pt circular plate electrodes are sealed to the holder as shown in Figure 1. The upper stopper of the cell was filled with a few grams of mercury to keep the sample from escaping out of the holder in the case when the latter is pushed upward while the cell is set in the pressure reservoir vessel.

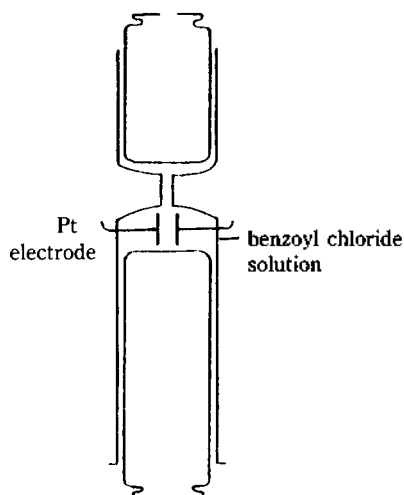


Figure 1. Schematic drawing of the electroconductance cell.

The cell was made by using two glass hypodermic syringes and by modifying them. The pressure measurement system was described elsewhere.¹²

C. Density Measurement of Water-Acetone Mixture Solvents. The piezometer originally due to Aime¹³ is used as the density measurement cell. The sample bottle is made of hard glass, about 10 cm³. The upper stopper of the cell prevents the oil, which is used as the transmittance medium of pressure, from infiltrating into the bottle. A small mercury reservoir is attached to the bottle. An inlet projector is attached to the bottom of the bottle. The increase of pressure makes mercury drop into the interior of the bottle through the projector. Before measuring the density of solvent mixtures, the exact volume of the sample bottle, V_{bottle} , was determined under pressure and at several temperatures with necessary corrections. The density of water-acetone mixture at a given pressure and temperature is determined by the following procedure: (1) the sample bottle is filled with the water-acetone

mixture, the mercury volume V_{Hg} entered into the bottle, when the latter is under pressure, was evaluated with corrections of the compressibility and expansion coefficient¹⁴ of mercury, (2) the solvent-mixture weight W_{mix} was measured at a given temperature, and then (3) the density of the mixture ρ_{mix} is calculated by $\rho_{\text{mix}} = W_{\text{mix}}/(V_{\text{bottle}} - V_{\text{Hg}})$.

The mole concentration of water [H_2O] in the mixture solvent, which is important in the later calculation, is obtained from the following equation:

$$[\text{H}_2\text{O}] = \frac{1000 \rho_{\text{mix}}}{18.016} \chi_{\text{H}_2\text{O}} \quad (17)$$

where, $\chi_{\text{H}_2\text{O}}$ is the mole fraction of water in the water-acetone mixture.

D. Kinetic Measurement. The conductance cell (Figure 1) is also used as a reaction vessel. The conductance cell is suspended in a high pressure vessel¹² with electrode leads, the vessel being set in a thermostat.

The rates of the solvolysis are determined by measuring the conductance of the solution since the conductance increases with time because of the production of O^-COO , H^+ and Cl^- ions as shown in Eq.(1). All kinetic runs were carried out under pseudo first order conditions¹⁵. The Guggenheim plots¹⁶ were used in this experiment since the conductance at infinite time was not determined. All the conductance measurements in this experiment were conducted from 1 to 2500 bars and from 15° to 30°C.

Result

A. Densities of Water-Acetone Mixtures. Table 1 shows the density data of water-acetone mixtures measured at various pressures and temperatures. In Table 1, they are also included the mole concentrations of water, [H_2O], in the mixtures which were calculated by using Eq.(17).

B. Conventional and Complete Rate Constants. The conventional rate constant k_c , Eq.(4) observed for the solvolysis

Table 1. Densities (g/cm³) and mole Concentrations (mole/l) of Water in Water-acetone Mixtures*

| P (bars) | | 1 | 500 | 1000 | 1500 | 2000 | 2500 |
|-----------------------|----|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| wt%(H ₂ O) | | | | | | | |
| 15°C | 5 | 0.8147 (6.5594) | 0.8667 (6.7981) | 0.9085 (7.3147) | 0.9428 (7.5908) | 0.9721 (7.8267) | 1.0012 (8.0610) |
| | 10 | 0.8329 (12.1921) | 0.8816 (12.9049) | 0.9223 (13.5007) | 0.9552 (13.9823) | 0.9846 (14.4127) | 1.0135 (14.8357) |
| 20°C | 5 | 0.8097 (6.5192) | 0.8621 (6.9411) | 0.9048 (7.2849) | 0.9397 (7.5654) | 0.9693 (7.8042) | 0.9985 (8.3093) |
| | 10 | 0.8285 (12.1276) | 0.8781 (12.8536) | 0.9192 (13.4553) | 0.9523 (13.9398) | 0.9824 (14.3801) | 1.0117 (14.8093) |
| 25°C | 5 | 0.8048 (6.4797) | 0.8575 (6.9040) | 0.9011 (7.2551) | 0.9366 (7.5409) | 0.9666 (7.7824) | 0.9959 (8.1083) |
| | 10 | 0.8241 (12.0632) | 0.8747 (12.8039) | 0.9161 (13.4099) | 0.9496 (13.9003) | 0.9803 (14.3497) | 1.0100 (14.7845) |
| 30°C | 5 | 0.7999 (6.4403) | 0.8530 (6.8678) | 0.8975 (7.2261) | 0.9336 (7.5167) | 0.9639 (7.7607) | 0.9923 (7.9974) |
| | 10 | 0.8198 (12.0003) | 0.8713 (12.7542) | 0.9131 (13.3660) | 0.9471 (13.8623) | 0.9782 (14.3190) | 1.0084 (14.7610) |

*In this table, the parenthesized data are the mole concentrations of water whereas the unparenthesized data indicate the densities of water-acetone mixture solvent.

Table 2. Conventional rate Constants (k_c), Complete rate Constants (k_c) and Hydration Number Change (n) of the Solvolysis of Benzoyl Chloride in Water-acetone Mixtures

| | | $k_c \times 10^{10a}$ sec ⁻¹ (l/mole) ^b | $k_c \times 10^4$ (sec ⁻¹) | | | | | |
|------|----|--|--|--------|--------|--------|--------|--------|
| | | | 1 | 500 | 1000 | 1500 | 2000 | 2500 |
| | | | (bar) | (bars) | (bars) | (bars) | (bars) | (bars) |
| 15°C | 5 | 5.78 (6.33) | 0.84 | 1.28 | 1.76 | 2.19 | 2.65 | 3.07 |
| | 10 | 0.07 (6.79) | 1.82 | 2.51 | 3.39 | 4.59 | 5.47 | 6.76 |
| 20°C | 5 | 17.35 (5.92) | 1.16 | 1.71 | 2.21 | 2.75 | 3.32 | 3.84 |
| | 10 | 0.32 (6.35) | 2.39 | 3.47 | 4.59 | 5.92 | 7.41 | 8.48 |
| 25°C | 5 | 41.64 (5.59) | 1.42 | 2.08 | 2.67 | 3.30 | 4.00 | 4.75 |
| | 10 | 0.98 (6.02) | 3.18 | 4.56 | 6.05 | 7.38 | 9.75 | 10.35 |
| 30°C | 5 | 78.80 (5.37) | 1.74 | 2.45 | 3.21 | 4.01 | 4.77 | 5.53 |
| | 10 | 3.11 (5.70) | 4.34 | 6.37 | 8.41 | 10.16 | 11.91 | 13.68 |

^aThe parenthesized data are the hydration number changes (n).

of benzoyl chloride in water-acetone mixtures are shown in Table 2. The larger the weight percentage of water, the larger are the rate constants. The value of k_c increases with temperature and pressure.

The values of $\ln k_c$ from Table 2 are plotted against $\ln[\text{H}_2\text{O}]$ from Table 1 in Figure 2. The slopes of the straight lines give the values of n and are tabulated in Table 2. The intercepts give the values of the complete rate constant k_c , which are tabulated in Table 2. The quantities of k_c and n may change with pressures, but in the range of pressures studied in our experiment, they are about constant, and independent of pressures (see Figure 2). Marshall⁸ reported that the n value is independent of temperatures and pressures, this fact, however, is contradictory to our results, *i.e.*, in our case n is independent of pressures, but it decreases with increasing temperatures. Concerning to k_c , Marshall also noticed that it is independent of pressures in agreement with our result.

C. Compressibility and Thermal Expansion Coefficient.

The compressibility β of water at a given concentration and temperature is calculated from Eq.(8) by utilizing the $[\text{H}_2\text{O}]$ data in Table 1. [Note: The $\ln[\text{H}_2\text{O}]$ data were expressed in a power series, and β was obtained by differentiation in accordance with Eq.(8). Other differential quantities in this paper were also obtained by similar method.] The results are summarized in Table 3. The thermal expansion coefficient α is similarly calculated from Eq.(12) by using the $[\text{H}_2\text{O}]$ data of Table 1, and are also tabulated in Table 3. In Table 3, the square bracketed data of β were obtained from Eq.(7b), *i.e.*, from the rate data k_c . The agreement between the β values from the $[\text{H}_2\text{O}]$ and from the k_c values is very good. This shows that Eq.(5) is right.

D. Conventional Activation Volume Change. The con-

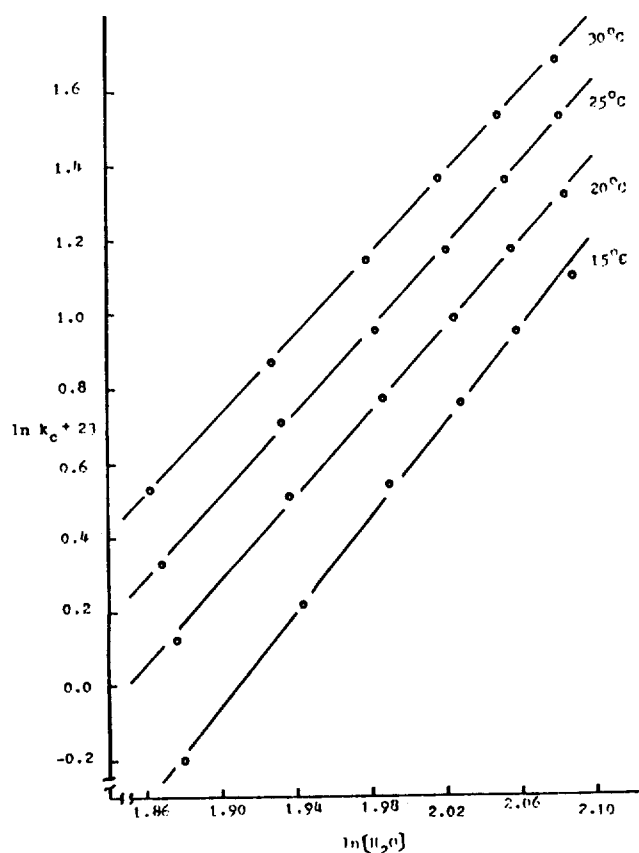


Figure 2. The plot of $\ln k_c$ vs. $\ln[\text{H}_2\text{O}]$ at 5 wt% of water. The temperature is indicated on each curve.

ventional activation volume change ΔV_c^\ddagger is calculated from Eq.(10) by using the n value in Table 4. From Table 4, we note that (1) all ΔV_c^\ddagger values are negative, (2) the value of $|\Delta V_c^\ddagger|$ decreases with increasing pressure and temperature, and (3) the value of $|\Delta V_c^\ddagger|$ increases with increasing wt% of water.

All the above experimental facts are consequence of Eq.(10). But it will be interesting to consider significant physical reasons embodied in each item. The ΔV_c^\ddagger is equal to $\Delta V_c^\ddagger - V_c$, where ΔV_c^\ddagger is the volume of the activated complex shown in the reaction mechanism Eq.(1), and V_c is the volume of reactants *i.e.*, $V_c = V[\text{COC}_6\text{H}_5(\text{aq})] + V(n \text{H}_2\text{O})$. The fact described in item (1) is natural since V_c should be larger than the volume of the hydrated activated complex. Next, we explain the fact of item (2). The value of $V[\text{COC}_6\text{H}_5(\text{aq})]$ does not change greatly with pressure and temperature, while $V(n \text{H}_2\text{O})$ decreases with pressure since $n \text{H}_2\text{O}$ is the free water acting as a reactant, and it decreases with increasing temperature because of the decrease of n with temperature (see Figure 2 and Table 2). Thus, V_c decreases with pressure and temperature. The ΔV_c^\ddagger value does not change with pressure and temperature, since the hydrated water strongly attached to the activated complex by dipole-dipole interactions. Consequently, $|\Delta V_c^\ddagger| (= |V_c^\ddagger - V_c|)$ decreases with increasing pressure and temperature since $V_c^\ddagger < V_c$, and, the latter decreases with P and T as mentioned above. The fact of item (3) is explained below. According to Table 2, the n value for 10 wt% water is larger than that for 5 wt%. Thus, $|\Delta V_c^\ddagger|$ becomes larger for 10 wt% water than for 5 wt% at a given temperature and pressure as expected from Eq.(10).

E. Activation Enthalpy and Activation Entropy. The

Table 3. Compressibilities ($\beta \times 10^4 \text{ bar}^{-1}$) and Thermal Expansion Coefficient ($\alpha \times 10^3 \text{ deg.}^{-1}$) of Water-acetone Mixtures^{a,b}

| P (bars) | | 1 | 500 | 1000 | 1500 | 2000 | 2500 |
|-----------------------|----|---|---|---|---|---|---|
| wt%(H ₂ O) | | | | | | | |
| 15°C | 5 | 1.4970 (1.2112) [1.3211] ^c | 1.0434 (1.0539) [1.1213] ^c | 0.9052 (0.8073) [0.9089] ^c | 0.7439 (0.6506) [0.6959] ^c | 0.5584 (0.5624) [0.4828] ^c | 0.3747 (0.5621) [0.2784] ^c |
| | 10 | 1.0870 (1.0486) | 0.9851 (0.7789) | 0.8574 (0.6651) | 0.7087 (0.5723) | 0.5457 (0.4334) | 0.3714 (0.3355) |
| 20°C | 5 | 1.1914 (1.2186) | 1.0752 (1.0595) | 0.9256 (0.8106) | 0.7507 (0.6528) | 0.5570 (0.5640) | 0.3798 (0.5275) |
| | 10 | 1.1052 (1.0541) | 1.0072 (0.7820) | 0.8731 (0.6673) | 0.7216 (0.5741) | 0.5557 (0.4343) | 0.3780 (0.3361) |
| 25°C | 5 | 1.2135 (1.2261) | 1.0952 (1.0652) | 0.9430 (0.8139) | 0.7642 (0.6549) | 0.5657 (0.5656) | 0.3830 (0.5289) |
| | 10 | 1.1358 (1.0592) | 1.0286 (0.7851) | 0.8919 (0.6696) | 0.7324 (0.5757) | 0.5577 (0.4353) | 0.3703 (0.3366) |
| 30°C | 5 | 1.2340 (1.2336) | 1.1123 (1.0781) | 0.9562 (0.8172) | 0.7718 (0.6570) | 0.5668 (0.5672) | 0.3868 (0.5303) |
| | 10 | 1.1440 (1.0653) | 1.0395 (0.7881) | 0.9046 (0.6718) | 0.7465 (0.5772) | 0.5601 (0.4362) | 0.3867 (0.3372) |

^aThe parenthesized data are the thermal expansion coefficients of water-acetone mixtures, and the unparenthesized data are the compressibilities. ^bThe β and α values of pure water at 15°C and one bar are; $\beta = 0.4678 \times 10 \text{ bar}^{-1}$ and $\alpha = 0.1507 \times 10^{-3} \text{ deg.}^{-1}$ (Handbook of Chemistry and Physics, 55th ed. CRC Press, Cleveland, Ohio, 1975, P. F-5). These values are smaller than our mixture values as expected. ^cThese compressibility data were calculated from Eq.(7b) i.e., from k_c . Similar calculations of β were conducted in other cases than at 15°C and 5 wt% water content. But the results are not shown in this table.

Table 4. Conventional Activation Volume Change (ΔV^\ddagger ; cm³/mole) for the Solvolysis of Benzoyl Chloride in Water-acetone Mixtures

| P (bars) | | 1 | 500 | 1000 | 1500 | 2000 | 2500 |
|-----------------------|----|--------|--------|--------|--------|-------|-------|
| wt%(H ₂ O) | | | | | | | |
| 15°C | 5 | -17.43 | -15.82 | -13.72 | -11.28 | -8.47 | -5.68 |
| | 10 | -18.15 | -16.45 | -14.31 | -11.83 | -9.11 | -6.20 |
| 20°C | 5 | -17.19 | -15.51 | -13.35 | -10.83 | -8.03 | -5.48 |
| | 10 | -17.70 | -15.96 | -13.51 | -11.17 | -8.60 | -5.85 |
| 25°C | 5 | -16.81 | -15.17 | -13.06 | -10.59 | -7.84 | -5.31 |
| | 10 | -16.95 | -15.35 | -13.31 | -10.93 | -8.32 | -5.52 |
| 30°C | 5 | -16.70 | -15.05 | -12.94 | -10.44 | -7.67 | -5.23 |
| | 10 | -16.83 | -15.13 | -12.99 | -10.72 | -8.04 | -5.55 |

conventional activation enthalpy change ΔH^\ddagger_c is obtained by a usual method, i.e., $\Delta H^\ddagger_c = RT^2 (\partial \ln k_c / \partial T)_P$, where k_c was experimentally obtained. The complete activation enthalpy change ΔH^\ddagger_s is similarly obtained by using k_s , which was also experimentally obtained [cf. Eq.(3)]. All the data of ΔH^\ddagger_c , ΔH^\ddagger_s and ΔH^\ddagger_e obtained from our experiment are summarized in Table 5.

The conventional and complete activation entropies are calculated by using Eq.(15a) from the k_c and k_s values in Table 2. The ΔS^\ddagger_c ($\equiv \Delta S^\ddagger_s - \Delta S^\ddagger_e$) is calculated from Eq.(15b). All the values of ΔS^\ddagger_c , ΔS^\ddagger_s and ΔS^\ddagger_e are summarized in Table 6.

Discussion

A. Model of the Activated Complex. At the outset, the physical meaning of the numbers, n^+ and n^- , should be clarified. As shown by Eq.(1), n^+ is the hydration number at the positive side of the activated complex whereas n^- is that at the negative

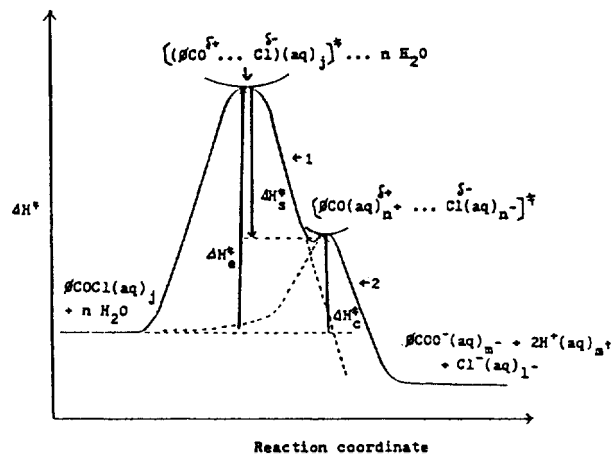


Figure 3. Diagram of ΔH^\ddagger vs. reaction coordinate. ΔH^\ddagger_c is the barrier height of the complete reaction (curve 1), ΔH^\ddagger_s is the electrostriction enthalpy in the activated complex, ΔH^\ddagger_e is the barrier height of the conventional reaction (curve 2). The upward direction of an arrow indicates a positive value whereas the downward arrow shows a negative value.

side. The sum, $(n^+ + n^-)$ is equal to $j + n$ [see Eq.(2a)].

Next, we consider the activated complexes corresponding to k_c and k_s . Since the two values are connected by Eq.(5), we obtain

$$\Delta G^\ddagger_c = \Delta G^\ddagger_s - nRT \ln(\text{H}_2\text{O}) \tag{18}$$

We have already obtained Eq.(13) which expresses the relation between ΔH^\ddagger_c and ΔH^\ddagger_s . Equations (13) and (18) suggest that the curve of ΔH^\ddagger vs. reaction coordinate is represented by Figure 3, i.e., curve 1 is for a complete reaction mech-

Table 5. Conventional Activation Enthalpy Change (ΔH^\ddagger), the Complete Activation Enthalpy Change (ΔH^\ddagger_c) and the Electrostriction Enthalpy Change in the Activated Complex ($\Delta H^\ddagger_e = \Delta H^\ddagger_c - \Delta H^\ddagger$) of the Solvolysis of Benzoyl Chloride in Water-acetone Mixtures

| | | ΔH^\ddagger (kcal/mole) | ΔH^\ddagger_c (kcal/mole)* | | | | | |
|------|-----------------------|---------------------------------|------------------------------------|-------------------|-------------------|-------------------|------------------|------------------|
| | | | 1 (bar) | 500 (bars) | 1000 (bars) | 1500 (bars) | 2000 (bars) | 2500 (bars) |
| 15°C | wt%(H ₂ O) | | | | | | | |
| | 5 | 28.26 | 8.46 (-19.80) | 7.38 (-20.88) | 6.24 (-22.02) | 5.89 (-22.37) | 5.49 (-22.77) | 5.48 (-22.78) |
| | 10 | 38.06 | 9.21 (-28.85) | 9.77 (-28.29) | 9.57 (-28.49) | 9.12 (-28.94) | 8.66 (-29.40) | 7.97 (-33.09) |
| 20°C | 5 | 29.25 | 8.76 (-20.49) | 7.63 (-21.62) | 6.46 (-22.79) | 6.10 (-23.15) | 5.69 (-23.56) | 5.67 (-23.58) |
| | 10 | 39.39 | 9.53 (-29.86) | 10.11 (-29.28) | 9.90 (-29.49) | 9.44 (-29.95) | 8.96 (-30.43) | 8.25 (-31.14) |
| 25°C | 5 | 30.26 | 9.06 (-21.20) | 7.90 (-22.36) | 6.68 (-23.58) | 6.31 (-23.95) | 5.88 (-24.38) | 5.86 (-24.40) |
| | 10 | 40.75 | 9.86 (-30.89) | 10.46 (-30.29) | 10.25 (-30.50) | 9.77 (-30.98) | 9.27 (-31.48) | 8.53 (-32.22) |
| 30°C | 5 | 31.28 | 9.37 (-21.91) | 8.16 (-23.12) | 6.90 (-24.38) | 6.52 (-24.76) | 6.08 (-25.20) | 6.06 (-25.22) |
| | 10 | 42.13 | 10.19 (-31.94) | 10.81 (-31.32) | 10.59 (-31.54) | 10.10 (-32.03) | 9.56 (-32.54) | 8.82 (-33.31) |

*The parenthesized data are ΔH^\ddagger_e values.

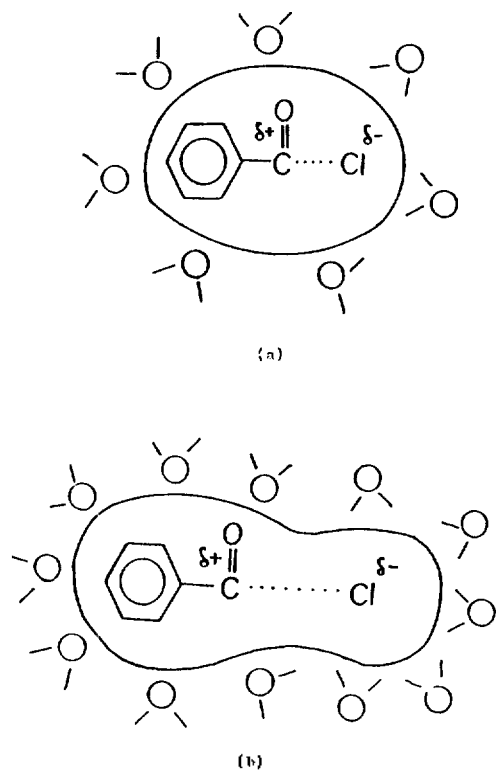


Figure 4. Models of activated complexes. Part (a) indicates an activated complex at 5% water content while (b) shows that at 10% water content. Note that the C - Cl bond elongated more at 10% water content than at 5% content, as a result, more charge separation occurred in the former (b) than in the latter case (a). Also one may note that more water dipoles are considered at 10% water content than at 5% content.

anisms, and curve 2 is a conventional reaction. It is assumed in Figure 3 that the critical bond (C-Cl) elongation in the activated complexes is about equal in the complete reaction and in the conventional reaction, the latter is hydrated [$\text{O}^-\text{C}(\text{O}^-\text{aq}) + \dots \text{Cl}^+(\text{aq})$], whereas the former is unhydrated i.e., [$\text{O}^-\text{C}(\text{O}^-\text{aq}) \dots \text{Cl}^+(\text{aq})$], where n H₂O molecules are attached loosely to the activated complex, but not hydrated as in the conventional activated complex. It is also assumed that the complete reaction is a two-step reaction, the first is a bond-elongation step, and the second is an electrostriction (hydration) step, the latter being very fast while the former is a rate determining step for the complete reaction. Thus ΔH^\ddagger_c ($\equiv \Delta H^\ddagger_e + \Delta H^\ddagger$), ΔS^\ddagger_c ($\equiv \Delta S^\ddagger_e + \Delta S^\ddagger$) and ΔV^\ddagger_c ($\equiv \Delta V^\ddagger_e + \Delta V^\ddagger$) are considered to be the quantities due to the electrostriction as previously mentioned.

Figure 4 shows schematically the activated complexes in 5 wt% and 10 wt% water. It is clear that in 10% solution, a greater charge separation and a more bond elongation occur, consequently, more condensation of water dipoles results than for 5% solution.

B. Variation of ΔH^\ddagger_c and ΔS^\ddagger_c with Temperature and Water Content. According to Table 5, ΔH^\ddagger_c with is independent of pressure, and increases with temperature and water content. As mentioned previously ΔH^\ddagger_c is required for forming the activated complex [$\text{O}^-\text{C}(\text{O}^-\text{aq}) \dots \text{Cl}^+(\text{aq})$], where the critical bond C - Cl is elongated, it seems that the bond elongation and the charge separation increases with increasing temperature and water content. Thus the above mentioned facts result.

The complete activation entropy change ΔS^\ddagger_c is a positive quantity (Table 6) except ΔS^\ddagger_c at 15°C and 5% water content, and it behaves in a similar way as ΔH^\ddagger_c , i.e., it increases with temperature and water content. The reason for these facts is similar to that for ΔH^\ddagger_c , i.e., the bond elongation and charge

Table 6. Conventional Activation Entropy Change (ΔS^\ddagger), the Complete Activation Entropy Change (ΔS_c^\ddagger) and the electrostriction Entropy Change in the Activated Complex ($\Delta S_e^\ddagger = \Delta S_c^\ddagger - \Delta S^\ddagger$) of the Solvolysis of Benzoyl Chloride in Water-acetone Mixtures

| | | ΔS_c^\ddagger (e.u.) | ΔS_e^\ddagger (e.u.) ^a | | | | | |
|------|-----------------------|------------------------------|---|--------------------|--------------------|--------------------|--------------------|--------------------|
| | | | 1 | 500 | 1000 | 1500 | 2000 | 2500 |
| | | | (bar) | (bars) | (bars) | (bars) | (bars) | (bars) |
| 15°C | wt%(H ₂ O) | | | | | | | |
| | 5 | -2.67 | -47.74 (-45.07) | -50.68 (-48.01) | -53.91 (-51.24) | -54.77 (-52.10) | -55.76 (-53.09) | -55.53 (-52.86) |
| | 10 | 22.59 | -43.63 (-66.22) | -41.04 (-63.63) | -41.13 (-63.72) | -42.08 (-64.67) | -43.33 (-65.92) | -45.31 (-67.90) |
| 20°C | 5 | 1.19 | -46.62 (-47.81) | -49.69 (-50.88) | -53.20 (-54.39) | -54.00 (-55.19) | -55.02 (-56.21) | -54.79 (-55.98) |
| | 10 | 27.87 | -42.57 (-70.44) | -39.84 (-67.71) | -39.99 (-67.86) | -41.05 (-68.92) | -42.24 (-70.11) | -44.42 (-72.29) |
| 25°C | 5 | 4.63 | -45.75 (-50.38) | -48.90 (-53.53) | -52.49 (-57.12) | -53.31 (-57.94) | -54.35 (-58.98) | -54.07 (-58.70) |
| | 10 | 32.37 | -41.48 (-73.85) | -38.75 (-71.12) | -38.89 (-71.26) | -40.10 (-72.47) | -42.21 (-74.58) | -43.58 (-75.95) |
| 30°C | 5 | 7.85 | -44.86 (-52.41) | -48.16 (-55.71) | -51.78 (-59.33) | -52.60 (-60.15) | -53.70 (-61.25) | -53.47 (-61.02) |
| | 10 | 36.91 | -40.34 (-77.25) | -37.53 (-74.44) | -37.70 (-74.61) | -38.95 (-75.86) | -40.32 (-77.23) | -42.57 (-79.48) |

^aThe parenthesized data are ΔS^\ddagger values.

separation in the formation of the activated complex increase with temperature and water content.

C. Variation of ΔH_c^\ddagger and ΔS_c^\ddagger with Pressure, Temperature and Water Content. According to Table 5 and 6, ΔH_c^\ddagger and ΔS_c^\ddagger are all negative, this is natural because ΔH_c^\ddagger and ΔS_c^\ddagger are the enthalpy and entropy changes due to the condensation of water dipoles on the activated complex. Also we note that $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ increases with increasing pressure, for 5% water content. This is explained by Eqs.(14) and (16), where $(\partial n / \partial T)_P$ is a negative quantity, and $[H_2O]$ increases with increasing pressure, thus $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ increase with P. In Tables 5 and 6, $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ for 10 wt% content show a minimum at 500 bars; then they increase regularly. At present, the reason for this phenomenon is not clear. We note, however, that $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ generally increase with P, this fact is physically understood in the following way: high pressure helps the condensation of water dipoles to the activated complex. Thus, $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ increase with pressure.

Equation (14) explains the variation of $|\Delta H_c^\ddagger|$ with temperature. On the r.h.s. of Eq.(14), the absolute value of the bracketed quantity decreases with temperature because of the factors n and $\ln[H_2O]$ in it. But, the decrease of the bracketed quantity is overpowered by the RT^2 outside the brackets. Thus $|\Delta H_c^\ddagger|$ increase with temperature.

The above fact is physically understood in the following way. Although the condensation of water dipoles decreases with temperature, the condensation at a high temperature accompanies $|\Delta H_c^\ddagger|$ which is larger than at a low temperature because the water dipoles have more kinetic energy than at a low temperature.

The value of $|\Delta H_c^\ddagger|$ increase with water content (Table 5). This is also clear from Eq.(14), where n increase with water content as we have already pointed out (see n values in Table 2 and Fig. 2). The increase of n values with water content

is caused in turn by longer extension of the critical bond and more charge separation in 10% water content than in 5% as we proposed (see Fig. 4).

The behavior of $|\Delta S_c^\ddagger|$ completely parallels that of $|\Delta H_c^\ddagger|$. Thus the behavior of $|\Delta S_c^\ddagger|$ is explained in a similar way with $|\Delta H_c^\ddagger|$.

Comparing Eq.(16) with (14), one notes that the first term on the right-hand-side of Eq.(16) is $\Delta H_c^\ddagger/T$ [see Eq.(14)] which is a negative quantity, and the second term is a positive term. But the latter term contribution is very small compared to that of the former term, thus ΔS_c^\ddagger becomes negative. From the similarity of the expressions of ΔH_c^\ddagger and ΔS_c^\ddagger [Eqs.(14) and (16)], one may understand the similar behaviors of the two quantities.

D. Variation of ΔH_c^\ddagger and ΔS_c^\ddagger with pressure, Temperature and Water Content. The quantities, ΔH_c^\ddagger and ΔS_c^\ddagger , are expressed by the following equations as previously mentioned:

$$\begin{aligned} \Delta H_c^\ddagger &= \Delta H_c^\ddagger + \Delta H_e^\ddagger \\ \Delta S_c^\ddagger &= \Delta S_c^\ddagger + \Delta S_e^\ddagger \end{aligned} \quad (19)$$

The variations of ΔH_c^\ddagger and ΔS_c^\ddagger with P, T and water content are explained by using Eq.(19) and by the following phenomenological relations: $\Delta H_c^\ddagger > |\Delta H_c^\ddagger|$ and $\Delta S_c^\ddagger < |\Delta S_c^\ddagger|$, where the behaviors of $|\Delta H_c^\ddagger|$ and $|\Delta S_c^\ddagger|$ were considered previously.

The quantity ΔH_c^\ddagger is independent of P. Since $\Delta H_c^\ddagger > |\Delta H_c^\ddagger|$, and since the latter increases with P, the ΔH_c^\ddagger decreases with pressure in agreement with experiment (Table 5). In Eq.(19), ΔS_c^\ddagger is independent of P, and is a positive quantity whereas ΔS_e^\ddagger and ΔS^\ddagger are negative. Since $\Delta S_c^\ddagger < |\Delta S_c^\ddagger|$, and since the latter increases with P, the ΔS_c^\ddagger increase with pressure, this also agrees with experiment (Table 6).

Concerning to the temperature effect on ΔH_c^\ddagger , both ΔH_c^\ddagger and $|\Delta H_c^\ddagger|$ increase with T, but the increase in ΔH_c^\ddagger overcomes that of $|\Delta H_c^\ddagger|$. Since $\Delta H_c^\ddagger > |\Delta H_c^\ddagger|$, the ΔH_c^\ddagger increase with temperature

(see Table 5). Next we consider the temperature effect on ΔS^\ddagger . In Eq.(19), both ΔS^\ddagger and $|\Delta S^\ddagger|$ increase with temperature (see Table 6). But the former increase overpowers the latter increase, and since $\Delta S^\ddagger < |\Delta S^\ddagger|$, the $|\Delta S^\ddagger|$ decreases with T.

The quantity ΔH^\ddagger increases with water content (Table 5). This fact is explained as follows. As previously explained, $|\Delta H^\ddagger|$ increases with water content, while ΔH^\ddagger also increases. But the latter increase overcomes the former. Thus, from Eq.(19) and the relation $\Delta H^\ddagger > |\Delta H^\ddagger|$, the quantity ΔH^\ddagger increases with water content. The decrease of ΔS^\ddagger with water content (Table 6) is similarly explained; in Eq.(19) both ΔS^\ddagger and $|\Delta S^\ddagger|$ increase with water content, but the former increase overcomes the latter increase keeping the relation $\Delta S^\ddagger < |\Delta S^\ddagger|$, as a result, $|\Delta S^\ddagger|$ decreases with water content.

E. Hydration Numbers and Rate Constants. We noted that $n = (n^+ + n^-) - j$ [see Eq.(2a)]. Previously it was mentioned that n is independent of pressure, but decreases with temperature. We also found that n is increases with water content. The hydration number j for the ground state molecule of $\text{O} \cdot \text{COCl}$ is considered to be constant independent of water content at a given pressure. Thus, the increase in n in high water content is due to the increase in $(n^+ + n^-)$ in agreement with our model (see Figure 4).

According to Table 2, the k_a value for 10% water content is larger than that for 5% water content by a factor of 25 to 83. This fact is explained below by taking an example. The ΔG^\ddagger for reaction (1) is expressed by $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. This equation is applied to the cases of 5% and 10% water contents at 15°C. The data of ΔH^\ddagger and ΔS^\ddagger are taken from Table 5 and Table 6, respectively. Thus the ratio of $k_a(5\%)/k_a(10\%)$, was calculated by the following equation:

$$k_a(5\%)/k_a(10\%) = \exp \{ (RT)^{-1} [-\Delta H^\ddagger(5\%) + \Delta H^\ddagger(10\%) + T(\Delta S^\ddagger(5\%) - \Delta S^\ddagger(10\%))] \} \quad (20)$$

The value calculated from Eq.(20) is equal to 81.75, and it is in a good agreement with experimental value of $5.78 \times 10^{-10} / 0.07 \times 10^{-10} = 82.57$ from Table 2.

Next, the ratio of $k_c(5\%)/k_c(10\%)$ is given by the following equation:

$$k_c(5\%)/k_c(10\%) = \exp \{ (RT)^{-1} [-(\Delta H^\ddagger)_{5\%} + (\Delta H^\ddagger)_{10\%} + T(\Delta S^\ddagger)_{5\%} - T(\Delta S^\ddagger)_{10\%}] \} \quad (21)$$

where, $\Delta G^\ddagger = (\Delta H^\ddagger) - T(\Delta S^\ddagger)$. From Tables 5 and 6, the corresponding data for ΔH^\ddagger and ΔS^\ddagger at one bar and 15°C are taken, and are introduced to Eq.(21), and the ratio is calculated to be 0.468; this value completely agrees with experimental value of $0.84 \times 10^{-4} / 1.82 \times 10^{-4} = 0.468$ from Table 2.

The ratio (k_c/k_e) at one bar, 15°C and 5% water content is calculated from the following equation:

$$(k_c/k_e)_{5\%} = \exp \{ (RT)^{-1} [-\Delta H^\ddagger + \Delta H^\ddagger + T(\Delta S^\ddagger - \Delta S^\ddagger)]_{5\%} \} \quad (22)$$

by using the value of $\Delta H^\ddagger (= \Delta H^\ddagger - \Delta H^\ddagger, \text{Table 5})$ and $\Delta S^\ddagger (= \Delta S^\ddagger - \Delta S^\ddagger, \text{Table 6})$, and it was found to be 1.47×10^5 , which is in a good agreement with experimental value, $8.40 \times 10^{-5} / 5.78 \times 10^{-10} = 1.45 \times 10^5$, from Table 2.

F. Constancy of k_a with Pressure. We have shown that k_a does not vary with pressure (see Fig. 2). Marshall also presented various cases in which k_a is nonvariable with respect to pressure. It was already mentioned that the constancy of k_a yields $\Delta V^\ddagger = 0$ at constant temperature [see Eq.(9b)]. We

consider the physical meaning of $\Delta V^\ddagger = 0$ below.

The quantity ΔV^\ddagger is represented by the following equation:

$$\Delta V^\ddagger = [V_o[MA(aq)] + \delta V^\ddagger(MA) - \delta V_o(aq) - \delta V(n \text{ H}_2\text{O})] - V_o[MA(aq)] \quad (23a)$$

In Eq.(23a), $MA(aq)$ represents $\text{O} \cdot \text{COCl}(Aq)$, $V_o[MA(aq)]$ is an intrinsic volume of $MA(aq)$, $\delta V^\ddagger(MA)$ is the volume change due to the critical bond extension of $M-A$, $-\delta V_o(aq)$ represents the volume contraction due to the redistribution of the hydrated water (aq), and $-\delta V(n \text{ H}_2\text{O})$ represents the volume contraction due to the loose attachment of $n \text{ H}_2\text{O}$ to the activated complex from the free state of water. From Eq.(23a),

$$\Delta V^\ddagger = \delta V^\ddagger(MA) - \delta V_o(aq) - \delta V(n \text{ H}_2\text{O}) = 0 \quad (23b)$$

i.e., the volume increase due to the critical bond extension, $\delta V^\ddagger(MA)$, equals the volume contraction due to $\delta V_o(aq)$, and $\delta V(n \text{ H}_2\text{O})$. Since $\Delta V^\ddagger = 0$, the following relations results:

$$\Delta G^\ddagger = \Delta A^\ddagger - \Delta H^\ddagger - T\Delta S^\ddagger \quad (23c)$$

and since ΔG^\ddagger is pressure independent, the pressure independency of ΔH^\ddagger and ΔS^\ddagger at constant temperature follows immediately from Eq.(23c) as experimentally found.

G. SN_1 or SN_2 . The criteria for deciding the SN_1 or SN_2 nature for a solvolysis, which are reported in the literature are summarized in the following.

(1) The first criterion comes from the activation parameters, *i.e.*, the SN_1 mechanism is predominant when ΔH^\ddagger value is large and $|\Delta S^\ddagger|$ value comparatively small, otherwise the SN_2 mechanism is dominant¹⁰.

(2) The second criterion uses the solvent effect; The SN_2 mechanism superior to the SN_1 mechanism when the m value of the Grunwald-Winstein plot¹⁷ is larger than 0.6 and when the m value is less than 0.5, the reverse is true.

(3) The third criterion depends on the number of water molecules(n) participating in the activated complex; The SN_1 mechanism is more influential than the SN_2 in the case when the n is large (*i.e.*, 6 or 7), if n is small (*i.e.*, 1 or 2) the reverse is the case¹⁸.

(4) The fourth criterion is based on the substituent effect to the reactant; The SN_1 mechanism is more favourable than the SN_2 when the Hammett plot¹⁹ is concave or convex, whereas the SN_2 is predominant if the plot yields a straight line.

In the above, each of the criteria has its own merit in deciding the SN_1 and SN_2 mechanisms. In the following, however, we propose our own criteria:

(1) If $|\Delta H^\ddagger|$, $|\Delta S^\ddagger|$, ΔH^\ddagger and ΔS^\ddagger are comparatively large the SN_1 type is predominant.

(2) If the above quantities are comparatively small especially when $\Delta S^\ddagger < 0$, then the SN_2 type is superior to the SN_1 type.

For deciding the largeness or smallness of the activation parameters, it is recommended to determine k_a and k_c at several water contents of a mixture solvent under pressure. Since the SN_1 mechanism appears generally at high water content, it is fairly easy to decide which mechanism is dominant.

From our criteria, the solvolysis of benzoyl chloride which we studied is mainly a SN_1 type reaction while the SN_2 mechanism appears to occur with the SN_1 type when the water content of the mixture solvent is small. This is evidenced by the appearance of the case of $\Delta S^\ddagger < 0$ at 15°C and 5 wt% water

content (see Table 6). Although we need more experimental data at various water content, in favor of our criteria, it can be said that our criteria are very simple and are trustworthy compared to the ones proposed so far.

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Effects of Hydration and Metal Ions on the Conformation of Daunomycin

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Daunomycin, an anthracycline antibiotic, has been found to inhibit virus multiplication and shows considerable activity against tumors. Its activity may be varied by conformational changes of daunomycin. The conformational changes are come from the pucker of D-ring and variation of environments. We have carried out conformational analyses by using empirical potential function. We found that when daunomycin is hydrated or bound to Mg²⁺ ion, the minimum conformer of each state is altered from α conformer to β conformer through the pathway having four local minima. Our calculated results are in good agreements with those of X-ray crystallography and biological experiments, in which metal ion inhibits the binding of daunomycin to DNA.

Introduction

The daunomycin is the anthracycline antibiotic with an amino sugar group. It is thought that the interference with DNA synthesis and function occurs via an intercalation of the anthracycline chromophore between base pairs in duplex DNA^{1,2}. Since small changes in the drug structure may lead to marked changes in the biological activity^{3,4}, the conformation study around the ether linkage connecting the chromophore and amino sugar is found to be very important⁵⁻⁷.

Several workers have studied the conformation of daunomycin according to potential energy calculations³⁻⁷ as well as the X-ray crystallography⁸⁻¹⁰. However, previous reports have shown conflicting results in comparing the conformation of minimum energy with those of the crystals^{5,6,11}. The conformation of daunomycin bound to DNA may be nearly identified with the crystal structure of daunomycin itself^{4,5,10}. However

NMR data in aqueous solution indicate that the conformation of daunomycin may differ from the preferred conformation found in the crystal form¹¹.

Several different conformations come from the pucker of cyclohexene ring (D-ring) within daunomycin. Prominent differences are that there is a hydrogen bond between C7 oxygen and C9 hydroxyl group (α conformer) or the amino sugar becomes oriented equatorially rather than axially (β form)^{4,5,11}.

The pucker of D-ring is occurred via the variation of environments around the daunomycin. That is, the internal hydrogen bond which may stabilize α conformer can be broken by water molecules in aqueous solution⁸.

The conformational analysis of daunomycin could be performed by examining relative dispositions of the sugar group, anthracycline chromophore, and functional groups bound to the phosphate backbone of DNA in various environments. Previous conformational analyses have centered on α , and β ,