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The Nature of a Bond between a Water Molecule and a Protonated Propylene in the Activated Complex for the Acid-catalyzed Hydration of Propylene

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The nature of a bond between a water molecule and a protonated propylene in the activated complex for the acid-catalyzed hydration of propylene was discussed. The number of water molecules contained in the activated complex, 1.3, was obtained by applying the acidity function, T_0, to the dependency of the log k_1 on the acid concentration for the hydration of various olefins. The general relationship between the electrostriction and the hydration number of various uni-valent cations was also discussed, and these ions were divided into two separate groups. In the first group, the hydration was caused by electrostatic interaction, while in the second group, the hydration was caused mainly by covalent bond formation. Since the representative point of the hydration of propylene was located near the first group, it was concluded that a molecule of water is held in the activated complex by electrostatic interaction. On the basis of these considerations, the present authors propose a hypothesis which is useful in characterizing the nature of a bond between a water molecule and a protonated substrate in an activated state: (a) If the log k_1 for a reaction increases linearly with $-H_0$, a water molecule (or molecules) is held in an activated complex by electrostatic interaction. (b) If the log k_1 for a reaction increases linearly with the log m_a, a water molecule is held in an activated complex by the formation of a covalent bond. k_1: the first order rate constant; H_0: Hammett's acidity function; m_a: acid concentration.

In an earlier paper[1], the following mechanisms of acid-catalyzed reactions in moderately concentrated acid solutions have been proposed:

$$\mathrm{S}\cdot h_5\mathrm{H_2O} + \mathrm{H^+}\cdot h_2\mathrm{H_2O} + (h_1-h_2-h_5)\mathrm{H_2O} \xrightleftharpoons{K_1} [\mathrm{SH^+}\cdot h_1\mathrm{H_2O}]^{\neq} \tag{1}$$

$$[\mathrm{SH^+}\cdot h_1\mathrm{H_2O}]^{\neq} \mathrel{-\!\!\!\Lambda\!\!\!\rightarrow} \text{Product} \tag{2}$$

where S is a substrate and where h_1, h_2, and h_5 are the hydration numbers of the activated complex, the proton, and the substrate respectively. The number of water molecules contained in an activated complex, h_1, can be calculated from the dependency of the log k_1 on the acid concentrations:

$$\log k_1 = C - T_0 \tag{3}$$

where k_1 and C are a rate constant and a constant respectively, and where T_0 is a new acidity function which varies with the hydration number, h_1, and with the acid concentrations. The respective acidity functions T_0, for various acid solutions are given by Eqs. (4)-(6): in hydrochloric acid solutions:

$$T_0 = 2.4(3.9-h_1+h_5)\log a_w - \log m_a \tag{4}$$

in nitric acid solutions:

$$T_0 = 2.3(3.9-h_1+h_5)\log a_w - \log m_a \tag{5}$$

in perchloric acid solutions:

$$T_0 = 2.3(3.9-h_1+h_5)\log a_w - \log m_a \tag{6}$$

where a_w is the activity of water and where m_a is the molality of acid. Usually, the hydration number of a substrate, h_5, is zero because, as was shown in the derivation process of T_0, the hydration number even of a water molecule, which has a larger affinity for water than hydrocarbons, is zero. These equations are derived in much the same manner as in the Glueckauf's calculation of the hydration numbers of ions in aqueous solutions,[2] therefore, the hydration number of an activated complex, h_1, as calculated by these equations, can be treated equally as the hydration numbers of various kinds of alkali metal ions as calculated by his method.

The present authors previously studied the pressure effect on the rate of the acid-catalyzed hydration of propylene and reported that the absolute values of the observed activation volume are approximately proportional to the value, $-\partial D/D^2\partial P$, derived from the Drude and Nernst equation; here D is a dielectric constant of water and p is a pressure.[3] From this result, it was concluded that the activation volume is caused by the contraction of water around a protonated propylene by electrostatic interaction; that is water molecules (or a water molecule) may be held in the activated complex by electrostatic interaction.

In this paper the above conclusion will be discussed in terms of the relationship between the hydration number and the electrostriction of various uni-valent cations.

Calculation and Discussion

Hydration Number of a Hammett Base. In order to examine the process of calculating the hydration number of an activated complex, h_1, first, the hydration numbers of a protonated Hammett base in various acid solutions were calculated.

The acidity function, T_0, for the protonation of a Hammett base is equal to the acidity function, H_0,[4] as defined by Eq. (7), because the value of $m_{\mathrm{AH}^+}/m_{\mathrm{A}}$ in Eq.(7) is equivalent to the first-order rate constant, k_1, in Eq.(3) and both the H_0 and T_0 functions are defined as being equal to $-\log m_a$ in a dilute acid solution[1]:

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[1] H. Takaya, N. Todo, and T. Hosoya, This Bulletin, **42**, 2748 (1969).

[2] E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

[3] H. Takaya, N. Todo, T. Hosoya, and T. Minegishi, This Bulletin, **44**, 1175 (1971).

[4] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

$$\log \frac{m_{\mathrm{AH}^+}}{m_{\mathrm{A}}} = C - H_0 \tag{7}$$

where A is a Hammett base and where AH^+ is a protonated Hammett base. By the substitution of the values in Table 1 into Eq.(5) and Eq.(6), the hydration number of a protonated Hammett base, h_1, can be calculated. The results obtained are 0.8 and 0.4 in nitric acid and in perchloric acid respectively, as is shown in the last column of Table 1. As for the value in hydrochloric acid, it was shown in an earlier paper that h_1 is 0.7.[1] It seems to be possible to decide that the hydration numbers do not vary with the kind of acid. The small disagreement among these values, which is caused probably by omitting a part of the salting-out effects in the course of the calculation of the T_0, may be interpreted on the assumption that the salting-out effects for a protonated Hammett base are almost completely canceled by those for the Hammett base. The fact that there was not so large a disagreement among the hydration numbers of a Hammett base in various acids suggests that the same procedure can be used in calculating the hydration numbers for other protonated activated complexes.

TABLE 1. HYDRATION NUMBER OF A HAMMETT BASE IN VARIOUS ACID SOLUTIONS

	Molality	$\log m_a$	H_0 or T_0	$\log a_w$	h_1
in HNO_3	3.0	0.477	−0.94	−0.065	0.8
in $HClO_4$	3.0	0.477	−1.07	−0.074	0.4

Numbers of Water Molecules Contained in the Activated Complexes for Hydration of Olefins. The dependency of $\log k_1$ on the acid concentrations for the hydration of propylene has not been observed. Therefore, the hydration numbers were calculated by using the results observed by Taft for the hydration of various olefins,[5] and the average value of these was used as the number of water molecules contained in the activated complex for the hydration of propylene. The $\log k_1$, which was represented by $\log k_c$ in Taft's paper, is represented by:

$$\log k_1 = -\rho' H_0 + C \tag{8}$$

where ρ' is a parameter to be determined by experiments. By comparing Eq.(8) with Eq.(3), it can be seen that $\rho' H_0$ must be T_0. In Table 2 the observed values of $-\rho' H_0$ (or $-T_0$) and also the hydration numbers of the various protonated olefins calculated by Eq.(5) are tabulated. From Table 2 it can be seen that the average hydration number is 1.3.

TABLE 2. THE OBSERVED $-\rho' H_0$ (OR $-T_0$) AND THE HYDRATION NUMBERS CALCULATED BY Eq. (5)

Substrate	HNO_3 Molarity	$-\rho' H_0$ or $-T_0$	Hydration number
Trimethylethylene	2.995[a]	0.88	1.7
Methylenecyclobutane	2.995[a]	1.00	1.0
Triptene	2.995[a]	0.89	1.6
Isobutene	2.525[b]	0.81	1.0

a) $\log m_a = 0.52$ and $\log a_w = -0.071$.
b) $\log m_a = 0.44$ and $\log a_w = -0.056$.

Relationship between the Conventional Electrostriction, $\Delta_c V_{\mathrm{el.}}$, and the Hydration Number, h_1, of Uni-valent Cations. The relationship between the conventional electrostriction, $\Delta_c V_{\mathrm{el.}}$, of various uni-valent alkali metal cations[6] and hydration number is shown in Fig. 1, where the value of $\Delta_c V_{\mathrm{el.}}$ is represented by setting the $\Delta_c V_{\mathrm{el.}}$ of H^+ as zero. The conventional electrostriction of a cation, $\Delta_c V_{\mathrm{el.}}$, is correlated with its electrostriction, $\Delta V_{\mathrm{el.}}$, as is shown by Eq. (9)[7]:

$$\Delta_c V_{\mathrm{el.}} = \Delta V_{\mathrm{el.}} - \Delta V_{\mathrm{el.H}^+} \tag{9}$$

where $\Delta V_{\mathrm{el.H}^+}$ is the electrostriction of the proton. From this figure, it can clearly be seen that the alkali metal ions are divided into the following separate two groups. In the first group, which consists of Rb^+, K^+ and Na^+, the values of $\Delta V_{\mathrm{el.}}$ can be represented by the value, $-Bz^2/r_s$,[8] derived from the Drude and Nernst equation. Here, r_s is the radius of an ion, which has a charge of z, and B is a constant. Since the Drude and Nernst equation was derived by using the theory of the electrostriction of a homogeneous dielectric around a charged sphere, it seems to suggest that the hydration of the ions in the first group is caused by electrostatic interaction. On the other hand, the $\Delta V_{\mathrm{el.}}$ of the second group, which consists of H^+ and Li^+, can not be given by the $-Bz^2/r_s$ value; moreover, the electrostriction of H^+ is small because of the large radius of the hydrated proton, the formula of which is accepted as $H^+ \cdot (H_2O)_4$.[2,8]

It may be generalized from the discussion above described that if the representative point for a reaction is located near the first group, the water molecules are held in an activated complex by electrostatic interaction and the number of water molecules may be 0, 1, or 2. On the other hand, if the representative point for a reaction is located near the second group, that is, if its hydration number is 3 and the activation volume is nearly zero, the structure of the activated complex may be similar to that of a hydrated proton, $H^+ (H_2O)_4$.

Consideration of an Activation Volume, $\Delta V^{\neq}$. It can be shown by the following treatment that the change in volume for the reaction of Eq. (1), $\Delta V^{\neq}$, as defined by Eq. (11), is equivalent to the electrostriction in Fig. 1, $\Delta_c V_{\mathrm{el.}}$:

$$\Delta V^{\neq} = \bar{V}_{\mathrm{act.}} - \bar{V}_{\mathrm{S}} - \bar{V}_{\mathrm{h.p.}} - (h_1 - h_2)\bar{V}_w \tag{11}$$

where $\bar{V}_{\mathrm{act.}}$, $\bar{V}_{\mathrm{S}}$, $\bar{V}_{\mathrm{h.p.}}$, and $\bar{V}_w$ are partial molar volumes of the activated complex, the substrate, the hydrated proton, and water respectively. Equation (11) can be re-written as Eq. (12) and Eq. (13):

$$\Delta V^{\neq} = (\bar{V}_{\mathrm{act.}} - \bar{V}_{\mathrm{S}} - h_1 \bar{V}_w) - (\bar{V}_{\mathrm{h.p.}} - h_2 \bar{V}_w) \tag{12}$$

$$= \Delta V_{\mathrm{act.}} - \Delta V_{\mathrm{H}^+} \tag{13}$$

where $\Delta V_{\mathrm{act.}}$ and ΔV_{H^+} are defined by Eq. (14) and Eq. (15) respectively:

$$\Delta V_{\mathrm{act.}} = \bar{V}_{\mathrm{act.}} - \bar{V}_{\mathrm{S}} - h_1 \bar{V}_w \tag{14}$$

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[5] R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *J. Amer. Chem. Soc.*, **77**, 1584 (1955).

[6] R. M. Noyes, *ibid.*, **86**, 971 (1964).

[7] The electrostriction of an ion is defined by Eq. (10) where the partial molar volume, $\bar{V}_0$, can be determined by experiments, however, the intrinsic ionic volume, V, can not be done by experiments but only deduced theoretically.

$$\Delta V_{\mathrm{el}} = \bar{V}_0 - V, \tag{10}$$

[8] P. Mukerjee, *J. Phys. Chem.*, **65**, 740 (1961).

$$\Delta V_{\mathrm{H}^+} = \bar{V}_{\mathrm{h.p.}} - h_2\bar{V}_w \tag{15}$$

Generally, the electrostriction of a proton, $\Delta V_{\mathrm{el.H}^+}$, is determined on the basis of the assumption that the intrinsic molar volume of H^+, V in Eq. (10),⁷⁾ is zero. However, if a proton is hydrated in water, the above assumption means that the intrinsic molar volume of $H^+\cdot h_2H_2O$ is equal to the volume of h_2H_2O, *i.e.*, h_2V_w. Therefore,

$$\Delta V_{\mathrm{H}^+} = \Delta V_{\mathrm{el.H}^+} \tag{16}$$

On the other hand, the electrostriction of an activated state, $\Delta V_{\mathrm{el.act.}}$, is given by Eq. (17):

$$\Delta V_{\mathrm{el.act.}} = \bar{V}_{\mathrm{act.}} - V_{\mathrm{SH}\cdot h_1\mathrm{H_2O}} \tag{17}$$

where $V_{\mathrm{SH}.h_1\mathrm{H_2O}}$ is the intrinsic molar volume of an activated complex, and where $SH\cdot h_1H_2O$ is a imaginary and non-cationic activated complex, one which is formed by the imaginary subtraction of an univalent charge from an activated complex, $[SH^+\cdot h_1H_2O]^{\neq}$. On the basis of the same assumption as was used in the case of H^+, the value of $V_{\mathrm{SH}.h_1\mathrm{H_2O}}$ can be determined by Eq. (18):

$$V_{\mathrm{SH}\cdot h_1\mathrm{H_2O}} = \bar{V}_{\mathrm{S}} + h_1\bar{V}_w \tag{18}$$

In this case, the substrate, S, corresponds to a water molecule in a hydrated proton, $H^+(H_2O)_4$. Therefore, from Eqs. (14), (17), and (18), we can obtain Eq. (19):

$$\Delta V_{\mathrm{act.}} = \Delta V_{\mathrm{el.act.}} \tag{19}$$

From Eqs. (13), (16), and (19), we can obtain Eq. (20):

$$\Delta V^{\neq} = \Delta V_{\mathrm{el.act.}} - \Delta V_{\mathrm{el.H}^+} \tag{20}$$

It is evident from a comparison of Eq. (20) and Eq. (9) that the $\Delta V^{\neq}$ is equivalent to $\Delta_c V_{\mathrm{el.}}$.

Application of the Relationship to Reactions. First, the relationship shown in Fig. 1 was applied to the classification of protonation of ammonia and enolization of acetone.

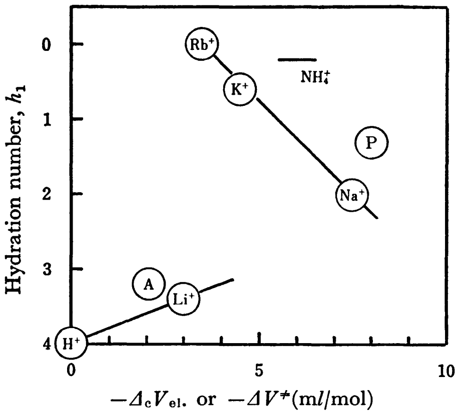

Fig. 1. Hydration number*¹ *versus* conventional electrostriction, $\Delta_c V_{\mathrm{el}}$, or activation volume, $\Delta V^{\neq}$, of uni-valent cations at 25°C.

Ⓟ: hydration of propylene ($\Delta V = -8$ml/mol Ref. 3, $h_1 = 1.3$)

Ⓐ: enolization of acetone ($\Delta V^{\neq} = -2.1$ ml/mol Ref. 11, $h_1 = 3.2$ Ref. 12)

*¹ The hydration number is obtained by calculating the entropy change; thus, the water molecules in hydration should be tightly bond with the ion.

The former reaction is represented by Eq. (21):⁹⁾

$$H_3{}^+O + NH_3 \rightleftarrows H_2O + NH_4{}^+ \tag{21}$$

For this reaction, $-\Delta V_{\mathrm{el.}}$ is 5.5—6.5 ml/mol⁹⁾ and the hydration number, h_1, is 0.2.²⁾ Since its position is located near the first group, the hydration may be caused by electrostatic interaction. The nature of the electrostriction of the ammonium ion is the same as those of alkali metal cations, since the hydration number of the ammonium ion can be correlated with Pauling's ionic radius in the same manner as in the case of the alkali metal cation.²⁾ In Fig. 1 the absolute value of the electrostriction of the ammonium ion deviates from that of the first group by 2 ml/mol. This may arise partly from the values of the electrostrictions of alkali metal cations used, since the $\Delta V_{\mathrm{el.}}$ is not a completely experimental value.⁷⁾

For the latter reaction there is general agreement that the slow step is the removal of a proton from the α-carbon of the protonated ketone by water acting as a base.¹⁰⁾ For this reaction, the $\Delta V^{\neq}$ is -2.1 ml/mol,¹¹⁾ and the h_1 is 3.2,¹²⁾ and the representative point is located near the second group; the probable structure of the activated complex is, then, similar to that of a hydrated proton, as is shown in Fig. 2. In this model the bond between the proton and the oxygen in the water molecule must be strong and covalent, since two hydrogen atoms of the water molecule must be cationic enough to attract two more water molecules.

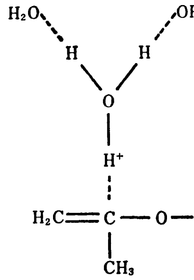

Fig. 2. Probable structure of the activated complex for enolization of acetone.

Consideration of the Activated Complex for the Hydration of Propylene. Since $\Delta V^{\neq}$ is -8 ml/mol¹³⁾ and h_1 is 1.3, the representative point of the hydration of propylene is located near the first group, as is shown in Fig. 1. As a consequence, it is a reasonable interpretation that the hydration of the activated complex is caused by electrostatic interaction and that the structure of the activated complex can not be similar to that of a hydrated proton.

Bunton¹⁴⁾ proposed two models for the activated state

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9) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959).

10) R. P. Bell, "Advances in Catalysis," Vol. IV, Academic Press Inc., New York (1952), pp.165—182.

11) E. Whalley, *Can. J. Chem.*, **42**, 1835 (1964).

12) The values of w^* from Bunnett's report for the reaction are 1.42 and 1.66 in hydrochloric acid. Hence 3.2 is obtained as h_1 by using Eq. (4). J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956 (1961).

13) At 25°C the $\Delta V^{\neq}$ is about -8 ml/mol from the Fig. 5 in an earlier paper,³⁾ since the value $-\partial D/D^2\partial p$ under S. T. P. is 0.8×10^{-6} cm²/kg.

14) C. A. Bunton and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **83**, 3207 (1961).

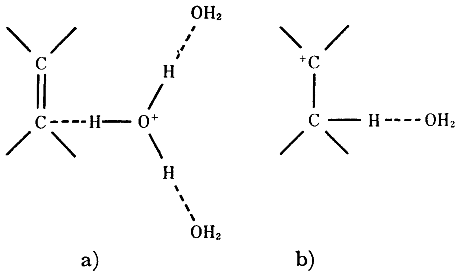

Fig. 3. Two models for the activated state of hydration of olefin proposed by Bunton (Ref. 14).
a) The activated state is similar to initial state.
In his paper a hydrated proton is represented by H_3O^+, however, in this paper it is done by $H(H_2O)_4{}^+$.
b) The activated state is akin to the carbonium ion.

of the hydration of various olefins; by the use of these models the observed isotope effect can be rationally explained: a) the activated state is similar to the initial state, and b) the activated state is akin to the carbonium ion, *i.e.*, the proton is bound to the reaction center (Fig. 3). In view of the hydration number, it is necessary to exclude the a) structure, since its hydration number, 3, is different from the value, 1.3, obtained in the present investigation. On the other hand, the b) model is in good agreement with the results of this study.

According to our results, the "free" carbonium ion model proposed by Taft[15] is plausible for the activated complex, and one molecule of water may be bound to the "free" carbonium ion by electrostatic interaction.

If the observed value of the activation volume[3], -8 m*l*/mol, is caused by the partially covalent bond formation between a protonated olefin and a water molecule, as was proposed by Baliga,[16] its bond must be strong and nearly equal to the covalent bond, since the value of 8 m*l*/mol corresponds to nearly half of the molar volume of water. The covalent bond may be formed by the transfer of an electron from the oxygen in a water molecule to the protonated olefin. Hence, the two hydrogen atoms of the water molecule become cationic and attract two more water molecules. This means that the number of the water molecules contained in the activated complex must be 3; this is inconsistent with the observed hydration number of 1.3.

New Hypothesis as to the Nature of a Bond between a Water Molecule and a Protonated Substrate in an Activated Complex. Zucker and Hammett have proposed a hypothesis which seemed useful in distinguishing the A-1 mechanism from the A-2 mechanism according to whether $\log k_1$ increases linearly with $\log c_{H^+}$ or with $-H_0$, where c_{H^+} is the concentration of the acid.[17] This hypothesis has, however, been sharply criticized by several authors[12,18] and has not been generally accepted.

The present authors hereby propose a hypothesis which is useful in characterizing the nature of a bond between a water molecule and a protonated substrate in an activated state: (a) If the $\log k_1$ for a reaction increases linearly with $-H_0$, a water molecule (or water molecules) is held in an activated complex by electrostatic interaction.

(b) If the $\log k_1$ for a reaction increases linearly with $\log m_a$, a water molecule is held in an activated complex by a covalent bond.

Strictly speaking, the water molecule held in an activated complex by a weakly and partially covalent bond can not be distinguished from that contained by electrostatic interaction. However, this does not seem significant, because, in the present state, a discussion of such a fine difference between the two cases seems meaningless.

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[15] R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5372 (1952).

[16] B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964); *ibid.*, **43**, 2453 (1965).

[17] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, **61**, 2791 (1939); F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[18] R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 306 (1958); R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y. (1959).