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S. G. ENTELIS, K. S. KAZANSKII, and N. M. CHIRKOV

THERMODYNAMICS OF THE PROTONATION OF ISOBUTYLENE

(Presented by Academician V. N. Kondrat' ev, January 19, 1960)

The question of the existence of aliphatic carbonium ions and the corresponding π-complexes has long been discussed in the literature. On the one hand, the numerous data obtained in the study of the kinetics of acid-catalyzed reactions persistently lead investigators to mechanisms involving aliphatic carbonium ions or π-complexes. On the other hand, the absence of facts concerning their direct detection and discouraging thermochemical calculations seem to prove the instability of these particles and the unfavorable nature of their formation, thereby casting doubt on the concept of carbonium ions in the interpretation of a number of reactions, for example transformations of olefins.

With regard to thermochemical calculations, it should be noted that the calculations available in the literature for the heat of the protonation reaction of olefins in aqueous solution

$$\textit{iso}\text{-}C_4H_8\ (aq) + H^{\oplus}\ (aq) = \textit{tert.}\text{-}C_4H_9^{\oplus}\ (aq) \qquad (1)$$

cannot provide the quantity of interest with the required accuracy. The data needed to carry out such calculations on the heats of solvation ΔH_s of carbonium ions are obtained approximately and are very unreliable (for *tert.*-$C_4H_9^{\oplus}$, $\Delta H_s = -40\text{–}69$ kcal/mole). Even such a fundamental quantity as the heat of solvation of the proton, according to data of different authors, is equal to -225, -257, -259, and -282 kcal/mole. It is therefore not surprising that the results of the calculations of Evans and Gal' pern (^{1}), who adopted $\Delta H_s(H^+) = -282$ kcal/mole, give for reaction (1) a heat $\Delta H_R = 26.1$ kcal/mole, whereas the same calculations carried out with the value $\Delta H_s(H^+) = -256$ kcal give $\Delta H_R = \pm 0$ kcal/mole.

The question of directly determining the equilibrium constant of the protonation reaction of olefins, its heat, and its entropy has become an important and fundamental problem, on the solution of which ideas concerning the nature and mechanism of acid catalysis depend.

Fig. 1. Absorption spectra of isobutylene in aqueous solution at various concentrations (in mol/l): 1—$2.2 \cdot 10^{-4}$; 2—$3.3 \cdot 10^{-4}$; 3—$5.7 \cdot 10^{-4}$; 4—$8.1 \cdot 10^{-4}$; 5—$1.27 \cdot 10^{-3}$

Figure 1: Fig. 1. Absorption spectra of isobutylene in aqueous solution at various concentrations (in mol/l): 1—$2.2 \cdot 10^{-4}$; 2—$3.3 \cdot 10^{-4}$; 3—$5.7 \cdot 10^{-4}$; 4—$8.1 \cdot 10^{-4}$; 5—$1.27 \cdot 10^{-3}$

Fig. 2. Extrapolation of kinetic curves for the consumption of isobutylene to $t = 0$

Figure 2: Fig. 2. Extrapolation of kinetic curves for the consumption of isobutylene to $t = 0$

We have attempted to solve this question by means of direct experiments. Isobutylene in the H_2SO_4—H_2O system was chosen as the object of investigation. In contrast to works described in the literature, in which the kinetics and thermodynamics of the absorption of isobutylene by acids were studied, in the present work a spectrophotometric method was used for direct observation of the transformation of *iso*-C_4H_8 in the liquid phase. The application of this method in the present case is possible owing to the absorption spectrum of unprotonated isobutylene that we found in aqueous solution (see Fig. 1). This absorption, lying near the transparency limit of quartz optics (210-220 mμ), is the slope of the *iso*-C_4H_8 peak with a maximum, according to literature data, at 185-190 mμ. We were unable to detect spectral manifestations of ionized particles ($BH^{\oplus}$), and their concentration was determined from the difference

$$C_{BH^{\oplus}} = C_0 - C_B^0, \tag{2}$$

where C_0 and C_B^0 are the total concentration of dissolved isobutylene and the concentration of its nonionized form, respectively.

With this method of calculation, we naturally cannot distinguish the π-complex from the carbonium ion and conventionally assume that all protonated isobutylene is present as tert.-$C_4H_9^+$.

In the system under study, the hydration reaction of isobutylene takes place with formation of tertiary butyl alcohol. To slow this reaction, which at ordinary temperatures is too fast to permit reliable extrapolation to zero time, we worked at reduced temperatures ($-15 \div -35°$). The value C_B^0, corresponding to equilibrium (1), was found by extrapolating the kinetic curves to $t = 0$ according to the monomolecular law (Fig. 2).

Fig. 1. Absorption spectra of isobutylene in aqueous solution at various concentrations (in mol/l): 1—$2.2 \cdot 10^{-4}$; 2—$3.3 \cdot 10^{-4}$; 3—$5.7 \cdot 10^{-4}$; 4—$8.1 \cdot 10^{-4}$; 5—$1.27 \cdot 10^{-3}$

Fig. 2. Extrapolation of kinetic curves for the consumption of isobutylene to $t = 0$

Experimental Part

Dissolution of gaseous isobutylene in sulfuric acid of the required concentration (25-50%) was carried out directly in a quartz all-welded cuvette connected to a glass apparatus by means of a ground joint and immersed in a thermostat at a temperature of -15, -25, or -35°. Mixing in the cuvette was accomplished by vigorous shaking with the aid of a special device*.

The total concentration of dissolved isobutylene C_0 was determined from the decrease in pressure in a known volume. After completion of absorption, which lasted 30-40 sec, the cuvette was transferred into the thermostated, at the same temperature, cuvette holder of an SF-4 spectrophotometer, where the change with time in optical density at 210 m (D_{210}) was recorded, occurring as a result of the decrease of C_{B} due to hydration (the time was counted from the moment saturation was stopped). By extrapolation in the coordinates $\lg D_{210}$—τ (Fig. 2), the value of the optical density corresponding to $C_{\mathrm{B}}^0 = D_{210}^0/\varepsilon l$ was found, where l is the cuvette length (1.5 cm), and ε is the molar absorption coefficient of the unprotonated form of isobutylene at the experimental temperature, expressed in l/mol • cm.

The absorption coefficients ε were found from the dependence of D_{210} on the concentration of isobutylene in aqueous solution; the concentrations were determined from the pressure above the solution by Henry' s law $C = hp$; the values of h were measured by us earlier ([2]). Beer' s law was obeyed over the entire investigated range of temperatures and concentrations. In view of the fact that measurement of the values of ε at negative temperatures is in principle impossible, the absorption coefficients were measured over a broad temperature interval (2—92.5°), and extrapolation to low temperatures was carried out according to the empirical formula

$$\frac{1}{\varepsilon} = a - bt, \tag{3}$$

which, as can be seen from Fig. 3, satisfactorily describes the dependence of ε on temperature ($a = 2.46 \cdot 10^{-3}$ mol $\cdot$ cm/l; $b = 2.38 \cdot 10^{-5}$ mol $\cdot$ cm/l $\cdot$ sec).

Fig. 3
Fig. 3. Dependence of the absorption coefficient of isobutylene in aqueous solution at λ 210 mμ on temperature

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* Without shaking, exchange between the liquid and gas phases is practically absent.

Fig. 4

Fig. 4. Dependence of $pK_{\text{iso-}C_4H_8}$ on reciprocal temperature

Knowing C_0, C_B^0 and, from equation (2), $C_{\text{BH}\oplus}$, one can find the value of pK by the known formula:

$$pK = H_0 - \lg\frac{C_\text{B}^0}{C_0 - C_\text{B}^0} = H_0 - \lg\frac{C_\text{B}^0}{C_{\text{BH}\oplus}}. \tag{4}$$

The values of the acidity function of H_2SO_4 solutions at the experimental temperatures were found by extrapolation from the data of A. I. Gelbshtein, G. G. Shcheglova, and M. I. Temkin (^{3}). The values of the basicity constants (pK) found by us are given in Table 1. The considerable error in determining the basicity constants and the observed small change in their magnitude with acidity are apparently associated with the large number of inevitable extrapolations in the calculations.

Table 1

t, °C	pK	$\pm\Delta$
−15	−1.89	0.10
−25	−2.05	0.15
−35	−2.21	0.16

In Fig. 4 is shown the dependence of pK on $1/T$, which gives the heat of protonation of iso-C_4H_8: $\Delta H_R = 4.3 \pm 4$ kcal/mol and the entropy of the reaction $\Delta S = +8.20$ e.u. (for the mean ΔH_R). The expression for the constant $K = h_0 C_\text{B}/C_{\text{BH}\oplus}$ is written as:

$$2.3R\,pK = -\frac{4300}{T} + 8.20. \tag{5}$$

Discussion of Results

The obtained values of pK indicate the presence of appreciable concentrations of protonated isobutylene at acid concentrations at which acid-catalytic transformations usually proceed. These concentrations are confirmed by calculations from kinetic data.

The heat of the protonation reaction of *iso*-C_4H_8 that was found, equal to $\Delta H_R = 4.3 \pm 4$ kcal, makes it possible to estimate the heat of solvation of the isobutylene carbonium ion, $\Delta H_s(R^\oplus)$.

The heat of the reaction of proton transfer from $H_3O^\oplus$ to *iso*-C_4H_8 in the gas phase

$$iso\text{-}C_4H_8 + H_3O^{\oplus} = \text{tert.-}C_4H_9^{\oplus} + H_2O \qquad (6)$$

is equal to the difference $(P_{itiso\text{-}C_4H_8} - P_{H2O})$, where P is the proton affinity of the corresponding molecule. If $P_{itiso\text{-}C_4H_8} = 198$ kcal/mol (4)*, and $P_{H2O} = 169$ kcal/mol (5), then reaction (6) is exothermic, with heat $\Delta H_R = -29$ kcal/mol. In order that, in the liquid phase, the heat of reaction (1), or, what is the same, of the reaction

$$iso\text{-}C_4H_8(aq) + H_3O^{\oplus}(aq) = \text{tert.-}C_4H_9^{\oplus}(aq) + H_2O_\ell \qquad (7)$$

be equal to 4.3 kcal/mol, the heats of solvation of the reactants on the right- and left-hand sides of equation (6) must differ by +33 kcal/mol:

$$\Delta H_s(\text{tert.-}C_4H_9^{\oplus}) + \Delta H_s(H_2O) - \Delta H_s(iso\text{-}C_4H_8) - \Delta H_s(H_3O^{\oplus}) = 33 \text{ kcal.} \quad (8)$$

Assuming that $\Delta H_s(H_2O) = -10.3$ kcal/mol (8); $\Delta H_s(iso\text{-}C_4H_8) = -4.6$ kcal/mol (2), and $\Delta H_s(H_3O^{\oplus}) = -102$ kcal/mol,** we obtain for the heat of hydration of the tert.-$C_4H_9{}^{\oplus}$ ion the value

$$\Delta H_s(\text{tert.-}C_4H_9^{\oplus}) = -64 \text{ kcal/mol } (\pm 4 \text{ kcal/mol}).$$

In an old paper Evans (6) takes as the most probable value for tert.-$C_4H_9{}^{\oplus}$ $\Delta H_s = -69$ kcal; according to Franklin (4) and V. N. Kondrat' ev and N. D. Sokolov (7), $\Delta H_s = -40$ kcal. Of the two cited values, preference should be given to the latter, more accurate one. The fact that the heat of solvation of the carbonium ion found by us exceeds by more than 20 kcal the value calculated by the authors (4,7) is natural, since the calculation by a formula relating ΔH_s to the ion radius takes into account only solvation due to purely electrostatic forces.

As V. N. Kondrat' ev and N. D. Sokolov correctly note, in these calculations nonelectrostatic interaction must also be taken into account, which evidently plays a considerable role. However, one cannot agree with these authors when, in calculating the affinity of $R^{\oplus}$ for the water molecule C_{H2O}, they assume that the carbonium ion in water exists only in the form of the oxonium ion $ROH_2^{\oplus}$. In reality, two types of interaction of the carbonium ion with water exist: solvation, which was discussed above, and the "strong," donor–acceptor interaction with one of the water molecules, with formation of an oxonium ion. These states are separated by a potential barrier.

Institute of Chemical Physics
Academy of Sciences of the USSR

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* The heat of formation of *iso*-C_4H_8 is equal to $\Delta H_f = -4.04$ kcal/mol (8).

** $-\Delta H_s(H_3O^{\oplus}) = \Delta H_f^0(H^{\oplus}\text{ gas}) + \Delta H_f^0(H_2O\text{ gas}) - P(H_2O) - \Delta H_f^0(H_3O^{\oplus}\text{ aq})$, according to the data of works (4) and (5).

Note: Figure translations are in progress. See original paper for figures.

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