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Abstract

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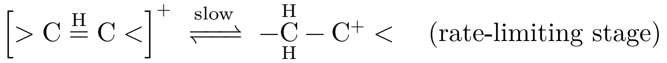
ON THE MECHANISM OF HYDRATION OF OLEFINS IN AQUEOUS SOLUTIONS OF STRONG ACIDS

The hydration of isobutylene (1), triptene, trimethylethylene, and methylenecyclobutane (2) in 1-5 M solutions of HNO_3 obeys a first-order equation. Between the observed reaction-rate constant k and the Hammett acidity function H_0 there is the relation

$$-\rho H_0 = \lg k + \mathrm{const}, \qquad (1)$$

where the coefficient $\rho \approx 1$ $(0.98 \div 1.11)$. The fulfillment of this equation served as the basis for the following mechanism (1) of olefin hydration:

$$> \mathrm{C} = \mathrm{C} < + \mathrm{H_3O^+} \xrightleftharpoons{\text{fast}} \left[> \mathrm{C} \overset{\mathrm{H}}{=} \mathrm{C} < \right]^+ + \mathrm{H_2O} \quad \text{(equilibrium)}$$



$$\left[> \mathrm{C} \overset{\mathrm{H}}{=} \mathrm{C} < \right]^+ \xrightleftharpoons{\text{slow}} -\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}} - \mathrm{C^+} < \quad \text{(rate-limiting stage)}$$

$$-\dot{\mathrm{C}} - \mathrm{C^+} < + 2\mathrm{H_2O} \rightleftharpoons \text{alcohol} + \mathrm{H_3O^+} \quad \text{(equilibrium)}$$

The heat effect of the first stage is composed of the heats of the following processes: a) desolvation of the proton –260 (3); b) addition of the proton to the olefin with formation of the π-complex Q_x; c) solvation of the formed π-complex Q_y; d) dissolution of the water molecule bound to the proton +10 kcal. To calculate Q_x within the framework of the LCAO MO method, it is necessary to know the value of the resonance integral γ of the bond between the C and H atoms in the π-complex.

The value of γ can be estimated by a procedure analogous to that used by Simonetta and Winstein (4). For this purpose let us consider the change in the overlap integral S as the proton approaches the π-electrons, which are described by pure p_z-functions.

Since the values of the p_z-function are maximal in the z direction, the values S' obtained for each C···H distance from tables (^{5}) were multiplied by $\cos\theta$ (θ is the angle between the z axis and the straight line joining the C and H atoms). The values $S = S'\cos\theta$ increase as the proton approaches, reach a maximum value of 0.36 at $R_{\mathrm{CH}} = 1.13$ Å, and decrease upon further decrease of R_{CH}, although the integral S' continues to increase. For an ordinary C–H bond $\gamma_1 \approx 45$ kcal at $S_1 = 0.69$ (^{6}). Using these values in the formula (^{6})

$$\gamma = \gamma_1[S/(1+S)] : [S_1/(1+S_1)],$$

we find at $S = 0.36$ the value $\gamma = 29.3$ kcal. At this value of γ, and at the value of the resonance integral of the π-bond $> \mathrm{C} = \mathrm{C} <$ equal to 20 kcal, the energy of two electrons in the field of the three nuclei amounts to 103 kcal. The energy gain upon addition of a proton to a double bond with formation of a π-complex is equal to $103 - 40 = 63$ kcal. This energy value is probably underestimated. An attempt to estimate the upper limit of this quantity within the MO method, taking into account the difference between the ionization potentials of the olefin and hydrogen, gives for isobutylene a value of ~ 145 kcal. The heat of solvation of the π-complex formed from isobutylene is probably close to the heat of solvation of the cation $\mathrm{N(CH_3)_4^+}$ (i.e., ~ 32 kcal $^{(3)}$), in which the positively charged atom is surrounded by hydrophobic $\mathrm{CH_3}$ groups.

Approximate calculations of this quantity by various methods $^{(7,8)}$ lead to values from 20 to 39 kcal. Thus, the heat effect of the first stage is: $-80-180+145+39+10 = -66$ kcal. To decide the question of the heat effect of the second stage it is necessary to know the heat of formation of the carbonium ion from isobutylene and a proton. Within the same approximation it can be shown that the complex of an olefin with a proton, in which the proton is shifted toward one of the carbon atoms of the bond $> \mathrm{C} = \mathrm{C} <$, is more favorable than the symmetrical π-complex, and transformation of the latter into the former is accompanied by a gain of more than 30 kcal. According to thermochemical data $^{(9-11)}$, the heat of addition of an unsolvated proton to gaseous isobutylene with formation of a carbonium ion is 194 ± 2 kcal*. Thus the carbonium ion proves to be more stable than the π-complex, and transformation of the former into the latter is accompanied by an expenditure of ~ 50 kcal. However, in order to satisfy relation (1) in Hammett' s interpretation $^{(12)}$, it is necessary to assume that the rate is limited not by the first stage, requiring an expenditure of 66 kcal, but by the second stage, which proceeds with evolution of heat. Obviously, such ideas cannot be regarded as substantiated. Even if one assumes that the activation energy of the first stage is equal to its heat effect, and takes into account that the activation energy of the slowest second stage must be at least somewhat greater than the activation energy of the first stage, it can be seen that the activation energy of the entire reaction as a whole is close to twice the heat effect of the first stage, i.e., -130 kcal, which is in contradiction with the experimental value $\Delta H^\ddagger = 13$-17 kcal $^{(26)}$ for gaseous olefins. Using the value 194 kcal for the heat of addition of a proton to gaseous isobutylene, it is easy to see that formation of solvated $(CH_3)_3C^+$ in solution from a gaseous olefin and an oxonium ion will require an expenditure of 17-20 kcal, which, within the accuracy of estimating this quantity, coincides with the experimental value of the activation energy of the reaction. Thus, in the case of isobutylene, the reaction can proceed through a carbonium ion. However, the absence of interconversion of 2-methylbutene-2 and 2-methylbutene-1 under conditions where dehydration does not occur excludes a mechanism involving a carbonium ion as an intermediate substance in equilibrium with the initial substances (13). At the same time, the closeness of the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for all these olefins and the presence of the same regularities in the kinetics (1,2) suggest that the hydration of these olefins and of isobutylene proceeds by one mechanism. The heats of formation of carbonium ions upon addition of a proton to a gaseous olefin, obtained from cyclic cycles, are: for $C_2H_5^+$, 149 kcal; $(CH_3)_2CH^+$, 179 kcal; $(CH_3)_3C^+$, 194 kcal. Thus, if the reaction proceeded through an activated complex—a carbonium ion—then the activation energies of isobutylene and propylene would differ by approximately 15 kcal, whereas the experimental difference in the heats of activation is 3.2 kcal (14). It also does not seem probable that $\Delta H^\ddagger$ for ethylene would be greater than the activation energy of isobutylene by 45 kcal. The decrease in the difference of the experimental values for olefins cannot be explained by the difference in the heats of solvation of the corresponding carbonium ions*. Let us also note that, in the case of propylene, between the value of the heat of formation of the carbonium ion in solution from the gaseous olefin and H_3O^+ and the experimental value of $\Delta H^\ddagger$ there is a discrepancy exceeding the error in determining the heat of formation of the carbonium ion, while in the case of ethylene a reaction through a carbonium ion is impossible. The more probable mechanism of this reaction in aqueous solutions, in our view, is a mechanism through the transition state shown in Scheme I. In the field of the six centers of the transition complex, six electrons move, which ensures a lowering of the activation energy; this is also promoted by the positive charge on the oxonium oxygen. We consider it essential that in one act the "stages" of transfer of a proton from H_3O^+ to the olefin molecule, formation of the alkoxonium ion, and regeneration of H_3O^+ are combined here. It is also possible that

Scheme I: transition complex

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in the transition complex H_3O^+, the olefin, and the H_2O molecule are arranged as an open chain, which leads to formation of an alkoxonium ion and water.

V. I. Tsvetkova (14) noted that the kinetic regularities observed in hydration in aqueous dioxane solutions (15) and in concentrated acid solutions (14) cannot

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* The heats of formation of carbonium ions from gaseous ethylene, propylene, isobutylene, and a proton were calculated from thermochemical data (9–11) for a cycle including hydrogenation of the olefin and dehydrogenation of the hydrocarbon thereby obtained through the stages of radical formation and ionization of this radical with formation of a carbonium ion.

be satisfactorily explained without taking into account that a water molecule is included in the transition complex. In addition, stepwise mechanisms require additional assumptions that are not consistent with the experimental data and theoretical arguments. Thus, for example, from Taft’ s mechanism (1) it follows that the equilibrium constant can be expressed through the ratio of the rate constants of the forward and reverse reactions only at equilibrium, which contradicts experiment (14). At the same time, according to Tsvetkova’s mechanism (14), the rate-limiting step is the reaction of the carbonium ion or π-complex with a water molecule, which is difficult to understand in light of the available data on the energetics of this reaction (8). In concentrated acid solutions, preliminary formation of a π-complex between the olefin and an acid molecule (and not a proton) is possible, a complex which in structure is close to an ion pair. In connection with the discussion of the reaction mechanism in aqueous acid solutions, we note that the values of H_0 over separate intervals or over wide concentration ranges may be satisfactorily represented, in addition to the expression $H_0 = -\lg(a_{\mathrm{H}^+} f_{\mathrm{B}} / f_{\mathrm{BH}^+})$, by other functional dependences (16–18). In this connection the interpretation of kinetic data sometimes becomes ambiguous, as was noted by A. I. Gelbshtein, G. G. Shcheglova, and M. I. Temkin (19) in the study of the decomposition of formic acid. S. G. Entelis (20) considers that dependence (1) may also be retained in the case when the reaction is limited by the stage of interaction of SH^+ with a neutral molecule (for example, the stage $\mathrm{SH}^+ + \mathrm{H_2O}$), provided that $a_{\mathrm{H_2O}} f_{\mathrm{SH}^+} / f_{\mathrm{M}^\ddagger} = \mathrm{const}$ ($f_{\mathrm{M}^\ddagger}$ is the activity coefficient of the transition state $\mathrm{M}^\ddagger$).

It can be shown that in this case dependence (1) will also be fulfilled under the condition $a_{\mathrm{H_2O}} f_{\mathrm{S}} / f_{\mathrm{M}_0^\ddagger} = \mathrm{const}$, or $\lg(a_{\mathrm{H_2O}} f_{\mathrm{S}} / f_{\mathrm{M}_0^\ddagger}) = \alpha + \beta H_0$ ($f_{\mathrm{M}_0^\ddagger}$ – the activity coefficient of the complex $M_0^\ddagger$, which differs from the activated complex $M_+^\ddagger$ only in that it does not contain a proton). It can similarly be shown that a reaction in whose activated complex two water molecules participate obeys the equation $k = k_0 h_0 f_S a^2_{\mathrm{H_2O}} / f_{M_0^\ddagger}$.

In this case $M_0^\ddagger$ corresponds to the stoichiometric composition $S \cdot 2\mathrm{H_2O}$. It is easy to see that the character of the kinetic dependence is preserved regardless of whether solvation precedes transfer of the proton to the complex of reacting molecules or, conversely, solvation follows protonation. Depending on the relation between the activity coefficients entering the equations for the reaction

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* According to Franklin’ s data (10), the difference in the heats of formation of gaseous sec-$\mathrm{C_3H_7^+}$ and tert-$\mathrm{C_4H_9^+}$ is 22 kcal, and in aqueous solution 16 kcal. According to the Kondrat’ ev-Sokolov formula (8), the difference in the heats of solvation of these ions is 4 kcal. Taking this figure into account, together with the heats of formation of gaseous ions adopted here, the difference in $\Delta H^\ddagger$ should be about 10 kcal in dilute aqueous solution and should increase, tending toward 15 kcal, as the acid concentration is increased.

rate constant, either equation (1) or

$$k_0' = k_0'[H_3O^+], \tag{2}$$

or, finally, intermediate dependences may hold.

On the basis of dependence (1) or (2), in the general case one can only assert that the transition complex contains a substrate molecule and a proton, but nothing can be said about the presence of other particles. Still less is it possible to determine with which of the constituent parts of the complex the proton is bound.

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