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An MO-theoretical Study on the Hydration of Simple Olefins

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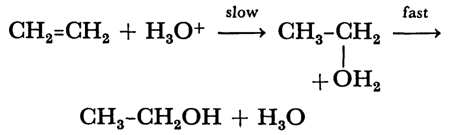
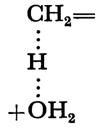
Synopsis. The acid-catalyzed hydration of simple olefins was studied on the basis of a semi-empirical SCF NDDO method. The substituent effect on the activation energy agreed well with experimental result.

Olefins can be hydrated by treatment with water and an acid catalyst. Though several mechanisms[1-3] have been proposed for the acid-catalyzed hydration of olefins, they may be written simply as:



$$CH_2{=}CH_2 + H_3O^+ \xrightarrow{\text{slow}} \underset{+OH_2}{\underset{|}{CH_3\text{-}CH_2}} \xrightarrow{\text{fast}}$$
$$CH_3\text{-}CH_2OH + H_3O$$

The rate-determining step, which is the first step, is slow proton transfer from H_3O^+ to the olefin, *via* I. This step is followed by the rapid addition of water.[1,2)]

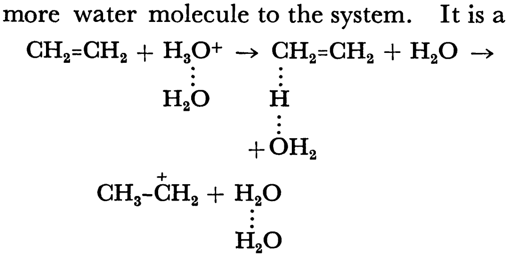


$$\begin{array}{c} CH_2{=}CH_2 \\ \vdots \\ H \\ \vdots \\ +OH_2 \end{array}$$

I

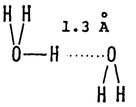
The hydration of simple olefins is a simple example of a catalytic reaction and a fundamental process for the preparation of alcohol from petroleum by-products. This note reports the results of an MO-theoretical study of this reaction mechanism and the substituent effect on the activation energy of the reaction. The MO method employed here is a semi-empirical NDDO method[4)] which gives well-balanced molecular geometries and reaction energies.

Though the solvent effect must be considered in this reaction, it is difficult to introduce it in a precise form since this effect has very complex aspects. Here the solvent effect was introduced simply by adding one more water molecule to the system. It is assumed that

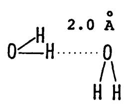


$$CH_2{=}CH_2 + \underset{H_2O}{\underset{\vdots}{H_3O^+}} \rightarrow \begin{array}{c} CH_2{=}CH_2 \\ \vdots \\ H \\ \vdots \\ +OH_2 \end{array} + H_2O \rightarrow$$
$$\overset{+}{CH_3\text{-}CH_2} + \underset{H_2O}{\underset{\vdots}{H_2O}}$$

the solvent water molecule, which bonds weakly to H_3O^+, leaves the H_3O^+ ion when a new bond is formed between the H_3O^+ and an olefin. The interaction energies for II and III, where each H···O distance was optimized, are 1.79 and 0.50 eV, respectively.



II



III

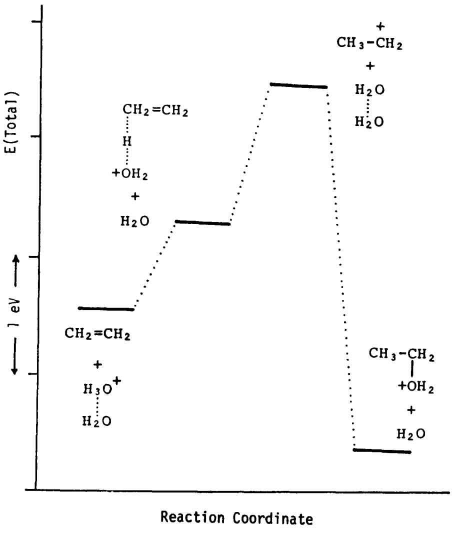
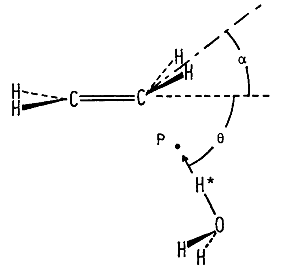


Fig. 1. Energy variation along the hydration of ethylene.

The energy diagram for this process is shown in Fig. 1. In Fig. 1, the energy of the carbonium ion, which is considered to be an intermediate of the process, is higher than that of I. In an actual water medium, the carbonium ion is stabilized by the solvent. This effect, however, is not considered in Fig. 1. The detailed calculation on the attack of H_3O^+ on ethylene from the direction shown in IV[5)] was performed to examine the most favorable path for the above process.



IV

The energy map of this process for $\theta = 45$ ° is shown in Fig. 2. It was found from Fig. 2 and from the calculated results that (1) H_3O^+ approaches the point P (the position of the H atom in the tetrahedral $-CH_3$ group) without any appreciable change in the H*–O bond length until the P–O distance becomes 1.5 Å, (2) the geometry of ethylene at P–O=1.5 Å is: C–C =1.30 Å, and $\alpha = 10$ °, (3) after the proton transfer from H_3O^+ to ethylene, H_2O leaves the carbonium ion, and (4) no appreciable change was observed in the energy maps for $45° < \theta < 90°$. In the calculation of the energy maps, the solvent effects of II and III

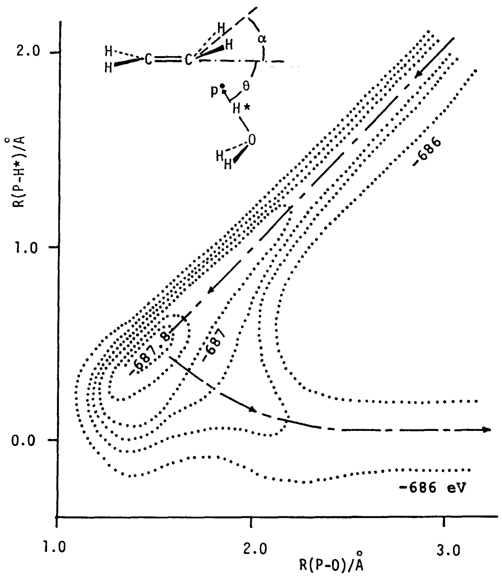


Fig. 2. Energy contours for the ethylene-H_3O^+ system. The C-C bond length and the angle α were optimized in the calculation.

were excluded. This is the reason why I is stable in Fig. 2.

The formation of the carbonium ion is followed by the rapid addition of water producing an oxonium ion (Fig. 1), and the carbonium ion does not correspond to the transition state. Nevertheless, it is expected that the transition state resembles the carbonium ion and I, and that the activation energy of the present process correlates with the difference between the energy of the carbonium ion and that of the initial state. The activation energies estimated under this assumption are listed in Table 1 as well as available experimental values.[1] The discrepancy between the calculated and experimetal activation energies is 20—30%. The activation energy for isobutene is very large, because the geometries of substituted carbonium ions were estimated from that of $CH_3\text{-}\overset{+}{C}H_2$ and this value reflects the overestimation of the steric interaction between the two CH_3 groups. The calculated values reproduce satisfactory the experimentally observed substituent effect on the activation energy. The Markownikoff rule is also reflected in the olefins listed in Table 1. The present authors thus feel that the present treatment correctly describes the reaction to some extent.

Table 1. Activation energies for the hydration of simple olefins

Olefins[a]	E_a (kcal/mol)	
	Calcd	Exptl[1]
$CH_2=\overset{*}{C}H_2$	44.5	32.4
$CH_2=\overset{*}{C}H\text{-}Me$	35.1	26.4
$Me\text{-}CH=\overset{*}{C}H_2$	63.4	—
$CH_2=\overset{*}{C}(Me)_2$	25.7	21.1
$(Me)_2C=\overset{*}{C}H_2$	169.8	—
$Me\text{-}CH=\overset{*}{C}H\text{-}Me$	48.4	—
$CH_2=\overset{*}{C}H\text{-}Et$	34.6	—
$Et\text{-}CH=\overset{*}{C}H_2$	45.0	—

a) The asterisk indicates the carbon atom which is attacked by the hydroxyl group.

References

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5) In a preliminary calculation, several interacting patterns for the H_3O^+-ethylene system were examined. The orientation of IV was the most favorable one.