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AN INVESTIGATION OF ACID CATALYSIS IN THE HYDRATION OF 2,3-DIMETHYL-2-BUTENE

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In the course of a comparative investigation of acid-catalyzed alkene hydrations,[1] we had occasion to investigate the susceptibility of the hydration of 2,3-dimethyl-2-butene to general acid catalysis. The reaction was followed spectrophotometrically at 201 mμ using a Beckman DU spectrophotometer. The alkene was maintained at very low concentration at all times to suppress reactions higher order in alkene (e.g., polymerization). This was conveniently accomplished by injection, via a glass syringe, of 2 cc. of 2,3-dimethyl-2-butene vapor into the buffer solution contained in the silica Beckman cell.[2]

The strong absorption at 201 mμ decreased in a first-order fashion to a value approximately 5% that of the initial absorbance. "Infinity" absorbances remained constant for several half-lives of reaction time. Buffer solutions were made so as to maintain $[NaHSO_4]/[Na_2SO_4] = 3.17$ and ionic strength was maintained constant at 3.04 using $NaClO_4$. Rate constants, k_{obs}, were measured in four buffer solutions covering the range 1.56 M to 0.626 M $NaHSO_4$ at 25°C. Although bisulfate ion concentration varied by 250%, $k_{obs} = 5.28 \pm .21 \times 10^{-4}$ sec^{-1}; i.e., the average deviation in k_{obs} is less than ± 4% which is within the experimental error. The data in Table I show that much of the slight variation of k_{obs} may be accounted for by slight changes in medium acidity, as measured by Ho.

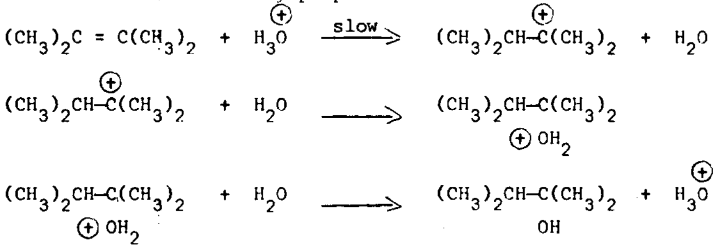
TABLE I

$[NaHSO_4]$	$-Ho^*$	$4 + \log k_{obs}$	$-Ho + 4 + \log k_{obs}$
1.56	0.03	0.73	0.76
1.25	-0.01	0.79	0.78
0.94	-0.03	0.81	0.78
0.626	-0.07	0.79	0.72

* 2-Nitroaniline was used as the Hammett indicator. See C. Perrin, J. Amer. Chem. Soc., 86, 256 (1964) for effects of ionic strength on Ho.

These data clearly demonstrate that hydration of 2,3-dimethyl-2-butene is not general acid catalyzed, in sharp contrast to hydration of styrenes.[3] The only previous indication that aliphatic alkenes are subject to specific acid catalysis was a study some twenty years ago that characterized electrolyte effects on the rate of hydration of isobutene.[4] In that study, the exact nature of specific acid catalysis was somewhat clouded by the fact that the pH was not held constant during the course of the search for general catalysis.

Absence of general catalysis in aliphatic alkene hydrations in aqueous acidic media is consistent with the Taft π complex mechanism[5] for alkene hydration; however, it is also consistent with the other commonly proposed mechanism[6]:



$$(CH_3)_2C = C(CH_3)_2 + \overset{\oplus}{H_3O} \xrightarrow{slow} (CH_3)_2CH\text{—}\overset{\oplus}{C}(CH_3)_2 + H_2O$$

$$(CH_3)_2CH\text{—}\overset{\oplus}{C}(CH_3)_2 + H_2O \longrightarrow (CH_3)_2CH\text{—}\underset{\oplus OH_2}{C}(CH_3)_2$$

$$(CH_3)_2CH\text{—}\underset{\oplus OH_2}{C}(CH_3)_2 + H_2O \longrightarrow (CH_3)_2CH\text{—}\underset{OH}{C}(CH_3)_2 + \overset{\oplus}{H_3O}$$

Absence of general acid catalysis is consistent with a reaction which involves a rate controlling proton transfer from hydronium ion to olefinic carbon, provided that proton transfer is quite extensive in the transition state (i.e., the Brönsted α approximates one[7,8]).

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