the different geometries assuming a specific rearrangement mechanism such as Berry pseudorotation.[13] The structures of the different five-coordinate 22-electron systems serve to indicate the various energetic minima on the potential surface for five-coordinate nitrosyl complexes, and these results underscore the dual coordinating ability of the nitrosyl ligand which makes these different relative minima possible. Recent studies by Collman, *et al.*,[14] and experimental observations by Wilson and Osborn[15] indicate that the barriers for interconversion between these minima in certain five-coordinate nitrosyl complexes may be relatively low. Collman, *et al.*,[14] have described these interconversions involving the tetragonal-pyramidal form of $C_s$ symmetry and the trigonal-bipyramidal structures as intramolecular redox reactions.

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(16) National Institutes of Health Predoctoral Fellow, 1969–1971.

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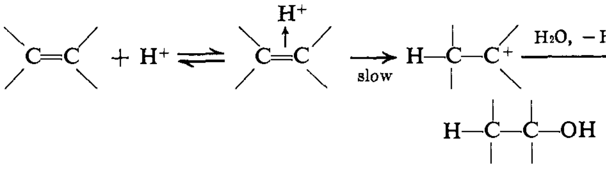
## General Acid Catalysis in the Hydration of Simple Olefins. The Mechanism of Olefin Hydration

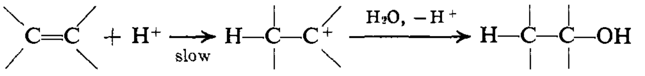
*Sir:*

The first thorough-going investigation of the mechanism of acid-catalyzed hydration of simple olefins produced the hypothesis that this reaction occurs through rapid and reversible formation of a $\pi$-complex intermediate; this intermediate then undergoes rate-determining collapse to a carbonium ion, which is hydrated in a subsequent fast reaction (eq 1).[1] This



(1)

reaction mechanism (A-1) was based principally upon three criteria, (1) kinetic acidity dependence in concentrated acids,[1] (2) solvent isotope effects,[2] and (3) entropies of activation,[1b,3] each of which was considered to be firmly diagnostic at the time but has since been shown to be incapable of ruling out a mechanism (A-SE2) which circumvents the $\pi$-complex intermediate (eq 2).[4] Recent measurements of volumes of activation[5] as well as solvent isotope effects in $H_2O$–$D_2O$ mixtures[6] have in fact been interpreted in terms of an A-SE2 mechanism.



(2)

A firm decision between A-1 and A-SE2 mechanisms can be made on the basis of the presence or absence of general acid catalysis, and the detection of this form of catalysis in the hydration of functionally substituted olefins such as styrenes,[7] vinyl ethers,[8] enamines,[9] and ketene acetals[10] has in fact led to the adoption of A-SE2 mechanisms for these reactions. The hydration of simple olefins has also been examined for general catalysis, but no reliable conclusion could be reached,[11] and the mechanism of this reaction has consequently remained in doubt. We wish to report here that we have now gained evidence which shows that general acid catalysis is present in the hydration of *trans*-cyclooctene and 2,3-dimethyl-2-butene.

It is difficult to examine the hydration of ordinary olefins for general acid catalysis because these substrates are comparatively unreactive. If general catalysis is to be established unequivocally, it should be demonstrated in dilute solution where the interpretation of salt effects is straightforward. This means that the catalysts must be fairly weak acids; otherwise, they will not remain sufficiently undissociated. Carboxylic acids meet this requirement, and buffers of these acids have traditionally been used for this purpose, but even olefins whose hydration generates tertiary carbonium ions react inconveniently slowly in these solutions. Recent investigations of A-SE2 reactions have shown, however, that some general acids, such as $H_3PO_4$ and $HSO_4^-$, have anomalously large catalytic coefficients;[12] these acids should therefore be especially suitable for the investigation of slow reactions to which conventional buffer techniques cannot be applied. We have found, in fact, that *trans*-cyclooctene and 2,3-dimethyl-2-butene react at convenient rates in phosphoric acid and bisulfate buffers above 50°.

We measured rates of hydration of these two olefins, by monitoring the decrease in uv absorption at 200 nm, in series of $H_3PO_4$–$H_2PO_4^-$ and $HSO_4^-$–$SO_4^{2-}$ buffer solutions of constant buffer ratio but changing buffer concentration. In each case, rates of reaction decreased

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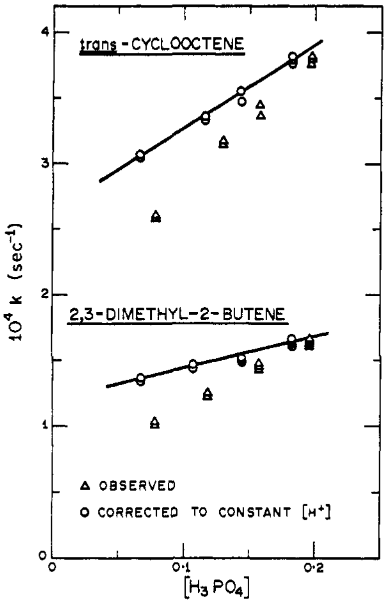

Figure 1. Relationship between undissociated acid concentration and specific rates of hydration of *trans*-cyclooctene and 2,3-dimethyl-2-butene in wholly aqueous $H_3PO_4$–$H_2PO_4^-$ buffer solutions at 52.4°; stoichiometric buffer ratio = 2, ionic strength maintained at 0.1 *M* with $NaClO_4$. Corrections to constant [H$^+$] were made by adjusting $k_{obsd}$ to the H$^+$ concentration (0.014 *M*) of the most concentrated buffer.

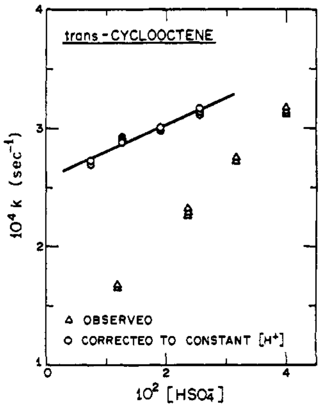

Figure 2. Relationship between undissociated acid concentration and specific rates of hydration of *trans*-cyclooctene in wholly aqueous $HSO_4^-$–$SO_4^{2-}$ buffer solutions at 52.4°; stoichiometric buffer ratio = 4, ionic strength maintained at 0.1 *M* with $NaClO_4$. Corrections to constant [H$^+$] were made by adjusting $k_{obsd}$ to the H$^+$ concentration (0.014 *M*) of the most concentrated buffer.

with decreasing buffer concentration (Figures 1 and 2). This, in itself, however, is not proof of catalysis by general acids, for neither $H_3PO_4$ nor $HSO_4^-$ is a sufficiently weak acid to give dilute buffer solutions whose hydrogen ion concentration does not decrease upon buffer dilution. The experiments were therefore performed at ionic strengths no greater than 0.1 *M*, for which the extended Debye–Hückel formula for calculating ionic activity coefficients is valid, and exact solution compositions were thus estimated. Figures 1 and 2 show that, when the necessary corrections to constant hydrogen ion concentration are made with $k_{H^+}$ values measured in dilute $HClO_4$ solution, marked dependences of reaction rate upon undissociated acid concentration still remain; least-squares analysis of the data gives $k_{H_3PO_4} = (6.4 \pm 0.5) \times 10^{-4}\ M^{-1}\ sec^{-1}$ and $k_{HSO_4^-} = (2.3 \pm 0.1) \times 10^{-3}\ M^{-1}\ sec^{-1}$ for *trans*-cyclooctene and $k_{H_3PO_4} = (2.46 \pm 0.03) \times 10^{-4}$ for 2,3-dimethyl-2-butene. The hydration of 2,3-dimethyl-2-butene was not examined as a function of $HSO_4^-$ concentration, but the velocity of this reaction measured in a single $HSO_4^-$ buffer proved to be significantly greater than that calculated for hydrogen ion catalysis alone, showing general acid catalysis in this system as well. Thus, all of the reactions investigated here are subject to catalysis by general acids.

The reason why general acid catalysis was not discovered in previous examinations[11] of aliphatic olefin hydration conducted for this purpose is now apparent. In both previous studies, large catalyst concentrations were employed to provide conveniently measurable reaction velocities, and, since buffer solutions were used, this led to high ionic strengths—in one case, as great as 3.0 *M*.[11b] Specific ionic interactions can be expected to come into prominence under these conditions, and it has in fact been recently demonstrated[13] that such effects can mask general acid catalysis completely. Thus, the present results are not incompatible with previous investigations, and the operation of an A-S$_E$2 mechanism for the hydration of simple olefins is finally firmly established.

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## Heats of Complexing of Alkali Metal Ions with a Crown Ether in Aprotic Solvents[1]

*Sir:*

Calorimetric results are reported here which show a large selectivity factor for the heat of complexing of dicyclohexyl-18-crown-6 ether[2] for different alkali cations and, furthermore, a considerable solvent effect on this selectivity.[3–5]

Data in Table I show dramatic differences in the complexing of the smaller cations, Li$^+$ and Na$^+$,

(1) Supported by National Science Foundation Grant No. GP-6550-X.

(2) Dicyclohexyl-18-crown-6 ether (2,5,8,15,18,21-hexaoxatricyclo[20.-4.0.0$^{9-14}$]hexacosane) was generously supplied as a mixture of isomers by H. K. Frensdorff of E. I. Du Pont de Nemours.

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