# The Kinetic Acidity Dependence of an *A*-1 Reaction in Concentrated Acids

By V. P. VITULLO†

(*Departments of Chemistry, University of Maryland Baltimore County, Baltimore, Maryland* 21228 *and University of Kansas, Lawrence, Kansas* 66044)

*Summary* The acidity dependence of the activity coefficient ratio, $f_{SH^+}/f_{\ddagger}$, for the isomerization of protonated 4,4-dimethylcyclohexadienone suggests that the transition state is less solvated than the ground state (SH$^+$) by one water molecule.

IN recent years there has been renewed interest in the mechanistic interpretation of kinetic data obtained in concentrated acids.[1–3] Our approach to this problem has been to examine in detail the kinetic acidity dependence of an *A*-1 reaction in which the concentration of the protonated intermediate SH$^+$ can be determined directly. Only in this way can the rate constant $k'$ be obtained unambiguously from experimentally determined quantities (Equations 1—3). In an *A*-1 reaction, the decomposition of SH$^+$ is truly unimolecular and changes in $k'$ with acid concentration

$$A\text{-1 Reaction: } S + H^+ \rightleftarrows SH^+ \xrightarrow{k'} \text{Products} \quad (1)$$

$$k_{obs} = (\text{fraction protonated})\, k' \quad (2)$$

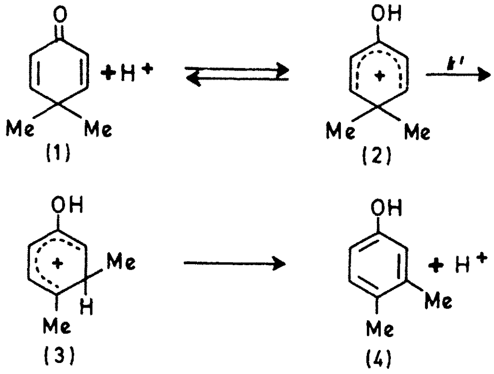
$$k_{obs} = \{[SH^+]/([S] + [SH^+])\}k' \quad (3)$$

must reflect changes solely in the ratio of the activity coefficient of the protonated intermediate, $f_{SH^+}$, to that of the transition state, $f_{\ddagger}$.[4] In this way the variation of

$$k' = k'_0\,(f_{SH^+}/f_{\ddagger}) \quad (4)$$

$f_{SH^+}/f_{\ddagger}$ becomes experimentally accessible.

In an earlier publication[5] we have provided unambiguous evidence that the acid-catalysed isomerization of 4,4-dimethylcyclohexadienone to 3,4-dimethylphenol occurs in three steps. Evidence was presented which suggests



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that (**2**), which can be detected spectroscopically, is formed rapidly and reversibly during the isomerization and the rate-determining step is the isomerization of (**2**) to (**3**). Thus, the dienone–phenol rearrangement is an example of an authentic *A*-1 reaction.

We have determined $k'$ (Equation 3) as a function of sulphuric acid concentration at 25°. These data are shown graphically in the Figure as a plot of log $k'$ against

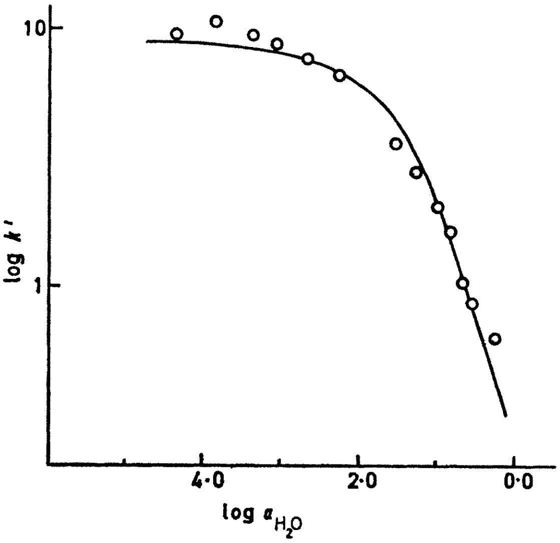
† Inquiries to: Department of Chemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228.

log $a_{H_2O}$.[6] The curve is calculated from Equation 5. Thus, $f_2/f_\ddagger$ appears to be inversely proportional to the

$$k' = (2{\cdot}68 \pm 0{\cdot}10) \times 10^{-5}/[(0{\cdot}0338 \pm 0{\cdot}0050) + a_{H_2O}]\mathrm{s}^{-1} \quad (5)$$

water activity at low acid concentrations and independent of water activity at high concentrations. Even though (**2**) and the transition state, which is intermediate in structure between (**2**) and (**3**), are very similar, their activity coefficient ratio is far from constant. We believe the following analysis accounts for these results.

The "p$K_a$" of (**2**) is approximately $-3{\cdot}8$‡ while that of (**3**) [and the transition state leading to (**3**)] is probably much larger. This difference in acidity is largely due to the inability of the unshared pair of electrons on the hydroxy-group of (**3**) to conjugate with the positive charge in the ring. We expect, therefore, that (**2**) will be more strongly solvated[7] (perhaps by one water molecule) than (**3**) and thus $f_2$ will increase[8,9] faster than $f_\ddagger$ as the activity of water is reduced. Hence $k'$ will increase with decreasing water activity. However, at very low water activities solvation factors are less important, $f_2/f_\ddagger$ remains constant, and $k'$ becomes independent of water activity. This suggests that 85—100% $H_2SO_4$ is an ideal solvent insofar as the activity coefficient ratio $f_2/f_\ddagger$ is constant over this range.[10]



FIGURE

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‡ Estimated from the intercept of a plot of log{[protonated dienone]/[neutral dienone]} against $-H_0$.

[1] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973.

[2] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899, 1917.

[3] A. J. Kresge, R. A. More O'Ferrall, L. E. Hakka, and V. P. Vitullo, *Chem. Comm.*, 1965, 46.

[4] J. N. Brønsted, *Z. phys. Chem.* (*Leipzig*), 1926, **119**, 19.

[5] V. P. Vitullo and N. Grossman, *Tetrahedron Letters*, 1970, 1559.

[6] W. F. Giauque, E. W. Horning, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1960, **82**, 60.

[7] The importance of hydrogen bonding to acidic hydroxy-groups has been noted earlier in studies of the equilibrium protonation of aromatic molecules. A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem. Soc.*, 1962, **84**, 4343.

[8] R. H. Boyd, *J. Amer. Chem. Soc.*, 1963, **85**, 1555.

[9] E. M. Arnett and R. D. Bushick, *J. Amer. Chem. Soc.*, 1964, **86**, 1564.

[10] This constitutes the first experimental demonstration of a suggestion made some years ago. C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2154.