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February 1968

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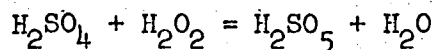
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THE FIRST DISSOCIATION OF SULFURIC ACID

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Some time ago¹ a kinetic study of the reaction



led to the conclusion that the undissociated molecule H_2SO_4 is the intermediate between an instantaneous and a subsequent slow reaction. It is of course true that in a case of this type the kinetic formalism, based on activities, is the same for a trimolecular reaction of H^+ , HSO_4^- and H_2O_2 and for a bimolecular reaction of H_2SO_4 and H_2O_2 . But a classical bimolecular reaction progress with a specific reaction rate increasing almost by 10^5 for an increase of the sulfuric acid concentration from 5 to 12.5 moles per liter appeared to be so interesting that some further experimental support was considered desirable.

The results are shown in Figure 1. The logarithms of the initial reaction with 1 mole H_2O_2 per liter at 25.0°C as found now are compared with the results of Monger and Redlich. The slope of the logarithm

(1) J. M. Monger and O. Redlich, J. Phys. Chem. 60, 797 (1956).

of the activity of sulfuric acid² and the slope of the acidity function³ $-H_0$ are also shown. The kinetic results (logarithmic slope value 0.64) are in reasonable agreement with the slope 0.71 of the activity. The acidity function with a slope 0.52 between $c = 5$ and 12.5 fits the data less well. More recent data⁴ for H_0 (slope 0.58 between $c = 9$ and 12.5) would fit in the smaller range about as well as the activity.

Measurements obtained in heavy solutions ($D/(H+D) = 0.86$) do not show any deviation from the light solutions. This result supports the assumption that the hydrogen ion is not rate controlling.

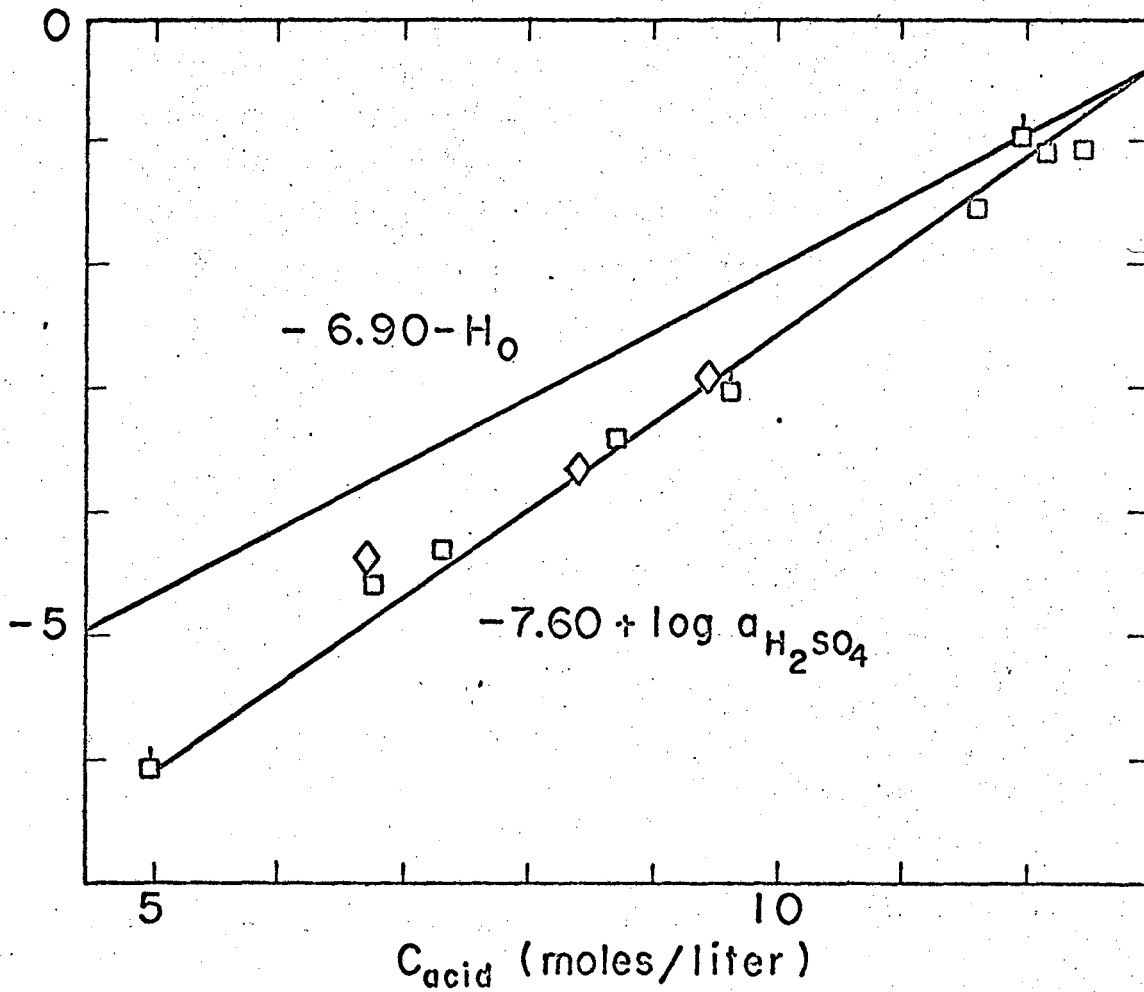
Naturally one may call the variation of the initial rate by a factor 10^5 a solvent effect. But it appears to be preferable to avoid this term in an example which can be explained by a simple and perfectly reasonable model, and to reserve the term "solvent effect" to cover those cases for which it has been invented, namely, where no simple model is applicable.

The measurement of reaction rates may be useful as the third method of investigating the molecular state of strong electrolytes, in addition to Raman intensities and nuclear magnetic resonance.

Acknowledgment

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- (2) J. I. Gmitro and T. Vermeulen, A.I.Ch.E. J. 10, 740 (1964); UCRL-10886 (1963).
 - (3) M. Paul and F. A. Long, Chem. Revs. 57, 1 (1957).
 - (4) M. J. Jorgenson and D. R. Hartter, J. Am. Chem. Soc. 85, 878 (1963).



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Fig. 1 Acidity function H_0 and logarithms of the activity $a_{H_2SO_4}$ and the initial reaction rate (\square H_2SO_4 Monger and Redlich; \square H_2SO_4 and \diamond D_2SO_4 present work).

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