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Some time ago\(^1\) a kinetic study of the reaction

\[ \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_5 + \text{H}_2\text{O} \]

led to the conclusion that the undissociated molecule \(\text{H}_2\text{SO}_4\) 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 \(\text{H}^+, \text{HSO}_4^-\) and \(\text{H}_2\text{O}_2\) and for a bimolecular reaction of \(\text{H}_2\text{SO}_4\) and \(\text{H}_2\text{O}_2\). 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 \(\text{H}_2\text{O}_2\) per liter at 25.0°C as found now are compared with the results of Monger and Redlich. The slope of the logarithm

\(\text{(1)}\) J. M. Monger and O. Redlich, J. Phys. Chem. 60, 797 (1956).
of the activity of sulfuric acid\(^2\) and the slope of the acidity function\(^3\) of \(-H_2O\) 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 data\(^4\) for \(H_2O\) (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.

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