

# Acid Catalyzed Decomposition of Ethyl Vinyl Ether in 2,2,2-Trifluoroethanol

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The acid catalyzed solvolysis of ethyl vinyl ether has been studied in 90% v/v 2,2,2-trifluoroethanol-methanol. A series of carboxylic and methanesulfonic acids were used as catalysts. The dissociation constants,  $K_{HA}$ , and the catalytic coefficients,  $k_{HA}$ , for these acids have been determined. A Brønsted plot was constructed, and the results were analyzed in terms of the Marcus' theory for proton transfer reactions. The results support the notion that part of the free energy of activation is required to desolvate the proton prior to the actual transfer.

The hydrolysis of vinyl ethers has been extensively studied in aqueous media<sup>1,2</sup> and the reaction has been shown to proceed *via* rate determining proton transfer to carbon. We have reported that the hydrolysis of ethyl vinyl ether in 80% DMSO-20% H<sub>2</sub>O by weight also occurs by the same A<sub>S</sub>E<sub>2</sub> mechanism as in water.<sup>3</sup> In that study, a Brønsted plot, as defined by a series of carboxylic acids, appeared to be curved. However, the pK<sub>HA</sub> range covered was insufficient to allow this to be unambiguously established and, therefore, the data could not serve as a test for the Marcus' theory of proton transfer. The number of carboxylic acids used in the study was limited by a combination of factors. Firstly, there are no carboxylic acids stronger than trifluoroacetic acid by at least a pK<sub>a</sub> unit. Secondly, carboxylic acids weaker than formic acid produce inconveniently slow rates. It was felt that a change in solvent may alleviate some of these problems.

It has been shown<sup>4</sup> previously that for rate

determining proton transfer to carbon the reaction rate increases upon changing the solvent from hydrogen bond accepting (DMSO) to hydrogen bond donating (methanol-trimethoxyborane). Thus, 2,2,2-trifluoroethanol was chosen for this study as it was expected to be a good hydrogen bond donating solvent.

## EXPERIMENTAL

Methanol (Merck "zur Analyse") was distilled prior to use. 2,2,2-trifluoroethanol (Fluka "puriss" grade) was purified by distillation from phosphorous pentoxide and then stored over 4 Å molecular sieves. Prior to use, it was distilled again from phosphorous pentoxide. All the acids were purified by distillation. Ethyl vinyl ether was purified as described before.<sup>1</sup>

The solvent mixed prior to use was 90% 2,2,2-trifluoroethanol and 10% methanol by volume (TFE-M). Stock solutions of the acids were prepared and standardized by the usual potentiometric techniques. A dilution series for each acid was prepared, and all subsequent measurements were made on these solutions. Conductance measurements on each solution were made using a Philips PW 9512 101 conductance cell with platinized electrodes and a Wayne Kerr B 642 Autobalance Universal Bridge. A Radiometer GK 2301 C combination electrode, which was preconditioned by soaking in 0.1 M hydrochloric acid, was used for all potentiometric measurements. The electrode could be used directly in the solvent.

Kinetic measurements were made by the usual spectrophotometric techniques in thermostatted cell holders. The reaction was monitored by following the decrease in absorption of ethyl vinyl ether at 225 nm. The kinetic runs were initiated by injecting 5-10 μl of 50% ethyl vinyl ether-50%

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methanol by volume into approximately 3 ml catalyst solution.

The viscosity of TFE-M was determined using an Ostwald viscosimeter with both 2,2,2-trifluoroethanol and methanol as standards.

All solutions were allowed to come to thermal equilibrium by standing for at least 15 min. Physico-chemical measurements were made at  $25.0 \pm 1^\circ\text{C}$  as maintained by a constant temperature bath.

## RESULTS

The acid dissociation constants ( $K_a$ ) for the acids used in this study (except the two weakest) were determined from a combination of conductance and potentiometric measurements. The dilution range used for each acid in both types of measurements was one thousandfold. From the conductance data, the iterative computational method of Fuoss and Kraus was used to evaluate  $K_a$ . These calculations require a value for the solvent viscosity coefficient ( $\mu$ ) which was determined to be  $1.58 \times 10^{-3} \text{ N s m}^{-2}$  from five separate measurements. All the calculations were performed using a computer. The limiting conductance,  $\Lambda_0$ , was calculated by choosing a large value and then going through several iterations. After each iteration, the calculated  $K_{\text{HA}}$  value was used with the potentiometric data to construct a  $mV$  vs.  $pH$  curve. The constants  $A$  and  $B$  of the equation  $mV = A \cdot pH$

+  $B$  were then evaluated. Iterations with both sets of data were continued until the best straight line was produced for both sets. The values of  $K_{\text{HA}}$  that were finally arrived at are shown in Table 1. It is felt that  $K_{\text{HA}}$  values determined in this way probably are in error within 20%. A final standard  $mV$  vs.  $pH$  curve was constructed, and a least squares analysis gave a slope of  $-61.2 \pm 2.3 \text{ mV/pH}$  and an intercept of  $600 \pm 8 \text{ mV}$ . This  $mV$  per  $pH$  response is in reasonable agreement with the theoretical response of  $-59.2 \text{ mV/pH}$ . For the two weakest acids, chloroacetic and acetic acids, the  $pH$  at each acid concentration was determined from the  $mV$  reading, and the acid dissociation constant was calculated. The dissociation constants for each acid were averaged, and the values are listed in Table 1. The standard deviation for both  $K_{\text{HA}}$  values is about 50%. This is rather large, but considering the weakness of the acids and the possible errors in dilution, it probably is not that bad.

The rates of acid catalyzed decomposition of ethyl vinyl ether were measured spectrophotometrically by monitoring the decrease in vinyl ether absorption at 225 nm. The pseudo-first-order rate constants,  $k_1$ , were evaluated graphically and could be replicated with discrepancies of about 5%. The acid solutions were unbuffered resulting in a changing solvated proton concentration throughout an acid concentration series. The expression for general acid catalysis is given by eqn. 1, where  $k_0$  is the rate constant for spontaneous decomposition,  $k_{\text{solv}}$  is the decomposition rate constant caused by the solvent, and  $k_{\text{H}^+}$  and  $k_{\text{HA}}$  have their usual meanings.

$$k_1 = k_0 + k_{\text{solv}} + k_{\text{H}^+}[\text{H}^+] + k_{\text{HA}}[\text{HA}] \quad (1)$$

It was assumed that  $k_0$  was negligible, but  $k_{\text{solv}}$  was measured directly. This left  $k_{\text{H}^+}$  and  $k_{\text{HA}}$  as the variables to be calculated. The  $[\text{H}^+]$  values were calculated from the quadratic equation solution to the normal acid dissociation expression assuming that the  $[\text{H}^+]$  is not negligible compared to  $[\text{HA}]$ . A regression analysis on the two independent variables,  $k_{\text{H}^+}$  and  $k_{\text{HA}}$ , was done for the trifluoromethane and methanesulfonic acid data using the MINITAB II computer program package.<sup>5</sup> The  $k_{\text{H}^+}$  calculated in this way is a second order rate constant; the concentration of  $\text{H}^+$  was that calculated from the dissociation expression and does not include the solvent concentration. Taking the average of the  $k_{\text{H}^+}$  values and then using this value for  $k_{\text{H}^+}$ , a regression analysis on the

Table 1. Catalytic coefficients and acid dissociation constants in 90% 2,2,2-trifluoroethanol–10% methanol (v/v).

| Acid                             | $k_{\text{HA}}/\text{M}^{-1}\text{s}^{-1}$ <sup>a</sup> | $K_{\text{HA}}/\text{M}$ <sup>b</sup> |
|----------------------------------|---|---------------------------------------|
| $\text{CF}_3\text{SO}_3\text{H}$ | $(5.58 \pm 0.63) \times 10^2$                           | $2.56 \times 10^{-2}$                 |
| $\text{CH}_3\text{SO}_3\text{H}$ | $(6.68 \pm 0.43) \times 10^2$                           | $4.26 \times 10^{-2}$                 |
| $\text{CF}_3\text{COOH}$         | $(2.36 \pm 0.13) \times 10^1$                           | $1.06 \times 10^{-4}$                 |
| $\text{CCl}_3\text{COOH}$        | $(6.02 \pm 0.27) \times 10^1$                           | $3.68 \times 10^{-5}$                 |
| $\text{CCl}_2\text{HCOOH}$       | $6.75 \pm 0.39$   | $4.24 \times 10^{-6}$                 |
| $\text{CClH}_2\text{COOH}$       | $(6.97 \pm 0.22) \times 10^{-1}$                        | $5.99 \times 10^{-8}$                 |
| $\text{CH}_3\text{COOH}$         | $(5.19 \pm 0.32) \times 10^{-2}$                        | $1.46 \times 10^{-9}$                 |
| $\text{H}^+$                     | $(4.40 \pm 1.10) \times 10^{2c}$                        |                                       |
| Solvent                          | $(5.71 \pm 0.10) \times 10^{-5d}$                       |                                       |

<sup>a</sup>The reported uncertainties are standard deviations. <sup>b</sup>Determined as described in the Result section and the error is estimated to be no worse than 20%. <sup>c</sup>This value is the mean of two determinations and the uncertainty is the average deviation of the mean. <sup>d</sup>This value is the average of four determinations and the uncertainty is the average deviation of the mean.

independent variable  $k_{\text{HA}}$  using MINITAB II was done on the data for the carboxylic acids. All these results are given in Table 1.

## DISCUSSION

The acid dissociation constants,  $K_{\text{HA}}$ , listed in Table 1 are "formal" dissociation constants. They were calculated using the mass action law assuming that the equilibrium involved only free ions and the unionized molecule. Since rather dilute solutions were used, it was felt that this may be a valid assumption. For the carboxylic acids plotting either  $\log K_a$  vs.  $\sigma^*$  or  $\text{p}K_a$  in the present solvent vs.  $\text{p}K_a$  in water yielded linear correlations. The latter linear plot was anticipated.<sup>7</sup> These observations indicate an internal consistency of the present data.

From an inspection of Table 1, it appears that methanesulfonic acid is stronger by a factor of two than trifluoromethanesulfonic acid. It is possible that part of this difference in  $K_{\text{HA}}$ 's is due to a fortunate combination of errors operating in opposite directions. A more likely explanation, however, may be that the trifluoromethanesulfonic acid is completely ionized to ion pairs in this solvent.<sup>6</sup> Dissociation would then occur from the ion pair, and the "normal" dissociation constant,  $K_{\text{HA}}$ , would most certainly be some function of the ion pair dissociation. Also, it seems unlikely that the acid dissociation constants for dissociation from the unionized and ionized molecule would be equivalent. Previous evidence<sup>4</sup> indicated that methanesulfonic acid may also form an ion pair. The extent to which this occurs was thought to be less than that for the trifluoro analog.<sup>4</sup>

It appears (Table 1) that the catalytic coefficients for the sulfonic acids and the solvated proton may be different. I do not think that this is the case, however. The  $k_{\text{H}^+}$  value was not determined by experiment but is rather a calculated value, and there is no statistical evidence that it is different from the other two strong acids. The difference in  $k_{\text{HA}}$ 's for the two sulfonic acids may or may not be statistically true but, if it is, an explanation is available. If trifluoromethanesulfonic acid does indeed exist primarily as an ion pair, then it seems reasonable that this ion pair would be strongly solvated. Part of the solvation could consist of a hydrogen-bond between the acidic proton and the solvent oxygen. For proton transfer to take place, the hydrogen-bonded solvent must be removed. The accompany-

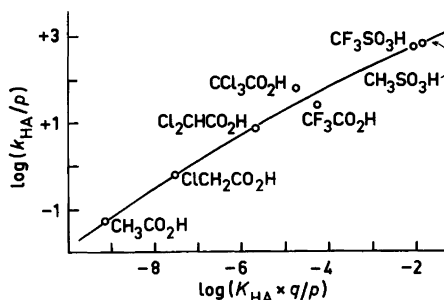


Fig. 1. Brønsted plot for acid decomposition of diphenyl diazomethane. The solid line represents the treatment of data according to Marcus' theory.

ing net energy input over that required for a similar process for methanesulfonic acid could be responsible for the lower catalytic power.

Fig. 1 shows a Brønsted plot of all the acids in Table 1 except the solvated proton. The data were fitted by a least-squares analysis to a quadratic expression in  $\log(q \cdot K_{\text{HA}}/p)$ . The line obtained is shown, and the data give a respectably curved plot. The coefficients of the quadratic expression can be related through Marcus' rate theory to the fundamental parameters by which proton transfer reactions can be characterized. This treatment gives an intrinsic barrier  $\Delta G_0^\ddagger = 79.9 \text{ kJ mol}^{-1}$  and a work term  $w^r = 41.8 \text{ kJ mol}^{-1}$ . ( $\Delta G_0^\ddagger$  is the purely kinetic component of the activation free energy for the hypothetical proton transfer reaction step whose  $\Delta G_0 = 0$ , and  $w^r$  is the free energy required to bring the reactants together and to form them into a reaction complex.) There are two obvious difficulties with this analysis. Firstly, two different acid types have been used to construct a curve, and there is no assurance that they may not each describe their own independent curves.<sup>7b</sup> Secondly, even with the sulfonic acids, the data do not show unequivocal curvature.

A similar analysis can be made with the data obtained in water<sup>1</sup> and in 80% DMSO–20% water<sup>3</sup> for the same reaction as here. In the former case  $\Delta G_0^\ddagger = 8.8 \text{ kJ mol}^{-1}$  and  $w^r = 68.2 \text{ kJ mol}^{-1}$ , and in the latter case  $\Delta G_0^\ddagger = 7.9 \text{ kJ mol}^{-1}$  and  $w^r = 82.4 \text{ kJ mol}^{-1}$ . Unfortunately, the data from which these Marcus' parameters are derived, do not show unequivocal curvature either. But, the trends are interesting,  $w^r$  increases on going from water to the better hydrogen bond acceptor<sup>8</sup> solvent 80% DMSO. Changing the solvent to TFE, which is

considered a good hydrogen bond donating species,<sup>9</sup> causes a decrease in  $w^r$ . This is exactly in the direction predicted assuming that part of the contribution to  $w^r$  involves the breaking of the acid – solvent hydrogen bond.<sup>4</sup> It should take more energy to break the acid-DMSO hydrogen bond than a similar bond with TFE.

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