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Acid Catalyzed Decomposition of Diphenyldiazomethane in Methanol—Trimethoxyborane Azeotrope

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The acid catalyzed decomposition of diphenyldiazomethane has been studied in the azeotropic solvent methanol-trimethoxyborane. The acids trifluoromethanesulfonic, methanesulfonic, trifluoroacetic, trichloroacetic, and dichloroacetic were employed as the catalysts. The catalytic coefficients, k_{HA}, and the dissociation constants, K_{HA}, for these acids have been determined. The kinetic results are compared with those found for the same reaction in 80 % DMSO – 20 % H_2O by weight. The results qualitatively support the notion that part of the observed free energy of activation arises from the energy required to desolvate the proton prior to the actual transfer.

It was also found that while trifluoromethanesulfonic acid is a stronger acid than methanesulfonic acid, it is a weaker acid catalyst.

In the three-step mechanism[1] for slow proton transfer reactions the first step is the formation of an encounter complex; the second step is the actual proton transfer step within the encounter complex; and, finally the last step involves separation of the products.

$$AH\cdots S + B \rightleftharpoons AH\cdots B + S \quad (1)$$

$$AH\cdots B \rightleftharpoons A^-\cdots HB^+ \quad (2)$$

$$A^-\cdots HB^+ \rightleftharpoons A^- + HB^+ \quad (3)$$

In equations 1 – 3 AH is an acid, B is a base and S is solvent. The Marcus theory[2] is based on this mechanism where the formation energy of the first step is separated from the remaining energy contributions to the observed free energy of activation. Among the contributions to the energy required in step (1) is that due to solvent reorganization.[3] In particular in protic solvents with a carbon base and an oxygen acid as the catalyst, the catalyst is most likely hydrogen bonded to the solvent while the carbon receptor center is not. Thus, step (1) would involve a sacrifice of at least one hydrogen bond and a corresponding amount of energy will be consumed. This amount of energy will depend on the strength of the original hydrogen bond. In two different solvents forming hydrogen bonds to the catalyst of differing strengths the reaction rates for the same substrate should vary on the basis of this effect alone. One would predict, therefore, that the poorer hydrogen bond accepting solvents will give rise to faster reaction rates.

Methanol and trimethoxyborane form an azeotrope (MTMB) which is composed of nearly equimolar quantities of each component and which is acidic.[4] The methanol oxygen is thought to be bound to the boron atom; thus, it was expected that MTMB would be a very poor hydrogen bond accepting solvent. A study of the acid catalyzed decomposition of diphenyldiazomethane (DDM) in MTMB was undertaken, and the results were compared to those obtained in DMSO[5] which is a very good hydrogen bond accepting solvent.[6] It was anticipated that the catalytic coefficients for the same acid strengths should be significantly higher in MTMB.

EXPERIMENTAL

Both methanol (Merck "zur analyse") and trimethoxyborane (Merck "zur synthese") were distilled prior to use. The methanol was dried by the

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addition of a small amount of trimethoxyborane followed by distillation. The methanol-trimethoxyborane azetrope was prepared by mixing equal quantities and then distilling. Only the fraction distilling at 54–55 °C (lit. 54.3 °C)[4] was retained for experiments. Trifluoromethanesulfonic acid (Merck "zur synthese") was twice distilled: b.p. 162–164 °C; lit. 162 °C.[7] Methanesulfonic acid (Koch-Light Laboratories) was twice distilled under vacuum: b.p. 168 °C at 10 mmHg; lit. 167 °C at 10 mmHg.[8] Trifluoroacetic acid (Fluka "purum") was distilled: b.p. 72 °C; lit. 71.5 °C.[9]

Diphenyldiazomethane (DDM) was prepared by adaption of the method of Nenitzescu and Solomonica[10] from benzophenone hydrazone which was prepared as previously described.[11] The dark purple-red crystals of diphenyldiazomethane were recrystallized twice alternately from methanol and light petroleum (30–60 °C). The DDM melted at room temperature and was used directly without further purification or characterization.

Stock solutions of the acids were prepared in methanol and standardized by the usual techniques.[12] A stock solution in the azeotrope for each acid was prepared by diluting a known amount of the methanol-stock solution with an equimolar amount of trimethoxyborane to artificially produce the azeotrope, and then diluting the resulting solution with the pure azeotrope. For each acid a series of dilutions was prepared, and all subsequent measurements were made on these solutions.

Conductance measurements were made with a Wayne Keer B642 Autobalance Universal Bridge and a Philips PW 9512/01 conductance cell with platinized electrodes. pH measurements were made using a Radiometer GK 2301 C combination electrode which had been preconditioned by soaking for 50 min in the azeotrope.

The viscosity coefficient of MTMB was measured by standard techniques[13] using an Ostwald viscosimeter and methanol as the standard.

Kinetic measurements were made by the usual spectrophotometric techniques by following the decrease in absorption of DDM at 530 nm. Either thermojacketed cells or cell holders were used, and all catalyst solutions were allowed to come to thermal equilibrium by standing for at least 15 min. The kinetic runs were initiated by injecting 5–10 μl saturated solution of DDM in methanol into about 3 ml catalyst solution. This introduced an error of about 0.3 % in the solvent composition.

All the physico-chemical measurements were made at 25.0±0.1 °C, maintained by a constant temperature bath.

In order to determine the solubilities of the acids, measured amounts of MTMB were titrated to a permanent cloudiness with the acids, trifluoromethanesulfonic and methanesulfonic, using a "Pressure-Lok" Series C liquid syringe from Precision Sampling Corporation.

RESULTS

The dissociation constants (K_{HA}) for trifluoromethanesulfonic acid and methanesulfonic acid were determined from conductance measurements. The computational method of Fuoss and Kraus[14] was used to evaluate K_{HA}. The calculations require values for the solvent viscosity coefficient (μ) and Λ_o, the limiting conductance. μ was determined to be 4.23×10^{-2} N s m^{-2}, and Λ_o for trifluoromethanesulfonic acid was taken to be 116 Ω^{-1} cm^{-1} from a plot of $[HA]^{\frac{1}{2}}$ *vs.* Λ. This Λ_o value was also assumed to apply for methanesulfonic acid. The results are

Table 1. Catalytic coefficients and acid dissociation constants in methanol-trimethoxyborane azeotrope at 25 °C.

Acid	K_{HA}/mol l^{-1}	k_{HA}/l mol^{-1} s^{-1} [a]	Intercept [a]
CF_3SO_3H	1.7×10^{-4}	5.5±0.4	(1.5±1.5)10^{-3}
CH_3SO_3H	9.3×10^{-6}	25.7±0.4	(2.3±2.3)10^{-3}
CF_3COOH	1.1×10^{-8}	1.67±0.04	(5.0±0.2)10^{-3}
CCl_3COOH	8×10^{-9}	3.0±0.2)10^{-1}	(1.3±2.6)10^{-4}
$CHCl_2COOH$	4.9×10^{-9}	(2.2±0.1)10^{-1}	(1.0±0.9)10^{-3}
Solvent		(1.2±0.4)10^{-4} [b]	
H^+		9.8 [c]	

[a] The reported uncertainties are standard deviations. [b] This value is the mean of nine determinations and the uncertainty is the average deviation of the mean. The concentration of the solvent was taken as 13 M. [c] Calculated as outlined in the Result section.

shown in Table 1 and since K_{HA} is a function of Λ_o, it is felt that the error for these values is probably within 20 %. These results show good agreement with previous values[15] determined in the same solvent CF_3SO_3H, $K_{HA}=1.5\times10^{-4}$; CH_3SO_3H, $K_{HA}=9.1\times10^{-6}$.

It has been reported[15] that the combination glass electrode gives the theoretical response of -59.2 *m*V per *p*H unit, and an emf *vs.* *p*H calibration curve was constructed. For the carboxylic acids the emf was measured on a series of unbuffered solutions. The *p*H at each concentration was determined and the dissociation constant, K_{HA}, was calculated. The results for these acids are given in Table 1. The average deviation of the mean of the trifluoroacetic acid value was 10 % but the average deviation of the mean for both tri- and dichloroacetic acid was 25 %.

The pseudo-first-order rate constants, k_1, for the acid catalyzed decomposition of DDM were determined using unbuffered solutions. Thus, the concentration of the solvated proton changed in a concentration series. The general-acid catalytic coefficients, k_{HA}, for the two sulfonic acids were calculated by a least squares analysis of a plot of $k_1-k_S-k_H[H^+]$ *vs.* [HA] where k_S is the solvent catalytic coefficient and k_H is the solvated proton catalytic coefficient. Since k_H was unknown but the other quantities either known or calculated from experimental quantities, the value of k_H was found by systematic trial and error computer routines until a minimum value for the error of the intercept was obtained. The two calculated k_H values agreed by 10 %; the values for k_H and K_{HA} are given in Table 1. Using the value for k_H, k_{HA} for the carboxylic acids was calculated from plots of $k_1-k_H[H^+]-k_S$ *vs.* [HA]; these values are listed in Table 1.

MTMB was titrated by several acids, and it was found that trifluoroacetic acid was completely miscible in all proportions while trifluoromethanesulfonic acid and methanesulfonic acid required 33.7 μl/ml MTMB and 57.1 μl/ml MTMB, respectively, to reach the cloudy endpoint as mentioned in the experimental section. These values are the averages of three determinations. This means that the strongest acid solutions that can be prepared from trifluoromethanesulfonic or methanesulfonic acid are 0.383 mol l^{-1} and 0.880 mol l^{-1}, respectively. It was noted that neither of these two acids was soluble in the upper of the two layers which formed after the endpoint was reached. The acids were also insoluble in the pure trimethoxyborane suggesting that the upper layer consists mainly of that component. Trifluoroacetic acid, however, is soluble in pure trimethoxyborane.

DISCUSSION

An interesting feature of the data in Table 1 is that trifluoromethanesulfonic acid is a poorer catalyst than methanesulfonic acid. Both these acids, while weak in one sense, are strong enough to disrupt the internal structure of MTMB causing it to separate into two layers. A possible cause of this phenomenon may be that the acids exist to some extent as ion pairs which involves solvation from the methanol molecules. As the acid concentration is increased, a point is reached where so many methanol molecules are involved in ion-pair solvation that the internal solvent structure is disrupted. The solvent then separates into two layers: one consisting of methanol-solvated acid and the other of the less polar trimethoxyborane. The differing abilities of the acids to cause the bi-layer phenomenon may reflect the extent each acid exists as ion-pairs. If it is assumed that proton transfer only takes place from the molecular acid and not the ion pair, then k_{HA} would be dependent on the molecular-acid concentration. This could easily account for the discrepancies between the k_{HA} values for trifluoromethane- and methanesulfonic acid. The k_{HA} values reported were corrected only for the calculated dissociation, and it was assumed that the acid concentration was molecular acid. So, the k_{HA} for trifluoromethanesulfonic acid may actually be larger than that for methanesulfonic acid, and what is seen here may be an artifact.

Since the solvated proton catalytic coefficient could not be measured directly but could only be inferred from iterative calculations, k_H is not known to a high degree of accuracy. Its value is, however, probably of the right order of magnitude. It has been noticed that hydronium ion is not necessarily the most effective catalyst.[5,17] In the present case the solvated proton is about as effective as the sulfonic acids. The value of k_H in the present solvent is about an order of magnitude larger than it is in 80 % DMSO – 20 % H_2O by weight.[5] This is in the direction expected as MTMB should solvate the proton less than DMSO – H_2O. Thus, the solvated proton would be a more effective catalyst.

In the Marcus formulation[2] for the interpretation of proton transfer reaction rates there is a substantial

contribution to the free energy of activation of the reaction by the thermodynamic free energy for the formation of an encounter complex (eqn. 1). The free energy of formation of the encounter complex is thought to involve, among other things, the energy required to break the acid-solvent hydrogen bond less the energy recovered by the formation of an acid-substrate hydrogen bond. In the present case there will be a net input in energy to form the encounter complex if DDM is assumed to be a poor hydrogen bond acceptor. A change in solvent would also affect the free energy of encounter complex formation by changing the strength of the acid-solvent hydrogen bond to be broken.

In a previous study[5] of the acid catalyzed decomposition of DDM in 80 % DMSO – 20 % water (by weight) a curved Brønsted plot, in accord with Marcus theory,[2] was obtained. DMSO readily accepts hydrogen bonds[6] while MTMB exhibits acidic characteristics[4] and could be assumed to be a poor hydrogen bond acceptor. Thus, it was felt that rates of DDM decomposition should be faster in MTMB than in 80 % DMSO – 20 % water due to a lower free energy of encounter complex formation. In order to test this proposition it seemed reasonable to compare the catalytic coefficients, k_{HA}, between the two solvents at the same K_{HA}. From the Brønsted plot in 80 % DMSO – 20 % water k_{HA} values can be calculated that correspond to K_{HA} values of the acids studied. The ratios $k_{HA}^{MTMB}/k_{HA}^{DMSO}$ could then give an indication of the rate acceleration due to a change in solvent at a constant K_{HA}. These ratios for the sulfonic and carboxylic acids in the order listed in Table 1 are 29, 287, 4250, 598 and 696. While these results are in the direction expected, their significance can be questioned inasmuch as all the solvent sensitive factors are not known.

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