

## The Upper Limit on Rates of Proton Transfer

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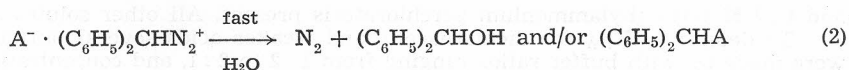
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The Brønsted plot for hydrolysis of diphenyldiazomethane by carboxylic acids is smooth but curved, approaching an asymptotic limit below  $10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . Regardless of the details of the theory used, such a limit requires that the transition state is approached via a state (or virtual state) substantially ( $\sim 70 \text{ kJ mol}^{-1}$ ) above the starting state in free energy, but still having an intact bond from  $\text{H}^+$  to its original conjugate base. Such a state has been called a reaction complex,<sup>6</sup> and is thought to be analogous to the intimate ion pair of solvolysis reactions.

### INTRODUCTION

It is evident from the recent Faraday Symposium on Proton Transfer,<sup>1</sup> and from earlier publications,<sup>2</sup> that the curvature of Brønsted plots can be interpreted in a number of quantitatively different ways. The approximate nature of these relations and the fact that Brønsted relations are, generally, limited to »homogeneous« classes of acids, the membership of which is not always completely unambiguous, make it difficult to distinguish among these possibilities, or, indeed, to know if any of them is valid. However, if increasingly stronger acids are studied until the catalytic coefficients reach or approach an asymptotic limit,  $k_{\text{lim}}$ , the interpretation of that limit is fairly clear. The difference between  $-RT \ln \{k_{\text{lim}}/(kT/h)\}$  and the free energy of activation for diffusion, about  $10 \text{ kJ mol}^{-1}$ , is that part of the activation barrier which is insensitive to the strength of the acid.<sup>3</sup> In terms of the Marcus theory of proton transfer<sup>4,5</sup> it is  $W^{\ddagger}$ , and this will remain true regardless of the form which is given to the relation between acid strength and  $\Delta G^{\ddagger}$ , the height of that part of the barrier which is sensitive to acid strength. At that symposium it was asserted that rates of reactions of the type shown in eq 1, carried out in 80% dimethylsulphoxide (DMSO) — 20% water, have an asymptotic limit below  $10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , about 9 powers of ten below the diffusion limit.<sup>6</sup> This observation has serious consequences for the model which must be used for such reactions. It is the purpose of the present paper to present, in considerably greater detail and supported by new results, the experimental foundation for the assertion, in the particular case that the acids are carboxylic acids.



## EXPERIMENTAL

*Materials*

Diphenyldiazomethane was prepared by oxidising the hydrazone of benzophenone<sup>7</sup> with yellow mercuric oxide.<sup>8</sup> It was purified by alternate recrystallizations from methanol and low-boiling petroleum ether, and had m. p. 28–29 °C (d.) lit.,<sup>8,9</sup> 29 °C. The infrared spectrum of this material showed neither benzhydrol nor benzophenone.

Trifluoroacetic acid was purchased at various times from PCR, Inc., and from Aldrich Chemical Co., and used without purification, as was heptafluorobutyric acid which was purchased from PCR, Inc., and oxalic acid, which was a Baker Analyzed Reagent. Our 3,5-dinitrobenzoic acid was purchased from Aldrich Chemical Co., Inc., and recrystallized from water containing 20% methanol; m. p. 205–207 °C. lit.,<sup>10</sup> 205–207 °C. Pentafluorophenoxyacetic acid was purchased from PCR, Inc., and recrystallized from petroleum ether; m. p., 111–112 °C (lit.,<sup>11</sup> 107.5–109 °C). Benzoic acid was purchased from Aldrich Chemical Co., Inc., and recrystallized from petroleum ether; m. p. 122–122.5 °C (lit.,<sup>12</sup> 122.4 °C). Acetic, chloroacetic and dichloroacetic acids have been previously described.<sup>13</sup>

Tetramethylammonium salts of trifluoroacetic acid, heptafluorobutyric acid and dichloroacetic acid were prepared by neutralizing concentrated aqueous solutions of those acids with tetramethylammonium hydroxide, purchased from Sigma Chemical Co. The water was boiled off under vacuum and the crude products were recrystallized. The trifluoroacetate was recrystallized from butanol, the heptafluorobutyrate from an acetone-water mixture, and the dichloroacetate from a mixture of acetone and 2-propanol. After drying under vacuum these materials were subjected to elemental analysis to establish their identity and purity.<sup>14</sup>

*Anal.* C<sub>3</sub>F<sub>7</sub>H<sub>12</sub>NO<sub>2</sub> (287.17) calc'd.: C 33.46; H 4.21; N 4.88%  
found: C 33.19; H 4.40; N 4.66%

*Anal.* C<sub>6</sub>F<sub>3</sub>H<sub>12</sub>NO<sub>2</sub> (187.07) calc'd.: C 38.50; H 6.42; N 7.48%  
found: C 38.33; H 6.41; N 7.36%

*Anal.* C<sub>6</sub>H<sub>13</sub>Cl<sub>2</sub>NO<sub>2</sub> (202.09) calc'd.: C 35.66; H 6.48; N 6.93%  
found: C 35.34; H 6.41; N 6.83%

Dimethylsulphoxide was purchased from the Aldrich Chemical Co. In order to make up the mixed solvent reproducibly it was first purified and dried to about 0.03% water,<sup>15</sup> then mixed with water in exactly the ratio of 4 : 1 by weight.

All other materials used were of Reagent grade or better, purchased from reliable commercial sources, and used without purification.

*Acid Dissociation Constants, K<sub>HA</sub>*

Hydrogen ion activities were determined at (25.0 ± 0.2) °C, electrometrically,<sup>16</sup> using a water jacketed 3-compartment cell, the compartments separated by glass frits. One end compartment contained 10<sup>-2</sup> mol dm<sup>-3</sup> AgNO<sub>3</sub> in contact with a silver wire electrode. The other end compartment contained the solution whose pH was required, in contact with a Radiometer type C glass electrode. The middle (bridging) compartment contained 10<sup>-2</sup> mol dm<sup>-3</sup> tetramethylammonium perchlorate. The potential difference between the two electrodes was determined using a Radiometer pH meter equipped with a scale expander. The electrodes were calibrated each day using 1.59 × 10<sup>-3</sup> mol dm<sup>-3</sup> HClO<sub>4</sub> and a 1 : 1 acetic acid potassium acetate buffer, both concentrations about 10<sup>-2</sup> mol dm<sup>-3</sup>. Enough tetraethyl ammonium perchlorate was added to each of the calibrating solutions to raise their ionic strength to 0.19 mol dm<sup>-3</sup>. The K<sub>HA</sub> for acetic acid in this medium was obtained from its value in dilute solution in the same solvent<sup>17</sup> using the Debye-Hückel equation.<sup>18</sup> An interionic distance of 0.6 nm<sup>19</sup> and a dielectric constant<sup>20</sup> of 65 were used to evaluate the parameters of the Debye-Hückel equation. The calibrating solutions differ by about 5 units of pH. The difference in measured potentials was 59.5 mv per pH unit with deviations never larger than 2 mv per pH unit. Values of pH determined in this way refer to a standard state in which the solvent is 80% DMSO-20% water by weight and 0.19 M tetraethylammonium perchlorate is present. All other solutes are dilute.

To determine K<sub>HA</sub> for dichloroacetic and weaker acids several buffer solutions were made up with buffer ratios ranging from 1 : 2 to 2 : 1, and concentrations in the

range  $1 - 2 \times 10^{-2}$  mol dm<sup>-3</sup>. This was done by partially neutralizing solutions of the acids with KOH solutions in the same solvent. The ionic strength was made up to 0.19 mol dm<sup>-3</sup> with tetramethylammonium perchlorate and the pH determined as described above. The antilog of the pH, multiplied by the stoichiometric anion to acid ratio, gives  $K_{HA}$ . The standard state is as described.

The stronger acids were too extensively ionized for this procedure to be useful. Instead, therefore, half of, or, in some cases the entire electrolyte was replaced with the tetramethylammonium salt of the acid, and small, known amounts of HClO<sub>4</sub> were added. Such solutions gave pH values considerably above those obtained from the same concentrations of HClO<sub>4</sub> in tetraethylammonium perchlorate, and  $K_{HA}$  values were readily calculated. However they refer to the same standard state as those for the weaker acids only under the (reasonable) assumption that the tetramethylammonium salts of the acids provide a medium equivalent to the same concentration of tetraethylammonium perchlorate.

### Determination of Rate Constants

Rate constants were determined by the conventional spectrophotometric technique, following the disappearance of the diphenyldiazomethane absorbance,  $A$ , at 530 nm or the more intense absorbance at 305 nm. The reactions were carried out either in 1.0 cm cells in a water-jacketed cell compartment or in a 10.0 cm, water-jacketed cell. Exposure to light was avoided as much as possible. The temperature was monitored in a similar cell in the absence of the reaction mixture and was found to be  $(25.0 \pm 0.1)$  °C.

For acids weaker than dichloroacetic, buffer ratios ranged from 10:1 to 1:1, with the acid at the higher concentrations. The conjugate base concentration was always below 0.1 mol dm<sup>-3</sup>; usually considerably below. The ionic strength was brought up to 0.19 molar with tetraethylammonium perchlorate. For the stronger acids such solutions were too extensively dissociated to be useful, so the tetraethylammonium perchlorate was replaced with the tetramethylammonium salt of the acid in question. The solutions were made up as described in the section on acid dissociation constants. Both techniques were used for dichloroacetic acid, with entirely consistent results. The  $H^+$  catalytic coefficient was obtained in HClO<sub>4</sub> solutions, brought to the required ionic strength with tetramethylammonium perchlorate.

The acid was always present in at least ten fold excess over the diphenyldiazomethane. In the case of the strong acids, which were present in concentrations between  $10^{-3}$  and  $10^{-4}$  mol dm<sup>-3</sup>, this required the use of very dilute diphenyldiazomethane solutions, so the 10 cm cell was used to get sufficient absorbance changes, or else the reaction was monitored at 305 nm, where the extinction coefficient of diphenyldiazomethane is much larger. In any event, only the formation of ester (about half of the total product) consumes acid, so that, in the worst cases, the change in acid concentration during the course of an experiment was only about 5%. As would be expected under these conditions,  $\log A$  was an accurately linear function of time in all experiments up to at least 75% completion. Pseudo-first order rate constants,  $k_1$ , were evaluated graphically in the usual way.<sup>21</sup> They could be replicated with a scatter of  $\pm 2 - 3\%$ .

### Products

Products were isolated from reactions with HClO<sub>4</sub> acid and with an acetic acid-potassium acetate buffer. The reactions were carried out in the usual way but on a 250 cm<sup>3</sup> scale. After 10 half lives the reaction mixtures were neutralized with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> and diluted with 200 cm<sup>3</sup> of water. They were then extracted with three 100 cm<sup>3</sup> portions of toluene, and the combined toluene solutions were washed repeatedly with water to remove the DMSO. The toluene was then removed by evaporation under reduced pressure leaving about 0.1 g (~ 50% yield) of product. This product consisted solely of benzhydrol in the case of the reaction with HClO<sub>4</sub>. It showed only one band, at the appropriate place, in a thin layer chromatogram. After two recrystallizations from petroleum ether (probably required to remove residual DMSO) it had m. p. 65–66 °C; lit.,<sup>22</sup> 66–67 °C. The product from the acetic acid-potassium acetate buffer was isolated in similar quantity. It showed bands for both benzhydrol and benzhydryl acetate in its thin layer chromatogram, in approxi-

mately equal proportions. Both substances, and no others, were also apparent in the IR spectrum of this product. No attempt was made to separate it into its constituents. Products of reactions with stronger acids could be expected to contain more benzhydrol and less of its ester, because the conjugate bases of such acids would be poorer nucleophiles than acetate ion.

## RESULTS AND DISCUSSION

The required  $K_{HA}$  values are shown in Table I, along with their probable errors. Each value is the average of at least 4 determinations. Probable errors of about 4% would be expected due to the scatter in potentiometer readings, both in calibration and in pH measurement. It is likely that errors in excess of 4% are due to small errors in the composition of the mixed solvent, to which  $K_{HA}$  is quite sensitive. The probable errors for the two perfluorinated carboxylic acids, for which  $K_{HA}$  values had to be measured in poorly buffered solutions, are not strikingly worse than those for the other members of the series. A plot of  $pK_{HA}$  in 80% DMSO — 20% water, in the presence of 0.19 mol dm<sup>-3</sup> tetraethylammonium perchlorate, against  $pK_{HA}$  in dilute aqueous solution, is shown in Figure 1. Such plots usually show approximate linearity,<sup>23,24</sup> and so does the present one. In any event, it is certainly a smooth curve, suggesting that the acids are free of extraneous effects, such as internal hydrogen bonding.<sup>24</sup> The fit of the trifluoroacetic acid point to the curve provides further support for that  $K_{HA}$  value.

The spontaneous decomposition rate of diphenyldiazomethane in the present medium was obtained in the presence and in the absence of 10<sup>-3</sup> mol dm<sup>-3</sup> NaOH. The two rates are indistinguishable and their rate constant,  $k_0$ , less than 1% of any of the  $k_1$  values to be dealt with in the rest of this paper. (This decomposition presumably includes the variant of eq 1 in which water is the acid, as well as thermal and photochemical decompositions.) Therefore  $k_0$  was neglected in the remainder of this work.

TABLE I

Rate Constants and Acid Dissociation Constants for Carboxylic Acids in 80% DMSO<sup>a,b</sup>

| No | Acid  | $K_{HA}/\text{mol dm}^{-3}$    | $k_{HA}/\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ |
|----|---|--------------------------------|--|
| 1  | C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> H                                     | $4.2 \pm 0.5 \times 10^{-2}$   | $1.7 \pm 0.3$                                      |
| 2  | CF <sub>3</sub> CO <sub>2</sub> H   | $2.7 \pm 0.6 \times 10^{-2}$   | $1.4 \pm 0.3$                                      |
| 3  | (CO <sub>2</sub> H) <sub>2</sub>  | $3.9 \pm 0.2 \times 10^{-4}$   | $9.3 \pm 0.1 \times 10^{-1}$                       |
| 4  | Cl <sub>2</sub> CHCO <sub>2</sub> H   | $2.7 \times 10^{-4c}$          | $4.9 \pm 0.1 \times 10^{-1}$                       |
| 5  | 3,5-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> H | $4.0 \pm 0.7 \times 10^{-5}$   | $1.80 \pm 0.05 \times 10^{-1}$                     |
| 6  | ClCH <sub>2</sub> CO <sub>2</sub> H   | $4.1 \times 10^{-6c}$          | $5.6 \pm 0.3 \times 10^{-2}$                       |
| 7  | C <sub>6</sub> F <sub>5</sub> OCH <sub>2</sub> CO <sub>2</sub> H                    | $3.5 \pm 0.9 \times 10^{-6}$   | $5.5 \pm 0.2 \times 10^{-2}$                       |
| 8  | 4-(NO <sub>2</sub> )C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H                 | $2.4 \pm 0.3 \times 10^{-6}$   | $4.0 \pm 0.2 \times 10^{-2}$                       |
| 9  | C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H                                     | $1.21 \pm 0.04 \times 10^{-7}$ | $8.1 \pm 0.4 \times 10^{-3}$                       |
| 10 | CH <sub>3</sub> CO <sub>2</sub> H   | $2.00 \times 10^{-8d}$         | $1.9 \pm 0.1 \times 10^{-3}$                       |

<sup>a</sup> In a medium containing 80% DMSO and 20% water, by weight, and an ionic strength of 0.19, made up, for the most part, of tetraethylammonium perchlorate.

<sup>b</sup> The uncertainties are probable errors of the mean values, which are shown.

<sup>c</sup> Adapted from ref 13.

<sup>d</sup> Adapted from J.-P. Morel, *Bull. Soc. Chim. France* (1967) 1405.

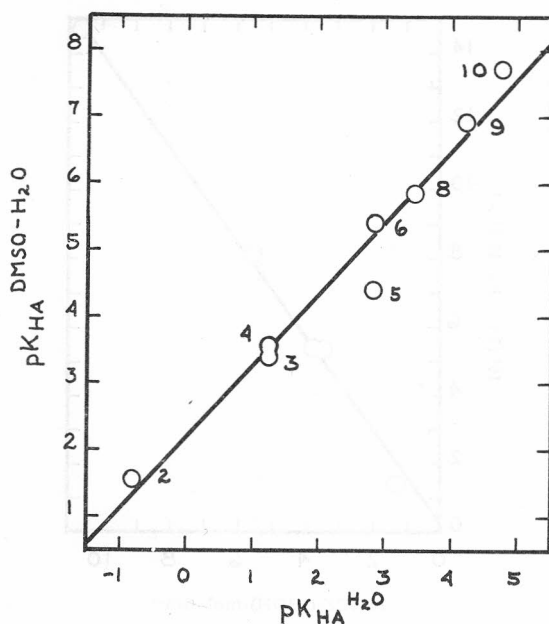


Figure 1. A plot of  $pK_{HA}$  values in 80% DMSO-20% water, in the presence of 0.19 M tetraethylammonium perchlorate, against those in dilute aqueous solution.<sup>25,26</sup> The numbering is the same as that in Table I. Heptafluorobutyric acid and pentafluorophenoxyacetic acid have been omitted because their aqueous solution dissociation constants do not appear to be known.

In  $HClO_4$  solutions  $k_1$  was accurately proportional to the acid concentration, and the average value of  $k_1/[H^+]$ ,  $(0.746 \pm .017) \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , was taken as  $k_H$ , the catalytic coefficient for  $H^+$ .

To get the catalytic coefficients of the general acids,  $k_{HA}$ , eq 3 was assumed, and  $\{k_1 - k_H [H^+]\}$

$$k_1 = k_H [H^+] + k_{HA} [HA] \quad (3)$$

was plotted against  $[HA]$ . (In eq 3,  $k_0$  is neglected.) Wherever it was significant, the partial dissociation of  $HA$  was taken into account in calculating its concentration. The pH was measured, and, from it and the known composition of the reaction mixture,  $[HA]$  could be evaluated. In general the plots were linear for  $[HA]$  up to at least  $0.1 \text{ mol dm}^{-3}$ , and the scatter from such a plot did not exceed the uncertainty in  $k_1$ . They had intercepts not significantly different from zero, as required by eq 3. The slopes,  $k_{HA}$ , and intercepts of these plots were obtained by the method of least squares, and the  $k_{HA}$  values are given in Table I. Figures 2 and 3 show typical examples of such plots. The former is for one of the stronger acids and the latter for one of the ordinary acids. All the resulting  $k_{HA}$  values are shown in Table I, along with the  $k_H$  values.

The Brønsted plot is shown in Figure 4. Data for a number of acids which are not carboxylic acids are also shown.<sup>6</sup> Phenols which are not nitrophenols appear to form a homogeneous series, along with carboxylic acids; nitrophenols appear not to be part of this series, and  $H^+$  also is not. Two miscellaneous oxygen acids give points which are somewhat displaced from the smooth curve defined

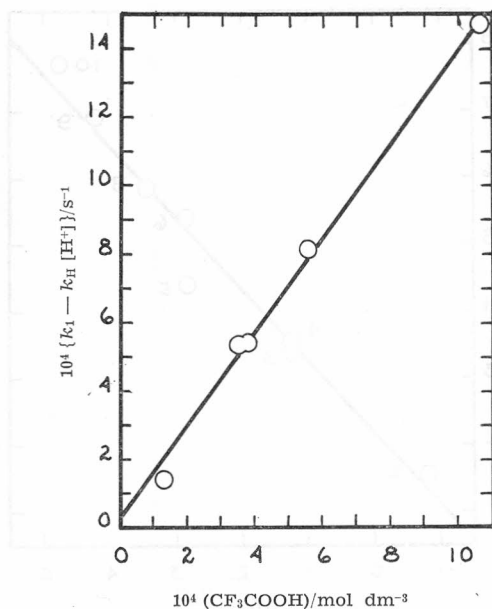


Figure 2. Rate as a function of acid concentration in 0.19 molar tetramethylammonium trifluoroacetate to which small amounts of perchloric acid were added.  $[H^+]$  and  $[CF_3COOH]$  were calculated using the known  $HClO_4$  concentration and the measured pH. The slope,  $k_{HA}$  for  $CF_3COOH$ , is  $1.4\ mol^{-1}\ dm^3\ s^{-1}$ .

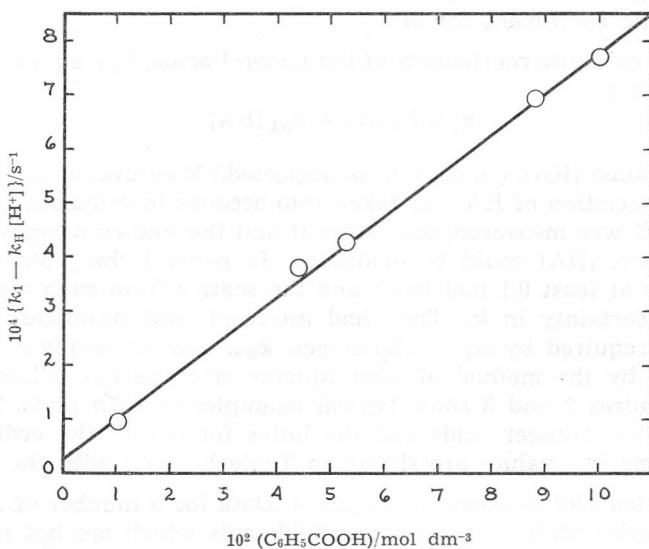


Figure 3. Rate as a function of acid concentration in 1:1 benzoic acid — potassium benzoate buffers which were brought up to an ionic strength 0.19 by addition of an appropriate amount of tetramethylammonium perchlorate. The slope,  $k_{HA}$  for benzoic acid, is  $7.5 \times 10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$ .

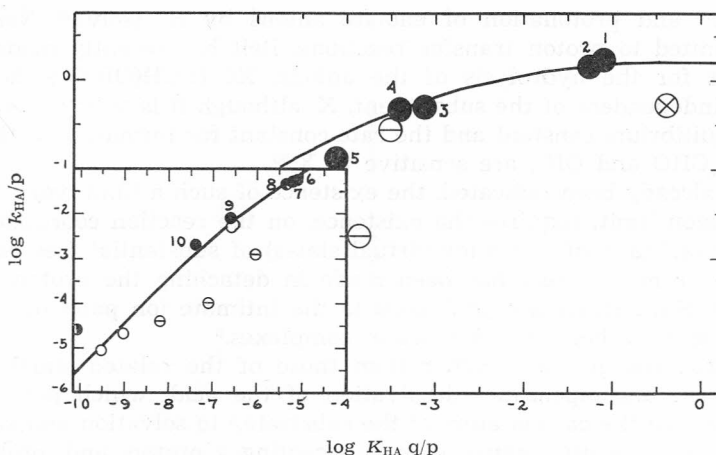


Figure 4. The Brønsted plot for attack by neutral oxygen acids on diphenyldiazomethane in 80% DMSO-20% water, also containing 0.19 molar electrolyte, mostly tetraethylammonium perchlorate. Closed circles are carboxylic acid points, numbered as in Table I. Open circles are phenols other than nitrophenols. Barred circles are nitrophenols.<sup>6</sup> The crossed circle is methanesulfonic acid.<sup>6</sup> The half-filled circle is the point generated by hexafluoroacetone hydrate.<sup>6</sup> The solid line represents the prediction of eqs 4-7.

by the carboxylic acid and phenol points. Figure 4 also shows the prediction of eqs 4-7, which constitute a particular formulation of Marcus theory of atom transfer,<sup>2,4-6</sup>

$$\Delta G^* = W^r + \Delta G^\ddagger \quad (4)$$

$$\Delta G^\ddagger = \{1 + (\Delta G_{\text{HA}}^0 + C)/\lambda\}^2 \lambda/4 \quad (5)$$

$$(\lambda > \Delta G_{\text{HA}}^0 + C > -\lambda)$$

$$\Delta G^\ddagger = 0 \quad (6)$$

$$(-\lambda > \Delta G_{\text{HA}}^0 + C)$$

$$\Delta G^\ddagger = \Delta G_{\text{HA}}^0 + C \quad (7)$$

$$(\Delta G_{\text{HA}}^0 + C > \lambda)$$

using parameters adjusted to give the best fit to the carboxylic acid and non-nitro phenol data. In this way a value of  $71.5 \pm 0.1$  was obtained for  $W^r$ ,  $22 \pm 2$  for  $\lambda$ , and  $-25 \pm 2$  for  $C$ , all in  $\text{kJ mol}^{-1}$ .<sup>6</sup> The uncertainties in this treatment include the formulation of  $\Delta G^\ddagger$  (eq 5)<sup>1,2</sup> and the choice of points to include in the correlation, as well as the experimental uncertainties (the latter do not appear to be significant in the present context). However, we believe it is clear by inspection of Figure 4 that an asymptotic limit is being approached below  $10 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , and that no combination of the uncertainties cited above threaten this conclusion. In fact, the same conclusion was reached by fitting all the points, instead of the selection indicated, or by fitting only the carboxylic acid points. The same conclusion was also reached if a general power series in  $\log K_{\text{HA}}$  was used to fit  $\log k_{\text{HA}}$ , instead of eqs 4 and 5 (and the fit was not appreciably improved).

The same conclusion can be reached for protonation of diazoacetate by tertiary ammonium ions,<sup>27</sup> protonation of benzylmalononitrile anions by carbo-

xylic acids,<sup>28</sup> and protonation of enolate anions by  $H^+$  (solv).<sup>29</sup> Nor is this behavior limited to proton transfer reactions. Bell has recently made similar observations for the hydrolysis of the anions,  $XC_6H_4CH(OH)O^-$ ; the rate is essentially independent of the substituent, X, although it is only  $\sim 5 \times 10^3 \text{ s}^{-1}$ .<sup>30</sup> Both the equilibrium constant and the rate constant for formation of the anion, from  $XC_6H_4CHO$  and  $OH^-$ , are sensitive to X.<sup>30</sup>

As has already been indicated, the existence of such a limit, very far short of the diffusion limit, requires the existence, on the reaction coordinate, prior to the transition state, of states (or virtual states) of substantial free energy, in which little or no progress has been made in detaching the proton from its original site. Such states are analogous to the intimate ion pairs of solvolysis reactions, and have been called reaction complexes.<sup>6</sup>

Their free energies are higher than those of the related starting states because of the uncompensated desolvation of the acid, which permits it to directly approach the carbon atom of the substrate,<sup>5</sup> to solvation and structural changes in the substrate, preparatory to accepting a proton, and, probably, to the endoergic formation of a short hydrogen bond between the acid and the carbon base. There is probably little or no activation energy for the reversion of a reaction complex to an encounter complex, so the formation of a reaction complex will rarely, if ever, be rate determining.<sup>31,32</sup>

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#### REFERENCES

1. R. P. Bell, *Faraday Symp. Chem. Soc.* **10** (1975) 17; R. A. Marcus, *ibid.* p. 60; A. J. Kresge, *ibid.* p. 89.
2. G. W. Koeppl and A. J. Kresge, *J. Chem. Soc., Chem. Comm.* (1973) 371.
3. M. M. Kreevoy, *Faraday Symp. Chem. Soc.* **10** (1975) 92.
4. R. A. Marcus, *J. Phys. Chem.* **72** (1968) 891.
5. M. M. Kreevoy and D. E. Konasewich, *Adv. Chem. Phys.* **21** (1971) 243.
6. A. I. Hassid, M. M. Kreevoy, and T.-M. Liang, *Faraday Symp. Chem. Soc.* **10** (1975) 69.
7. A. Schonberg, A. E. K. Fateen, and A. E. M. A. Sammour, *J. Amer. Chem. Soc.* **79** (1957) 6020.
8. C. D. Nenitzescu and E. Solomonica, *Org. Syn.*, Coll. Vol. 2, 1943, p. 496.
9. D. Bethell and J. D. Callister, *J. Chem. Soc.* (1963) 3801.
10. R. W. Brewster and B. Williams, *Org. Syn.*, Coll. Vol. 3, 1955, p. 327.
11. F. I. Abezgauz and S. V. Sokalov, *Zh. Obsch. Khim.* **38** (1968) 2502.
12. F. W. Schwab and E. Vickers, *J. Res. Natl. Bur. Std.* **34** (1945) 333.
13. E. H. Baughman and M. M. Kreevoy, *J. Phys. Chem.* **78** (1974) 421.
14. The analyses were performed by M-H-W Laboratores, Garden City, Michigan, U.S.A.
15. L. M. Abts, J. T. Langland, and M. M. Kreevoy, *J. Amer. Chem. Soc.* **97** (1975) 3181.
16. I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.* **1** (1962) 189.
17. J.-P. Morel, *Bull. Soc. Chim. France*, (1967) 1405.
18. R. G. Bates, *Determination of pH*. John Wiley & Sons, Inc., New York, N. Y., 1964, p. 11. The Debye-Hückel equation is unreliable for solutions as concentrated as our present ones. To check these estimates of activity coefficients several  $pK_{HA}$  values were measured in dilute solution and also estimated from pH measurements in the more concentrated electrolyte. The agreement was entirely satisfactory.
19. J. Kielland, *J. Amer. Chem. Soc.* **59** (1937) 1675.
20. E. Tommila and A. Paajunen, *Suom. Kemist.* **41 B** (1968) 172.



21. A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, 2nd ed., John Wiley and Sons Inc., New York, N. Y. 1961, p. 29.
22. F. Y. Wiselogle and H. Sonneborn, III, *Org. Syn.*, Coll. Vol. I, revised ed., 1971, p. 90.
23. M. M. Kreevoy and E. H. Baughman, *J. Amer. Chem. Soc.* **95** (1973) 8178.
24. I. M. Kolthoff and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.* **93** (1971) 3843.
25. G. Kortum, W. Vogel, and K. Andrussov, *Dissociation Constants of Organic Acids*, Butterworth and Co. (Publishers) Ltd., London, 1961.
26. A. K. Covington, J. G. Freeman, and T. H. Hiley, *J. Phys. Chem.* **74** (1970) 3773.
27. M. M. Kreevoy and S-W. Oh, *J. Amer. Chem. Soc.* **95** (1973) 4805.
28. R. P. Bell and S. Grainger, *J. Chem. Soc., Perkin II* (1976) 1367.
29. A. J. Kresge, D. S. Sagtys, and H. L. Chen, *J. Amer. Chem. Soc.* in press, have concluded that rates of enolate reprotonation by  $H^+$  (aq.) are limiting, in the present sense. Their rate constants are between  $10^6$  and  $10^7$   $mol^{-1} dm^3 s^{-1}$ .
30. R. P. Bell and P. E. Sørensen, *J. Chem. Soc., Perkin II* (1976) 1594.
31. M. M. Kreevoy, *Faraday Symp. Chem. Soc.* **10** (1975) 97.
32. J. R. Murdoch, *J. Amer. Chem. Soc.* **94** (1972) 4410.

### SAŽETAK

#### Gornja granica brzine prijenosa protona

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Određene su Brønstedove relacije za hidrolizu difenildiazometana u nizu karbonskih kiselina. Dobivene krivulje asimptotski se približavaju graničnoj vrijednosti, koja je znatno ispod  $10 mol^{-1} dm^3 s^{-1}$ . Postojanje ove granične vrijednosti upućuje da prelaznom stanju istraženih reakcija prethodi reakcijski kompleks. Slobodna energija ovog potonjeg je bitno viša od energije ishodnog spoja ( $\sim 70 kJ mol^{-1}$ ), ali je  $H^+$  još uvijek vezan na konjugiranu bazu. Prema tome, reakcijski kompleks odgovara intimnom ionskom paru kod solvolitskih reakcija.

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