

$H^+ = 0.67$. These overall distributions obviously indicate extensive randomization in the ethyl ion. This conclusion is in disagreement with that of a recent ICR study^{2b} in which it was reported that D^+ transfer occurred quantitatively in the reaction of $C_2D_3H_2^+$ from $(CD_3CH_2)_2NNO$ with the parent molecule. It is probable that the interpretation of the latter experiment was complicated by the large number of potential D^+ donors, including the parent ion and fragment ions other than $C_2D_3H_2^+$.⁵

b. Isotopic Analysis of Ethane Produced in the H^- (D^-) Transfer to $C_2D_3H_2^+$ and $C_2D_2H_3^+$. The ethyl ions from various sources (first column of Table I) have been produced in the presence of the H^- and D^- donors given in column 3 of Table I. If all $C_2D_3H_2^+$ retain the structure indicated by the precursor only CD_3CH_3 will be formed in the reaction $C_2D_3H_2^+ + RH \rightarrow CD_3CH_3 + R^+$ ($k \sim 10^{-9}$ cc/(mol sec)).⁶ If, however, the D and H atoms in $C_2D_3H_2^+$ are completely scrambled, 90% of the $C_2D_3H_2^+$ should react with RH to yield CD_2HCDH_2 . The same holds for $C_2D_2H_3^+$ ions accepting a D^- entity from a deuterated reactant (RD). The position of the deuterium atoms was established by analysis of the ethane fraction on a high-resolution mass spectrometer using verified standard mass spectral cracking patterns for CD_3CDH_2 , CD_2HCD_2H , CD_3CH_3 , and CD_2HCDH_2 , which were run on the same instrument. The latter were in consistent agreement with those reported by Bell and Kistiakowski.⁷ A complete detailed analysis of the data as well as the interpretation of other facets relating to the photolysis and radiolysis of alkyl halides would require an inordinate amount of space and will be presented later.⁸ The distributions given in the last column represent that of the ethane- d_3 product formed in the H^- (D^-) transfer reaction within the indicated error limits. All thermal free radicals were removed by O_2 or NO and a small unscavengeable contribution from "hot" ethyl radicals abstracting⁹ a H (D) atom has been taken into account. In the 11.6–11.8-eV CD_3CH_2I-RH photolysis experiments the reaction $CD_3CH_2^* + RH \rightarrow CD_3CH_3 + R$ accounts for 5% of the ethane fraction under conditions ($RH/CD_3CH_2I > 5$) where over 90% of the $C_2D_3H_2^+$ ions are intercepted by RH . From the limiting value of ethane observed at high RH concentrations, it is estimated that at 11.6–11.8 eV (pressure, 5 Torr), 20% of the photons absorbed by ethyl iodide result in the formation of ethyl cations ($\Phi(C_2H_5^+) = 0.2$). In the photolysis of pure ethyl iodide the quantum yield of ethane which can be ascribed to hot ethyl radicals is 0.011, 0.009, and 0.004 at 8.4, 10, and 11.6–11.8 eV, respectively. In contrast with the 11.6–11.8-eV photolysis, no increase of Φ (ethane) is noted when RH is added to CD_3CH_2I-NO (1:001) mixtures at photon energies (8.4–10.0 eV) below the threshold for $C_2D_3H_2^+$

formation (appearance potential = 10.6 eV). In the radiolysis of ethyl iodide (pressure, 200–500 Torr) the G value of hot ethyl radicals and of ethyl cations is 0.08 and 1.2, respectively. As expected in both the photolysis and radiolysis, the ethane- d_3 produced by thermal as well as by hot CD_3CH_2 radical reactions consists exclusively of CD_3CH_3 .

The proton transfer (Figure 1) and the hydride transfer (Table I) results taken together can only be accounted for by a statistical scrambling of the hydrogen atoms in the ethyl cation irrespective of its structure. Furthermore, the fact that at pressure up to 1000 Torr of reactant gas (RH or RD) the H and D atoms in the ethyl cation are statistically scrambled shows that 1,2 hydride shift occurs with a high rate constant ($k > 10^{10}$ sec⁻¹). Of particular importance is the observation that the $C_2D_3H_2^+$ formed (appearance potential = 11.4 eV) in the photoionization of CD_3CH_2Br is statistically scrambled. It follows that, in agreement with recent calculations,^{2a,11} the energy barrier of a 1,2 hydride shift in the ethyl cation must be less than about 5 kcal/mol. This is in agreement with the observation that an energy barrier of not more than 6 kcal/mol can be attributed to the 2,3 hydride shift in 2-butyl cations formed in $SbF_5-HSO_3^{21}$ or $SO_2ClF-SbF_5$.^{2k}

The present results do not throw any light as to the structure of the $C_2X_3^+$ ion at the time of reaction. Also, it should be emphasized that the present study does not exclude the existence of unscrambled ethyl cations at the shorter reaction times encountered in condensed phase systems.

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Rates of Exchange of Acetic Acid Molecules at the Amide Hydrogen-Bond Acceptor Site of Aniline Bases

Sir:

Recent work has established that there is a relationship between hydrogen-bond acceptor strength and base strength only for bases of closely related structure.^{1,2} Equilibrium constants for hydrogen-bond formation then increase slowly with K_B , the slope of the linear free-energy correlations being about 0.2.¹ We now wish to report some results concerning the kinetics of hydrogen bonding for a number of meta- and para-substituted anilines. Basicity and hydrogen bond strength should be well correlated in this series.

Using methods described previously,³⁻⁵ we have obtained rate constants (k_H) for the exchange of acetic acid molecules at the $-NH_2$: hydrogen-bond acceptor

(5) "Eight Peak Index of Mass Spectra," compiled by ICI Industries Ltd., Mass Spectrometry Data Centre, AWRE, U. K., 1970.

(6) (a) J. H. Futrell and T. O. Tiernan, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968, Chapter 4; (b) P. Ausloos and S. G. Lias, "Ion-Molecule Reactions," J. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 16.

(7) J. A. Bell and G. B. Kistiakowski, *J. Amer. Chem. Soc.*, **84**, 3417 (1962).

(8) P. Ausloos and R. E. Rebbert, *J. Res. Nat. Bur. Stand.*, to be published.

(9) R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, **47**, 2849 (1967).

(1) R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer, and J. W. Rakshys, *J. Amer. Chem. Soc.*, **91**, 4801 (1969).

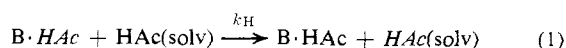
(2) E. M. Arnett, R. P. Quirk, and J. J. Burke, *ibid.*, **92**, 1260 (1970); E. M. Arnett and E. J. Mitchell, *ibid.*, **93**, 4052 (1971).

(3) E. Grunwald and E. M. Price, *ibid.*, **86**, 2970 (1964).

(4) E. Grunwald and M. S. Puar, *ibid.*, **89**, 6842 (1967).

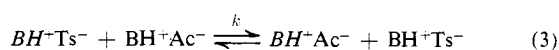
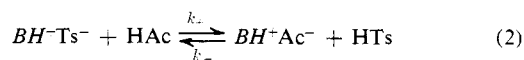
(5) M. R. Crampton and E. Grunwald, *ibid.*, **93**, 2987 (1971).

site of the aniline (B) in anhydrous acetic acid (eq 1).

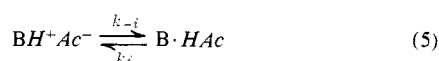


Values of k_{H} were obtained by a kinetic analysis of proton exchange rates determined by nmr techniques. In brief, the method requires the measurement of the T_1 and T_2 relaxation times of the carboxyl proton resonance of the solvent for a series of solutions containing the *p*-toluenesulfonate salt (BH^+Ts^-) of the aniline of interest and a variable concentration of *p*-toluenesulfonic acid (HTs).^{4,5} The determination of T_2 by the pulsed nmr spin-echo method³ was simplified considerably by coupling the spectrometer with a Wang Model 700 calculator using an Adams-Smith Model 100-3 interface.⁶

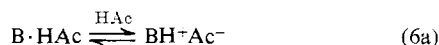
Rate constants for the following processes were derived from the nmr results.⁷ Proton exchange ac-



According to eq 4 very probably occurs by a mechanism involving proton transfer (k_{-i} , eq 5), rate-determining



exchange of HAc (eq 1),^{3,4} and reverse proton transfer (k_i , eq 5). That is to say, $k_i \gg k_{\text{H}}$, and consequently $k_e = k_{-i}k_{\text{H}}/k_i$. The ratio k_i/k_{-i} is equal to the base ionization constant K_i^{B} (eq 6), a known quantity.⁵ If



$$K_i^{\text{B}} = [\text{BH}^+\text{Ac}^-]/[\text{B}] \quad (6b)$$

this be granted, then the values obtained for k_{H} are accurate to at least 20% for all our substrates except *p*-anisidine where the error is about 30% (on the basis of the combined errors in k_e and K_i^{B}).

Results are summarized in Table I. We note in

Table I. Kinetic Summary of Proton Exchange and Hydrogen Bond Replacement for Substituted Anilinium *p*-Toluenesulfonates in Acetic Acid at 30°

| Substituent | k_{H} , sec ⁻¹ | K_i^{B} | pK_{A} (water) ^a | k_{-} , sec ⁻¹ M^{-1} | k_i , sec ⁻¹ M^{-1} |
|--|------------------------------------|------------------|--------------------------------------|---|---------------------------------------|
| <i>p</i> -OCH ₃ | 3×10^9 | 32.8 | 5.24 | | |
| <i>p</i> -CH ₃ ^b | 2.0×10^9 | 19.2 | 4.99 | 7.5×10^9 | 8.2×10^8 |
| <i>m</i> -CH ₃ | 3.3×10^9 | 9.56 | 4.64 | 8.1×10^9 | 11×10^8 |
| <i>p</i> -F | 2.6×10^9 | 4.66 | 4.56 | 10×10^9 | |
| <i>m</i> -OCH ₃ | 1.8×10^9 | 4.71 | 4.15 | 9.9×10^9 | $\sim 9 \times 10^8$ |

^a A. I. Biggs, *J. Chem. Soc.*, 2573 (1961). ^b Reference 5.

passing that values obtained for k_{-} and k_i are consistent with values reported previously.^{4,5}

According to eq 1, the exchange process characterized by k_{H} involves the breaking of an $\text{N} \cdot \text{HAc}$ hydrogen bond and the formation of a new one. If hydrogen-

(6) Adams-Smith, Inc., Needham Heights, Mass.

(7) Required values of the equilibrium constant $K = k_+/k_-$ were taken from C. S. Leung and E. Grunwald, *J. Phys. Chem.*, **73**, 1822 (1969).

(8) G. W. Ceska and E. Grunwald, *J. Amer. Chem. Soc.*, **89**, 1371 (1967).

bond strength were an important factor, we would expect k_{H} to increase with decreasing bond strength and hence with decreasing basicity.⁹ However, it is clear from the data in Table I that there is no correlation at all between k_{H} and basicity as measured either by K_i^{B} in acetic acid or by pK_{A} in water. Although the variation of k_{H} is not large (the range of $\log k_{\text{H}}$ is 0.3 while that of $\log K_i^{\text{B}}$ is 0.85), it seems safe to conclude that factors other than basicity have an overriding effect. This conclusion is consistent with earlier observations of the effect of structure on k_{H} for amines in water¹⁰ and for *N*-alkylanilines in acetic acid^{4,10} where basicity was also shown to be relatively unimportant and where it was indicated that London dispersion forces contribute a dominant interaction. The present communication offers evidence supporting the claim that hydrogen bond strength is not an important consideration for the rate-determining process measured by k_{H} .

Acknowledgments. This work was supported in part by grants from the National Science Foundation and by Brandeis University's Biomedical Science Research Committee. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(9) We are assuming that the equilibrium constant for H-bond formation is greater than 1. That is, in eq 1, the breaking of the H bond is the rate-determining step for the overall exchange process.

(10) E. Grunwald and E. K. Ralph, *Accounts Chem. Res.*, **4**, 107 (1971).

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A ¹³C Nuclear Magnetic Resonance Study on the Biosynthesis of Pyrrolnitrin from Tryptophan by *Pseudomonas*

Sir:

Previous studies^{1,2} with *Pseudomonas aureofaciens* have shown that the antifungal antibiotic pyrrolnitrin (I) is derived from tryptophan. Using various isotopically labeled tryptophan species it was demonstrated³ that C-2 of the indole nucleus is retained, the amino nitrogen becomes the pyrrole nitrogen, the indole nitrogen gives rise to the nitro group, and tritium from C-2 of the side chain of L- but not D-tryptophan is retained during the biosynthesis. These studies supported the proposed⁴ biosynthetic sequence shown in Scheme I, path a. This sequence suggests that the two chlorine atoms found in pyrrolnitrin are introduced late in the biosynthesis, presumably immediately before the last step,² the oxidation of the amino to the nitro group. However, this requires introducing chlorine into the 3 position of the pyrrole ring, whereas the normal patterns of electrophilic substitution of pyrroles predict

(1) D. H. Lively, M. Gorman, M. E. Haney, and J. A. Mabe, *Antimicrob. Ag. Chemother.*, 462 (1966).

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(3) H. G. Floss, P. E. Manni, R. L. Hamill, and J. A. Mabe, *Biochem. Biophys. Res. Commun.*, **45**, 781 (1971).

(4) M. Gorman and D. H. Lively in "Antibiotics," Vol. II, D. Gottlieb and P. D. Shaw, Ed., Springer-Verlag, New York, N. Y., 1967, p 433.