

10,400), 295 (1850), 305 sh (1550), 328 sh (119), 343 (143), 358 (137), and 375 (66), and  $\lambda_{\max}$  5.86  $\mu$  (C=O).

*Anal.* Calcd. for  $C_{42}H_{22}O_4$ : C, 84.54; H, 4.73; mol. wt., 596.6. Found: C, 84.47; H, 4.58; mol. wt. (thermal osmometer), 574.

On standing, the mother liquors deposited an additional 1.9 g. of solid which was extracted with 80 ml. of a hot 1:1 mixture of ethanol-acetonitrile and then recrystallized by dissolution in acetonitrile and addition of water to the hot solution. On cooling, 0.32 g. of VIIIb was collected, m.p. 235° (red coloration). An additional 0.10 g. (total yield 4.2%), m.p. 233° (red coloration), was isolated by dilution of the hot extracts with water followed by cooling. A second recrystallization of the combined product from acetonitrile-water gave 0.38 g., m.p. 238° (red coloration). The compound displayed absorption maxima at  $\lambda_{\max}^{CH_2CN}$  245 (sh)  $m\mu$  ( $\epsilon$  9300), 292 (1730), 300 sh (1550), 332 sh (80), 343 (104), 355 (100), and 372 sh (50), and  $\lambda_{\max}$  5.80  $\mu$  (C=O).

*Anal.* Calcd. for  $C_{42}H_{22}O_4$ : C, 84.54; H, 4.73; mol. wt., 596.6. Found: C, 84.56; H, 5.42; mol. wt. (thermal osmometer), 619.

By evaporation of the original mother liquors, dissolution of the residue in alcohol, and fractional precipitation with water, 0.1 g. of 2,3-diphenylindenone oxide could be isolated from the more soluble fraction. The mother liquors were shown spectrally to contain about 10% of the original weight of the starting material.

In a second run using conditions similar to those used in the formation of the dimethyl acetylenedicarboxylate adduct IV, a solution of 0.14 g. (0.47 mmoles) of the indenone oxide in 125 ml. of freshly distilled diethyl succinate was rapidly heated under nitrogen up to 175° and maintained at this temperature for 24 min. After cooling and allowing to stand for 65 hr., the resulting red solution was evaporated *in vacuo* and the residue crystallized from methanol to give 0.055 g. of crude dimer. The mother liquors yielded a total of 0.025 g. (18%) of unchanged 2,3-diphenylindenone oxide.

**Acid Hydrolysis of Dimer VIIIa.**—To a solution of 1.05 g. (1.76 mmoles) of the dimer in 20 ml. of benzene was added 60 ml. of acetonitrile followed by 3.0 ml. of concentrated hydrochloric acid. After stirring for 1 hr. at room temperature, the mixture was poured into water and the organic solvents were removed *in vacuo*. The aqueous solution was decanted from the gummy precipitate and the latter washed, dried, and recrystallized by dissolving in 5 ml. of ethanol at room temperature and then cooling. The product 0.750 g., after trituration with three ~4-ml. portions of acetonitrile weighed 0.159 g., m.p. 230–232° (red coloration).<sup>14</sup> The combined extracts were concentrated to ~7 ml., added to an equal volume of ethanol, and diluted with water to the cloud point to give 0.450 g., m.p. 200–220° (red coloration). Dissolution of this product in a little alcohol at room temperature followed by cooling gave an additional 0.441 g. (total yield of XII, 55%), m.p. 220–222° (red coloration),<sup>14</sup> which was spectrally indistinguishable from the higher melting product. If the product was heated at any stage during the work-up, purification became more difficult and lower yields were obtained. The product showed only benzenoid absorption in the ultraviolet and no carbonyl absorption in the infrared:  $\lambda_{\max}$  2.82  $\mu$  (OH).

*Anal.* Calcd. for  $C_{42}H_{20}O_6$ : C, 82.08; H, 4.89. Found: C, 81.93; H, 5.21.

**Reaction of Dimer VIIIa with Dimethyl Acetylenedicarboxylate.**—A mixture of 0.211 g. (0.354 mmole) of the dimer in 0.5 ml. (4.1 mmoles) of dimethyl acetylenedicarboxylate was heated under nitrogen for 20 min. in a bath maintained at 190–200°. The excess reagent was removed under reduced pressure at 100° and the resulting residue trituated with methyl alcohol to give 0.250 g. (0.581 mmole, 82%) of the adduct IV, m.p. 169–171°.

**Reaction of Dimer Hydrate XII with Dimethyl Acetylenedicarboxylate.**—The preceding procedure was repeated using 0.197 g. (0.32 mmole) of the hydrate XII. The crude product crystallized from methanol to give 0.100 g. (0.228 mmole, 71%) of IV, m.p. 165–169°. No other product was isolated.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PENNSYLVANIA]

## General Base Catalyzed Ethanolsis of Ethyl Trifluoroacetate

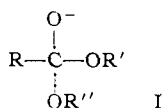
BY S. L. JOHNSON

RECEIVED MARCH 28, 1964

General base catalyzed ethanolsis of ethyl trifluoroacetate has been found. This finding is inconsistent with a concerted mechanism. The numerical value of the catalytic constant is consistent with a mechanism involving the base-assisted formation of an anionic tetrahedral intermediate but is not consistent with the alternative mechanism which involves the specific base-general acid catalyzed formation of a neutral tetrahedral intermediate.

### Introduction

In substitution reactions on the carbonyl carbon of carboxylic esters of the type  $RCO_2R'$  no reaction intermediate definitely lying on the reaction path has ever been detected by kinetic means, or by the observation of a transient intermediate during the course of the reaction.<sup>1</sup> A tetrahedral intermediate, I, has been observed from the reaction of  $RCO_2R'$  with  $M^+OR''^-$  in



dibutyl ether as detected by the disappearance of  $\nu_{C=O}$  in the infrared.<sup>4,5</sup> The acyl part of  $RCO_2R'$  must con-

tain strongly electron-withdrawing groups for this reaction to take place and the solvent must have a very low dielectric constant in order to favor I over  $M^+OR''^-$ . The tetrahedral intermediate formation has been observed for a number of  $R''$  groups,<sup>5</sup> including ethyl, *n*-butyl, isopropyl, and *t*-butyl. It is at least reassuring when postulating tetrahedral reaction intermediates that such intermediates can be observed under special conditions.

Further evidence<sup>6–11</sup> of tetrahedral intermediate formation comes from concurrent hydrolysis and  $O^{18}$  exchange into the ester when hydrolysis is carried out in  $H_2O^{18}$ . The partitioning of the intermediate as measured by the ratio of the rates of hydrolysis and  $O^{18}$  exchange into the ester is equal to  $2k_2/k_{-1}$  in the scheme

(6) M. L. Bender, *ibid.*, **73**, 1626 (1951).

(7) M. L. Bender, R. D. Ginger, and K. C. Kemp, *ibid.*, **76**, 3350 (1954).

(8) C. A. Bunton, T. A. Lewis, and D. H. Llewellyn, *Chem. Ind. (London)*, 1154 (1954).

(9) M. L. Bender, R. D. Ginger, and J. P. Unik, *J. Am. Chem. Soc.*, **80**, 1044 (1958).

(10) C. A. Bunton and D. N. Spatcher, *J. Chem. Soc.*, 1079 (1956).

(11) M. L. Bender, H. Matsui, R. J. Thomas, and S. W. Tobey, *J. Am. Chem. Soc.*, **83**, 4193 (1961).

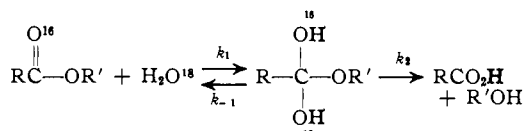
(1) However, Bruce and Fedor have kinetically demonstrated the necessity for an intermediate in the reaction of hydroxylamine with a thiol acetate,<sup>2</sup> and Hand and Jencks have similarly demonstrated the necessity for an intermediate in the reaction of amines with imido esters.<sup>3</sup>

(2) T. C. Bruce and L. R. Fedor, *J. Am. Chem. Soc.*, **86**, 738 (1964).

(3) E. S. Hand and W. P. Jencks, *ibid.*, **84**, 3505 (1962).

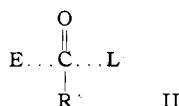
(4) M. L. Bender, *ibid.*, **75**, 5986 (1953).

(5) A. Moffat and H. Hunt, *ibid.*, **81**, 2082 (1959).



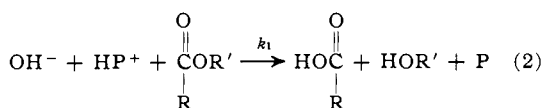
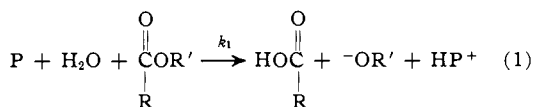
The values of  $k_2/k_{-1}$  for such systems vary from 0 to  $\infty$ ; these values can generally (but not always<sup>11</sup>) be correlated with the leaving ability of OR'. The variation of acidic *vs.* basic hydrolysis rates of ethyl benzoate by a factor of  $10^4$  as contrasted<sup>9</sup> to the variation in the  $k_2/k_{-1}$  values of only two is evidence that the intermediate lies *on* the reaction path.

The mere observation that O<sup>18</sup> exchange occurs during the hydrolysis of an ester does not necessarily mean that such an intermediate lies *on* the reaction path. This intermediate has never been observed as a transient during the course of the reaction,<sup>12</sup> nor has the intermediate ever been demonstrated by conclusive kinetic evidence. An S<sub>N</sub>2 mechanism for ester hydrolysis is an alternative mechanism, with O<sup>18</sup> exchange into the ester occurring *via* a blind alley. The square-planar S<sub>N</sub>2 transition state II has been favored<sup>14</sup> because of the overlap between the  $\pi$ -orbitals of the entering group E and leaving group L with the carbonyl group.

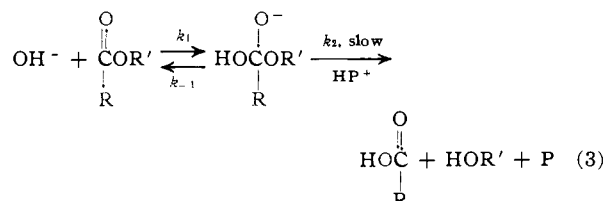


The mechanistic possibilities in ester hydrolysis (or solvolysis) are rather large in view of the possibility of intermediate formation. The transition state could be either the rate-determining formation of the intermediate, the rate-determining destruction of the intermediate, or the S<sub>N</sub>2-like transition state. No less than seven mechanistic schemes demonstrated by eq. 1-7 are consistent with the observation of general base catalysis for the hydrolysis (or solvolysis) of esters. In schemes 4 and 6 either the first step or the second step can be slow; the other two-step mechanisms in eq. 3, 5, and 7 have their slow steps marked. The general base in the following schemes is denoted by P.

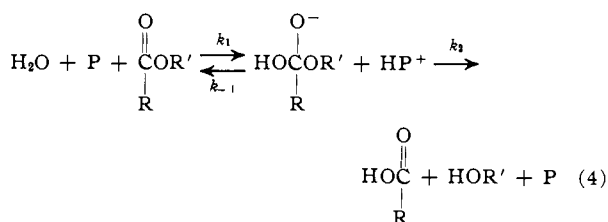
Concerted mechanisms:



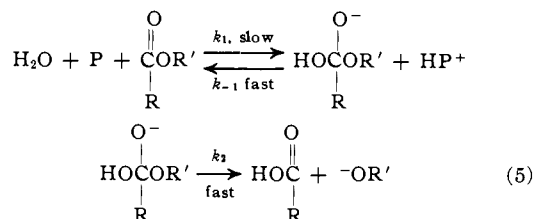
Specific base, general acid stepwise through an anionic intermediate:



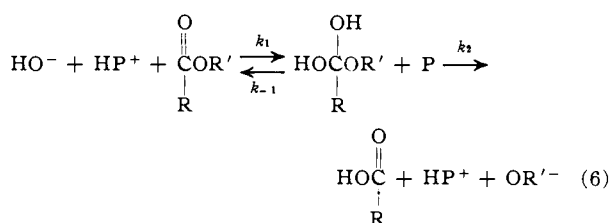
General base, general acid stepwise through an anionic intermediate:



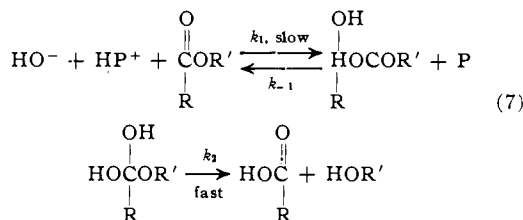
General base stepwise through an anionic intermediate:



Specific base, general acid, general base stepwise through a neutral intermediate:



Specific base, general acid stepwise through a neutral intermediate:



In order to simplify the above state of affairs, the general base-catalyzed ethanolysis of ethyl trifluoroacetate in heavy ethanol (C<sub>2</sub>D<sub>5</sub>OH) has been carried out. The entering group is chemically nearly identical with the leaving group; therefore there is nearly equal partitioning in the intermediate.

### Experimental

**Materials.**—Water-free acetaldehyde-free heavy ethanol was obtained from Merck of Canada. Ethyl trifluoroacetate (K and K) was carefully distilled twice using a packed column; b.p. 60.8° at 742 mm. Pyridine (Eastman Kodak) was refluxed over calcium hydride overnight and then distilled. Pyridinium nitrate, m.p. 118–119° cor., was prepared from nitric acid and pyridine in water, dried over phosphorus pentoxide, and then sublimed. Methanol and *t*-butyl alcohol were carefully dried by standard procedures.<sup>15</sup> Eastman Kodak 2,6-lutidine was treated with boron trifluoride, and the unreacted 2,6-lutidine was removed by distillation<sup>16</sup>; b.p. 143.5° at 744 mm. The purity of the reagents was checked by v.p.c. methods which indicate that all reagents were water free. The heavy ethanol was found to contain no acetaldehyde or paraldehyde, and the ethyl trifluoroacetate contained no trifluoroacetic acid.

(12) However, in the reaction of acid chlorides with amines a transient intermediate has been observed.<sup>14</sup>

(13) S. G. Entelis and O. V. Nesterov, *Dokl. Chem. Proc. Acad. Sci. U.S.S.R.*, **148**, 174 (1963).

(14) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1948, p. 117.

(15) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955.

(16) H. C. Brown, S. Johnson, and H. Podall, *J. Am. Chem. Soc.*, **76**, 5556 (1954).

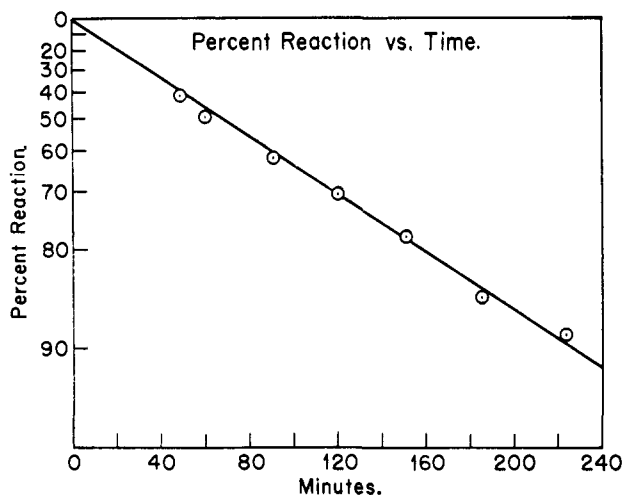


Fig. 1.—Percentage reaction *vs.* time for the reaction  $C_2H_5O_2CCF_3 + C_2D_5OH \rightarrow C_2D_5O_2CCF_3 + C_2H_5OH$  in a buffer mixture of 0.192 *m*  $C_5H_5N$ , 0.152 *m*  $C_5H_5NH^+NO_3^-$  in  $C_2D_5OH$  at 38°.

**Kinetics.**—The rate of the exchange reaction between  $C_2H_5O_2CCF_3$  and  $C_2D_5OH$  giving the final product  $C_2D_5O_2CCF_3$  and  $C_2H_5OH$  was followed by observing the decrease in the proton magnetic resonance signal of the methyl group in the ester ( $\tau = 8.63$ ) and the increase in the proton magnetic resonance signal of the methyl group of the alcohol ( $\tau = 8.72$ ). A Varian A-60 n.m.r. spectrometer was used for this purpose. The kinetic runs were thermostated in a  $38.0 \pm 0.1^\circ$  constant temperature bath; the probe temperature was  $38.0 \pm 0.5^\circ$ . The rate of increase of the ethanol signal was equal to the rate of decrease of the ethyl ester signal. Good first-order plots were obtained upon plotting  $\log h_t$  *vs.* time where  $h_t$  represents the height of the ester signal at any time *t*. This is the expected behavior for isotopic exchange reactions.<sup>17</sup> An example of such a plot is shown in Fig. 1.

The solutions were prepared by weighing up all of the required amount of reagents except for the ester in an n.m.r. tube. Ethyl trifluoroacetate was added to the thermostated tubes with the aid of a micropipet at time = 0. The approximate concentration of the ester was 0.2 *M*. A v.p.c. analysis of the products indicated no diethyl ether or diethyl carbonate formation; therefore, no side reactions leading to these products are taking place.

## Results

**General Base Catalysis of Ethanolsis.**—In Table I are the results of the pyridine-catalyzed ethanolsis of

TABLE I  
THE KINETICS OF ETHANOLYSIS OF ETHYL TRIFLUOROACETATE  
AT 38° IN  $C_2D_5OH$

B, <sup>a</sup> <i>m</i>	BH <sup>+</sup> , <sup>a</sup> <i>m</i>	NaClO <sub>4</sub> , <i>m</i>	<i>k</i> <sub>obsd.</sub> , sec. <sup>-1</sup> × 10 <sup>3</sup>
0.472	0.0766	...	32.0
.345	.0561	...	26.2
.266	.0432	...	17.5
.140	.023	...	10.5
.089	.0144	...	6.78
.192	.152	...	17.0
0	0	...	0.15
0.154	0.018	...	9.19 ± 0.43
.154	.018	0.119	12.0
.154	.018	0.429	16.0

<sup>a</sup> Pyridine-pyridinium nitrate buffer.

ethyl trifluoroacetate. The rate is dependent only upon the pyridine concentration in the buffer solutions; no general acid catalysis was found. No general acid catalysis would be expected on the basis of the work of Jencks and Carriuolo.<sup>18</sup> A positive salt effect was

(17) H. A. C. McKay, *Nature*, **142**, 997 (1938).

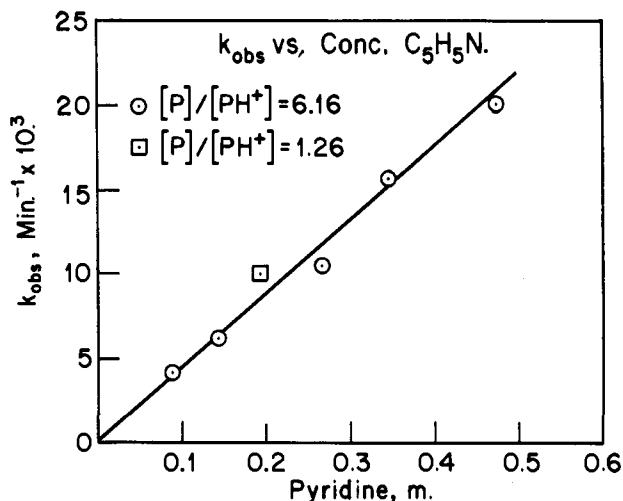


Fig. 2.—Plot of *k*<sub>obsd</sub> for the rate of ethanolsis of ethyl trifluoroacetate *vs.* pyridine concentration in buffered solutions of pyridine and pyridinium nitrate: ○,  $P/PH^+ = 6.16$ ; □,  $P/PH^+ = 1.26$ .

separately measured. Figure 2 is a plot of *k*<sub>obsd</sub> *vs.* the pyridine concentration in the buffer. The catalytic coefficient obtained from this plot is  $7.4 \times 10^{-4} m^{-1} sec^{-1}$ .

**General Base Catalyzed Methanolysis and *t*-Butanolysis.**—As part of the investigation of solvolysis of ethyl trifluoroacetate, two more alcohols, methanol and *t*-butyl alcohol, were used as solvolytic media. These two alcohols have n.m.r. signals that are well separated from the ethyl ester and ethanol signals. Using a 2,6-lutidine-2,6-lutidinium chloride buffer and a pyridine-pyridinium perchlorate buffer, strong catalysis was found for both bases in methanol, and a slow uncatalyzed solvolysis was observed. In *t*-butyl alcohol, no general base catalysis could be detected, even upon using buffer solutions as concentrated as 2 *M* in pyridine.

## Discussion

**Mechanistic Possibilities.**—In symmetrical exchange reactions the reaction path must be symmetrical. In the case of the concerted mechanism corresponding to eq. 1 or 2 the transition state itself must be symmetrical with respect to the entering and leaving groups. In the case of the stepwise mechanisms the formation of the symmetrical tetrahedral intermediate (through an unsymmetrical transition state) provides the point of symmetry in the reaction path. The possibility of nucleophilic catalysis which also provides a symmetrical reaction path can be ruled out because it was found that 2,6-lutidine catalyzes the methanolysis of the substrate almost as well as pyridine does. Such behavior would not be expected from nucleophilic catalysis,<sup>19</sup> but would be expected for general base catalysis.<sup>20</sup> Mechanisms involving acylium ion formation can be ruled out because of the improbability of introducing a full positive charge on a carbonyl atom with highly electron-withdrawing substituents on it.

Specific base, general acid stepwise mechanisms analogous to eq. 3 and 7 (substituting  $C_2D_5OH$  for  $H_2O$  and  $C_2D_5O^-$  for  $HO^-$ ) violate the principle of micro-

(18) W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **83**, 1743 (1961).

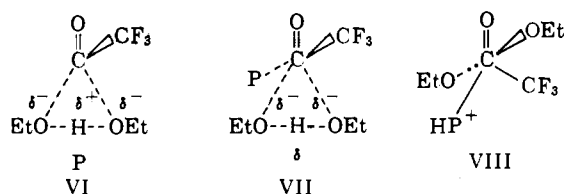
(19) V. Gold and A. R. Butler, *J. Chem. Soc.*, 4362 (1961).

(20) F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.* **85**, 1773 (1963).



ergies of interaction of P with X + Y which would allow two asymmetric paths to be taken as is illustrated by the hypothetical case in structure III. The real transition state corresponds to V (in Fig. 4) where the two C-O bonds in the transition state are symmetrical with respect to the position of PH<sup>+</sup>

In order to describe the transition state for a general base catalyzed process for a symmetrical reaction, it is necessary to include the base bound to the proton which is symmetrically situated with respect to both the entering and leaving groups. This proton then must be completely, or nearly completely, transferred to the P moiety. It is conceivable that the PH<sup>+</sup> unit is bound to the two OEt groups, but this bonding must be rather weak as this would represent a three-center hydrogen bond. The square-planar Dewar-type<sup>14</sup> transition state illustrated by V is not the only way to write a transition state which fulfills the requirement of leaving the carbonyl group largely intact while at the same time allowing the two C-OEt bonds to be equivalent; VI, VII, and VIII also fulfill this requirement. Transition state VI is a trigonal arrangement of the carbonyl



bond and the two C-OEt bonds, with the proton shared equally between the two partially negative alkoxy oxygens. In this case it is difficult to see what P is doing other than solvating the transition state as specifically drawn in VII. Certainly the proton is not partially transferred to the general base as is required in reactions catalyzed by general bases.<sup>23</sup> Furthermore, 2,6-lutidine would be expected to be much poorer in solvating a transition state than pyridine. In VIII, there is no possibility that the proton be hydrogen bonded between the two ethoxide oxygens because of their linear arrangement perpendicular to the plane of the paper and the proton is completely transferred to the general base. No postulated transition state which can be drawn for the concerted symmetrical general base-catalyzed reaction makes much sense in terms of a partial proton transfer to P. Each suffers from either no proton transfer to P or from complete proton transfer to P, and therefore does not constitute true general base catalysis. Furthermore, if mechanisms A and B were postulated such that there is no stable tetrahedral intermediate formed, but rather that the tetrahedral intermediate represented the transition state itself, then these two situations would not represent general base catalysis because all proton transfers would be complete by the time the highest energy region of the reaction path was achieved. On the basis that the proton must be *partially* transferred to the general base in order to observe general base catalysis, all concerted mechanisms may be discarded for this symmetrical exchange reaction. This constitutes very strong evidence that an intermediate lies *on* the reaction path in the solvolysis of a carboxylic ester of type RCO<sub>2</sub>R'.

(23) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

Of the two possible mechanisms A and B, B may be ruled out from the knowledge of the catalytic and protolysis rate constants and complex formation equilibrium constants. The catalytic constant expression for a reaction proceeding through transition state B may be written  $(k^*/2)(K_{\text{EtOH}}/K_{\text{C}_6\text{H}_5\text{NH}^+})K_{\text{complex}}$  assuming that the reaction proceeds in a stepwise manner by prior formation of an ester ··· HP<sup>+</sup> hydrogen-bonded complex at the carbonyl oxygen followed by the reaction of this complex with an ethoxide ions. The autoprotolysis constant of ethanol,  $K_{\text{EtOH}}$ , is equal<sup>24</sup> to  $10^{-19.1}$  and the acid dissociation constant of pyridine,  $K_{\text{C}_6\text{H}_5\text{NH}^+}$ , is approximated<sup>25</sup> by  $10^{-6.4}$  because of the generality that protonated bases of type PH<sup>+</sup> in ethanol have a pK<sub>a</sub> value *ca.* 1.2 units greater than in water. A *very generous* value for  $K_{\text{complex}}$ , the equilibrium constant for the formation of the ester ··· HB<sup>+</sup> hydrogen-bonded complex, is  $0.5 M^{-1}$ . This is because the complexing constants of a number of carbonyl compounds with phenol in carbon tetrachloride indicate a value<sup>25</sup> near unity or less, depending upon the electron-withdrawing groups in the carbonyl compounds. In non-hydroxylic solvents the complexing constant is at a maximum value because the equilibrium is between the two totally uncomplexed donor and acceptor and the complex. In a hydroxylic solvent the  $K_{\text{complex}}$  is expected to drop considerably because of the stabilization of the "uncomplexed" species by hydrogen-bonding interactions with the solvent. The free energy of the "reagents" will now be considerably lower than the same "reagents" in carbon tetrachloride. An example of this effect is the large change in dimerization constant of acetic acid in benzene and in water. The  $K_{\text{dimer}}$  values are 151 and  $0.037 M^{-1}$ , respectively,<sup>26</sup> a change by a factor of  $4.2 \times 10^3$ . The value of 0.5 for  $K_{\text{complex}}$  is undoubtedly too high by two or three orders of magnitude, but since we have no way of predicting it accurately without further data a value of  $0.5 M^{-1}$  will be taken as an upper limit.

Using the observed value of the catalytic coefficient,  $7.4 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ , the *lower limit* of  $k^*$ , the rate-determining step in mechanism B, is  $7.4 \times 10^9 M^{-1} \text{ sec}^{-1}$ . This value is in the midrange of what is expected for a diffusion-controlled reaction rate constant, and is certainly not the expected magnitude for a reaction involving covalent C-O bond making and breaking.<sup>27</sup> A reasonable value for the rate constant for the combination of a lyoxide ion with a positively charged carbonyl carbon is  $1.5 \times 10^5 M^{-1} \text{ sec}^{-1}$  obtained for the reaction of hydroxide and N-methyl-N'-acetyl-imidazolium ion.<sup>28</sup>

Alternatively, mechanism B may be postulated as a prior equilibrium formation of a complex between ethoxide ion and the ester followed by protonation of the complex with HP<sup>+</sup>. The catalytic constant may now be written  $k_{\text{cat}} = (k^*/2)(K_{\text{EtOH}}/K_{\text{C}_6\text{H}_5\text{NH}^+})K'_{\text{complex}}$ . The most reasonable complex is the anionic tetrahedral intermediate; the value of  $K'_{\text{complex}}$  in ethanol for this

(24) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(25) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963).

(26) M. Davies and D. M. L. Griffith, *Z. physik. Chem.*, **2**, 353 (1954).

(27) M. Eigen in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 1031.

(28) R. Wolfenden and W. P. Jencks, *J. Am. Chem. Soc.*, **83**, 4390 (1961).

type of complexing is<sup>4,29</sup>  $<0.05$ . On this basis the lower limit of  $k^*$  is  $2.4 \times 10^{11} M^{-1} \text{sec}^{-1}$ . This value is larger than the fastest protolytic constant yet measured,<sup>27</sup> that for the combination of hydroxide ion and hydronium ion in water, which gives the value  $1.4 \times 10^{11} M^{-1} \text{sec}^{-1}$ ; in this reaction the steric factors and acidity–basicity factors are optimum. Therefore mechanism B *via* a pre-equilibrium formation of an anionic tetrahedral intermediate formation followed by a rate-determining proton transfer may be ruled out. A mechanism which cannot be discredited is the formation of a weaker ethoxide–ester nontetrahedral complex followed by a rate-controlling proton transfer. The  $K'_{\text{complex}}$  for this association reaction would have to be one or greater in order to give a believable value for  $k^*$ . The formation of such a complex with a  $K'_{\text{complex}}$  value greater than one should be easily observable by a physical method, which has not been the case.<sup>29</sup> The

(29) An n.m.r. analysis of a dilute ethanol–sodium ethoxide–ethyl trifluoroacetate solution in benzene shows an unbroadened ester ethyl peak (in both the methyl and methylene regions) and an unbroadened ethanol–ethoxide signal. No other ethyl signals were detectable, even under high amplification, indicating that there is no appreciable concentration of a stable complex formed in which the ethoxide and ester ethyl groups are equivalent, and that there is no rapid exchange of the ethyls through an unstable intermediate. This does not, however, preclude a rapid exchange between the ethoxide of a complex in which the ethoxide is not equivalent to the ester ethyl group and the bulk ethoxide. Also an infrared analysis of an ethanol solution of sodium ethoxide and ethyl trifluoroacetate indicates no complex formation. See ref. 4 for a similar study of methyl trifluoroacetate in sodium methoxide–methanol.

only other possible mechanism for scheme B is an unlikely termolecular collision.

The most likely path for general base catalysis of ethyl trifluoroacetate ethanolysis is therefore mechanism A, the general base-catalyzed formation of the anionic tetrahedral intermediate. The lack of general catalysis for the *t*-butanolysis of ethyl trifluoroacetate must then be due to the low acidity of *t*-butyl alcohol<sup>30</sup> combined with the low dielectric constant for *t*-butyl alcohol.<sup>31</sup> The general base catalyzed solvolysis of ethyl trifluoroacetate would be expected to be decreased by a decrease in the medium dielectric constant because this is the case in the general base catalyzed hydrolysis reaction.<sup>18</sup> The lack of the *t*-butanolysis reaction cannot be due entirely to steric hindrance in the anionic tetrahedral intermediate<sup>5</sup> because ethoxide, *n*-butoxide, isopropoxide, and *t*-butoxide form the anionic intermediate with ethyl trifluoroacetate in di-*n*-butyl ether to the extent of 72, 72, 54, and 51%, respectively.

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## The Mechanism of the Acid-Catalyzed Rearrangement of Triarylmethyl Hydroperoxides

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The acid-catalyzed rearrangements of three triarylmethyl hydroperoxides in aqueous dioxane have been studied. Kinetic, exchange, and equilibrium data prove conclusively that complete equilibration among the triarylcarbinol, hydrogen peroxide, triarylmethyl hydroperoxide, and water occurs prior to any significant amount of rearrangement. The rates of the reactions were found to be proportional to  $k_0$ . A mechanism for the prerearrangement sequence is proposed and discussed.

### Introduction

Triphenylmethyl hydroperoxide undergoes acid-catalyzed rearrangement in a variety of solvents to yield phenol and benzophenone. A substituted triphenylmethyl hydroperoxide yields a mixture of substituted phenols and benzophenones, the composition of the mixture being dependent upon the relative rates of migration of the substituted and unsubstituted phenyl groups. At the outset of the present research we hoped that a quantitative kinetic and product analysis of this reaction would provide data which would be applicable to a modification of the Heck and Winstein treatment of the timing of covalency changes in competitive rearrangement reactions.<sup>3</sup> Such a treatment would have provided evidence concerning the synchronous or stepwise nature of the rearrangement reaction. However, major differences between the behavior of the triarylmethyl systems and that of other hydroperoxides appeared early in the work; consequently, we have concerned ourselves primarily

with the mechanism of the prerearrangement sequence of reactions. A preliminary communication describing these results has already been published.<sup>4</sup>

### Results and Discussion

**A. Rate Studies.**—The acid-catalyzed rearrangement of cumene hydroperoxide has been studied by a number of workers, but there is little agreement about the exact mechanism of the reaction.<sup>5–9</sup> However, there seems to be no question about the order of the reaction. Although complicated by several factors, the reaction was found<sup>8</sup> to exhibit a first-order dependence upon the hydroperoxide concentration and a first-order dependence upon acid concentration. The perchloric acid catalyzed rearrangements of three triarylmethyl hydroperoxides in aqueous dioxane, how-

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