completion and infinity absorbances were taken at 10 half-lives. The pH(D) of the solutions was measured at the end of each run. First-order rate constants were determined from plots of log $(A_t - A_\infty)$.

Experimental values of k_n, k_0, and n were used with a nonlinear least-squares computer program to fit the data to the various models using the fractionation factors as variable parameters.

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Gas-Phase Pathways for Ester Hydrolysis

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Abstract: The gas-phase reaction, $^{18}OH^- + RCOOR' \rightarrow RCO^{18}O^-$ (or $RCOO^-$) + neutrals, has been investigated by ion cyclotron resonance techniques at pressures of 10^{-5} Torr for R = H, $(CH_3)_3C$, CF_3, C_6H_5, CH_3O, and C_2H_5O. Analysis of the oxygen-18 content of the carboxylate anion reveals: (1) Methyl esters react preferentially by acyl-oxygen fission ($B_{AC}2$), but the S_N2 pathway is not negligible and amounts to 5–25% of the reaction. A notable exception is CF_3COOCH_3 for which the S_N2 reaction amounts to 75%. (2) Ethyl esters yield lower ^{18}O content in the ionic product. This observation is ascribed to an elimination-type reaction that results in water and ethylene as neutral products. The results are discussed in terms of a qualitative description of the potential energy hypersurface, recent theoretical calculations, and experimental observations of related reactions. It is argued that the efficiency of the gas-phase pathways is controlled by the ease with which the intermediates can evolve into the final products. A comparison is also made with some reactions of NH_2^-, alkoxides, and F^-.

The hydrolysis of esters constitutes one of the most thoroughly studied reactions in the history of chemistry with regard to rates, mechanisms, and catalytic agents.[1-4] A classical experiment using isotopically labeled water resulted in early evidence that alkaline saponification of amyl acetate proceeds exclusively by breakage of the acyl-oxygen bond,[5] through what was later defined as a $B_{AC}2$ mechanism.[6] Further ^{18}O experiments[7,8] were necessary to resolve some of the mechanistic ambiguities, and in particular to establish that the reaction involves the initial formation of a tetrahedral species by addition of the OH^- to the carbonyl group. The alternate mechanism, an S_N2 or $B_{AL}2$ process with alkyl-oxygen bond fission, is very rare. Such facts have contributed to the entrenched idea that displacement reactions at carbonyl carbon are more facile than at saturated carbon.

Recent experiments carried out by cyclotron resonance techniques have pointed out that several mechanisms may become competitive in the gas-phase reaction of nucleophiles with simple esters.[9-13] For example, OH^- in the gas phase has been shown to react with alkyl formates, $HCOOC_nH_{2n+1}$, to yield associated ions, $C_nH_{2n+1}OHOH^-$, by a decarbonylation process, and $HCOO^-$ by a displacement reaction.[12] More elaborate studies carried out with F^- as the nucleophile probe show that (a) S_N2 processes can become important with several esters; (b) esters with alkyl groups containing β hydrogens display drastic changes in the ionic product distribution.[12,13] This latter feature has been argued to originate from a preferred elimination type reaction (reaction 1), a channel which becomes the dominant reactive pathway, for example, eq 1. In

$$F^- + CH_3COOC_2H_5 \longrightarrow \left[\begin{array}{c} ^-O \quad\quad O{-}CH_2 \\ \diagdown \quad / \quad\quad \diagdown \\ C \quad\quad CH_2 \\ \diagup \quad \diagdown \quad\quad \\ H_3C \quad F \cdots H \end{array} \right]$$

$$\longrightarrow CH_3COO^- + HF + C_2H_4 \quad (1)$$

a related report, Comisarow[14] has shown that the reaction of alkoxide ions with methyl benzoate and methyl trifluoroacetate in the gas phase proceeds only by the S_N2 mechanism.

The above results have prompted us to investigate the gas-phase analogue of base hydrolysis to determine the pathways of this reaction under solvent-free conditions, and to assess the
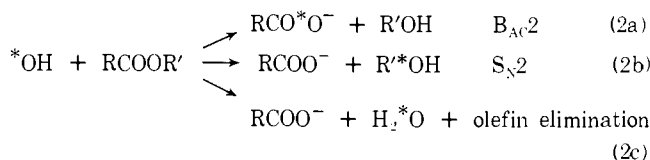
intrinsic reactivity of saturated and unsaturated carbon centers. Thus, a study was undertaken of the reactions of $^{18}OH^-$ with several esters. Measurements of the ^{18}O content in the ionic products were used to establish the relative contribution of the three processes which are operative in the gas phase, 2a-c, and the branching ratio dependence on R and R'

$$*OH + RCOOR' \longrightarrow \begin{cases} RCO^*O^- + R'OH & B_{AC}2 \quad (2a) \\ RCOO^- + R'^*OH & S_N2 \quad (2b) \\ RCOO^- + H_2^*O + \text{olefin elimination} \quad (2c) \end{cases}$$

where R contains no hydrogens α to the carbonyl group. The results of these experiments are compared with the behavior of other nucleophiles in the gas phase (NH_2^-, F^-, and alkoxides) to present an overall view of the reactivity of esters.

Experimental Section

Experiments were carried out in a Varian ICR spectrometer provided with a dual inlet system and a three-section flat cell. The spectrometer was operated in the drift mode with magnetic field modulation. Spectra were obtained by sweeping the magnetic field while the radio frequency remained constant, usually at 153.6 kHz. Typical ion residence times in the cell vary from 1 to 5 ms depending on the magnetic field.[15]

Hydroxide ions were generated from 20% oxygen-18 enriched water (Bio-Rad) by electron impact at 7.6 eV. The inlet system was heated (60-80 °C), but the analyzer system was kept at room temperature. This mode of operation resulted in good signals of OH^- at pressures of $5-8 \times 10^{-6}$ Torr and emission currents of the order of 150 nA. The resulting negative ICR spectra of water were usually free of any other contaminant negative ions.

The ^{18}O percentage of the hydroxide ions was calculated from the relative ion abundances (the marginal oscillator power absorption signal divided by ion mass) of the labeled and unlabeled ions. This percentage was found to vary by as much as $\pm 2\%$ in a given day. Since the ^{18}O content of the carboxylate anions must be normalized with respect to the ^{18}O content of the hydroxide ion, the accuracy of the results was limited in most cases by the above factor. These measurements did not show any noticeable dependence with inlet temperature.

The pulse method developed by Faigle[12,15] to determine ion residence times proved difficult for OH^- at 1700 G. Reliable measurements at the electrometer could only be obtained for analyzer drift fields above 0.35 V/cm, but such conditions yield very poor signals for OH^- under marginal oscillator detection. Therefore, absolute rate constants were not determined in the present experiments. Nevertheless, several attempts were made to determine qualitatively conversion ratios[16] for different esters under similar experimental conditions. Pressure was measured on an ionization gauge calibrated against an MKS Baratron micromanometer. The results of these experiments admittedly yield crude estimates of relative rates.

Alkoxide ions were generated from the corresponding alkyl nitrites,[9] while NH_2^- was obtained by electron impact of NH_3 at 6.5 eV. The corresponding ND_2^- was obtained from 20% ND_3 in D_2O (99% D content, Merck). The inlet system was also heated for NH_2^- operation. Typical pressures of NH_3 were of the order of $1-2 \times 10^{-5}$ Torr with emission currents of 300 nA.

The partial pressure of the esters was kept in the range of $1-3 \times 10^{-6}$ Torr. Since the main objective of our experiments was to study the initial process between the nucleophile and the ester, the pressure of the latter was adjusted so that conversion ratios were no larger than 10%.

Most of the esters used in the present work were of commercial origin. The purity of the samples was verified by positive ion low-pressure ICR, and they were distilled when necessary. Particular care was taken to remove traces of carboxylic acids and alcohols. The esters do not display a negative ion ICR. It should also be emphasized that the results obtained with $^{18}OH^-$ span 8 months and were obtained in two ICR cells made of different materials. The reproducibility of our measurements over this period of time (during which the system was repeatedly baked out and the cells were cleaned in ultrasonic baths and exposed to other chemicals) suggests that any possible in situ

Table I. Relative Contribution of the Different Mechanisms for the Gas-Phase Reaction of Hydroxide Ion with Esters as Measured by the ^{18}O Content of the Ionic Product[a]

	$B_{AC}2$	S_N2	S_N2 or elimination
$HCOOCH_3$	0.73 ± 0.04	0.27 ± 0.04	
$DCOOC_2H_5$[b]	0.23 ± 0.02		0.77 ± 0.02
$HCOOCH(CH_3)_2$	0.21 ± 0.02		0.79 ± 0.02
$(CH_3)_3CCOOCH_3$	0.90 ± 0.02	0.10 ± 0.02	
$(CH_3)_3CCOOC_2H_5$	0.72 ± 0.05		0.28 ± 0.05
$C_6H_5COOCH_3$	0.92 ± 0.05	0.08 ± 0.05	
$C_6H_5COOC_2H_5$	0.58 ± 0.05		0.42 ± 0.05
CF_3COOCH_3	0.24 ± 0.03	0.76 ± 0.03	
$CF_3COOC_2H_5$	0.20 ± 0.03		0.80 ± 0.03
$(CH_3O)_2CO$	0.68 ± 0.04	0.32 ± 0.04	
$(C_2H_5O)_2CO$	0.22 ± 0.02		0.78 ± 0.02

[a] Errors quoted represent the standard deviation of several independent measurements. [b] The use of this compound was necessary to separate the peaks due to formate ion and to $C_2H_5O^-$.

hydrolysis of the esters by heterogeneous catalysis is minimal. Processes of this type are known to be very sensitive to surface composition.
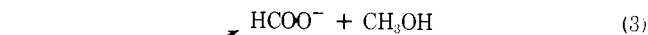
Methyl pivalate was prepared by reaction of distilled $(CH_3)_3$-CCOCl (Eastman) with dry methanol according to the procedure of Whitmore and Forster.[17] The ester was collected by distillation at 60 mmHg in the range of 42-43 °C.

Methyl trifluoroacetate was prepared by reaction of trifluoroacetic anhydride with dry methanol and distilled at 40-41 °C.

Ethyl trifluoroacetate was prepared by Dr. Peter Tiedemann, while $DCOOC_2H_5$ was kindly provided by Dr. Fernando Faigle.[15]

Results

Since methyl or methylene groups attached to a carbonyl group are substantially acidic in the gas phase, hydroxide ion reactions other than proton abstraction could only be studied for a selected number of groups (reaction 2). Except for alkyl formates, the gas-phase hydrolysis reactions with R' = CH_3, C_2H_5, and C_3H_7 yield exclusively $RCOO^-$ as the product ion. For alkyl formates, it has been shown that two other processes are possible.[12]

$$OH^- + HCOOCH_3 \longrightarrow \begin{cases} HCOO^- + CH_3OH \quad (3) \\ CH_3OHOH^- + CO \quad (4) \\ CH_3O^- + H_2O + CO \text{ (or HCOOH)} \quad (5) \end{cases}$$

In the ^{18}O experiments, relative ion abundances of carboxylate anions, $I_{RCOO^-}/I_{RCO^{18}O^-}$, were measured from spectra obtained at low product conversion. These values along with the experimental values of $I_{OH^-}/I_{^{18}OH^-}$ were used to calculate the fraction X of reactive encounters which proceed by the $B_{AC}2$ mechanism.

$$X = [(I_{OH^-}/I_{^{18}OH^-}) + 1]/[(I_{RCOO^-}/I_{RCO^{18}O^-}) + 1]$$

This equation neglects any possible isotope effects of $^{18}OH^-$ vs OH^-. The results of these experiments are listed in Table I.

Reaction 4 was used for calibration purposes in order to investigate any possible problems due to oxygen exchange and subsequent isotopic fractionation. A series of independent measurements revealed that $[CH_3OHOH]^-$ retains $(98 \pm 4)\%$ of the oxygen-18 content of the hydroxide ion. Reaction 5 does not affect the results with the alkyl formates as the alkoxides have been shown to be unable to yield $HCOO^-$.[9] Furthermore,

Table II. Relative Rate Constants for the Reaction of NH_2^- with Alkyl Pivalates

R'	k_7	k_8	k_9	k_{10}
CH_3	1.5	3.8	1	1.1
C_2H_5	0.5	1.8	1	1.1

Table III. Relative Rate Constants for the Reactions of Alkoxide Ions with Alkyl Pivalates

$R''O^-$	R'	k_{11}/k_{12}
CD_3O^-	CH_3	1.5
CD_3O^-	C_2H_5	2.5
$C_2D_5O^-$	C_2H_5	1.2

because the hydrolysis reactions are run under conditions of low conversion (typically 10%), it is unlikely that tertiary ion-molecule reactions of the carboxylate anions can significantly affect the results. This contention is supported by the fact that under these conditions the known fast reaction of CH_3O^- (generated in reaction 5) with methyl formate[9] is not detected.
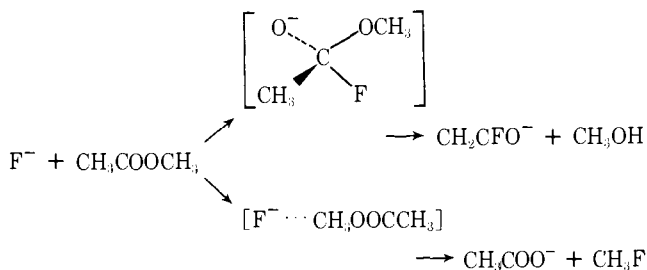
The values of X obtained for methyl esters where reaction 2c is endothermic (by 33 kcal mol^{-1} for $HCOOCH_3$) yield directly by difference the fraction of reactive encounters that proceed by the S_N2 pathway. For the higher R' groups, the value $(1 - X)$ represents the sum of the fraction of reactive encounters that proceed via 2b or via 2c.

The measurements of conversion ratios for the different esters showed the following relative rates for formation of the carboxylate anion: CF_3COOCH_3 > $(CH_3O)_2CO$ > $HCOOCH_3 \sim (CH_3)_3CCOOCH_3$ > $C_6H_5COOCH_3$.

Reaction with Other Nucleophiles. NH_2^-. The reactions of NH_2^- with alkyl formates[18] have been shown to yield $R'O^-$ by a mechanism similar to that of reaction 5. Alkyl trifluoroacetates and carbonates were observed to yield exclusively carboxylate anions by reaction with NH_2^-. These reactions which are presumably S_N2 processes are comparable in rates to the hydroxide ion reactions.

$$NH_2^- + RCOOR' \rightarrow RCOO^- + R'NH_2 \text{ (assumed)} \quad (6)$$

$$R = CF_3, CH_3O, C_2H_5O$$

$$R' = CH_3, C_2H_5$$

Alkyl pivalates display a much more complex reactivity pattern as described in the set of reactions 7-10. The product

$$NH_2^- + (CH_3)_3CCOOR' \longrightarrow \begin{cases} R'O^- + (CH_3)_3CCONH_2 & (7) \\ (CH_3)_3CCONH^- + R'OH & (8) \\ (CH_3)_3CCOO^- + R'NH_2 & (9) \\ \quad \text{(or olefin} + NH_3) \\ (M-1)^- + NH_3 & (10) \end{cases}$$

ion of reaction 8 was identified from two experimental facts: (a) the same ionic species is obtained for R' = CH_3 and C_2H_5; (b) when ND_2^- is used as the reagent ion, the product ion is displaced in mass by one mass unit leading to a very strong signal at m/e 101.[19] While reaction 10 appears as the questionable result of proton abstraction by the strong gas phase NH_2^-, we have been unable to assign it to any detectable impurities in the pivalates. As in most ICR experiments, the nature of the neutral products in the above reactions has been assumed. Relative rate constants for reactions 7-10 are listed in Table II.

Alkoxides and Fluoride Ions. The reaction of alkoxide ions with esters has been studies by several authors.[9,14,20] Additional data relevant to our discussion have been obtained for the alkyl pivalates.

$$R''O^- + (CH_3)_3CCOOR' \longrightarrow \begin{cases} R'O^- + (CH_3)_3CCOOR'' \quad B_{AC}2 & (11) \\ (CH_3)_3CCOO^- + R'OR'' \quad S_N2 & (12) \end{cases}$$

Relative rate constants are listed in Table III.

The reactions of fluoride ions with a number of esters has been previously discussed.[12,13] For the esters used in this work, and other than alkyl formates, the only reaction observed is that which leads to the formation of the carboxylate anions, $RCOO^-$.

Discussion

An initial survey of the ^{18}O data for methyl esters indicates that the $B_{AC}2$ mechanism is usually the dominant pathway for the gas-phase analogue of base hydrolysis. However, unlike its counterpart in solution, the S_N2 pathway is appreciably competitive and becomes the most important one for R = CF_3, a group traditionally viewed as enhancing the reactivity of the carbonyl group.

A comparison of the gas-phase and solution rate constants shows a second important and dramatic difference for the reactions in question. While absolute rate constants have been determined in the gas phase only for the alkyl formates[12] and CF_3COOCH_3,[20] our relative conversion ratio measurements allow us to estimate that the rate constants for the fastest (CF_3COOCH_3) and the slowest substrate ($C_6H_5COOCH_3$) differ at most by a factor of 5. The corresponding solution reactions show a difference of 10^8 in rates.[21,22] The data available for methyl formate suggest that the gas-phase reaction proceeds with little or no activation energy. For a hydroxide ion-methyl formate collision rate constant of 2.36×10^{-9} cm^3 molecule^{-1} s^{-1} calculated according to the ADO theory,[23,24] the efficiency of the hydrolysis reaction is 0.31.[25] Comparison of absolute values reveals that the $OH^- + HCOOCH_3$ reaction is about 10^{10} faster in the gas phase.[26] For the CF_3COOCH_3 reaction, the gas-phase efficiency has been measured to be 0.47.[20]

The branching ratio for the methyl esters, where reactions 2a and 2b have identical thermochemistry while 2c is endothermic, can be discussed in terms of a qualitative description of the potential energy hypersurface for these reactions. The approach of the OH^- to a complex molecule like an ester will be dominated at long range by the ion-induced dipole attraction leading to a net decrease in the potential energy of the system. At closer range, the energy surface is expected to display several energy minima corresponding to a balance in the overlap of the molecular orbitals of the reagents. This line of reasoning is best supported and exemplified by recent ab initio calculations of the reaction pathway for $OH^- + HCONH_2$.[27] In this system, energy minima were encountered for the species corresponding to the addition of the hydroxide to the carbonyl system, and another one for attachment of the OH^- to the acidic hydrogen of the amido group. Of course, a number of other theoretical calculations exist at present that predict the intermediates, or precursors, of $B_{AC}2$-type reactions[28] and S_N2 reactions[29] in the gas phase to lie *below* the energy of the reagents. This has been corroborated experimentally in a few favorable cases.[30,31] Thus, Scheme I is proposed to describe the gas-phase hydrolysis reactions.[32]

In this scheme, stable intermediates have been proposed on the reagent side as the first step. The exothermicity of this step is dictated by the stability of both species. On the product side, the expected stable intermediates have been considered to be the hydrogen-bonded carboxylate-methanol species in one

Scheme I

$$OH^- + RCOOCH_3$$

$$\longrightarrow \quad \longrightarrow \quad \text{products}$$

case, and the precursor of the reverse S_N2 reaction in the other. These two valleys in the energy surface have been assumed to be separated by energy barriers, $E_a^{\ddagger}$ and $E_b^{\ddagger}$, which must nevertheless lie below, or at worst very close to, the energy of the reagents, as the reactions proceed with high efficiency. The reason for the $E_b^{\ddagger}$ barrier for the S_N2 reaction is based on our previous experiments[31] and the lengthy semiquantitative treatment of gas-phase S_N2 reactions by Brauman.[20] The postulated energy barrier $E_a^{\ddagger}$ is based primarily on the results of the theoretical calculation of Tomasi,[27] which, although suspect in its quantitative aspects, is probably valid in its qualitative details.

The scheme presented above implies that the critical parameter for these reactions will be the ease with which the intermediates can evolve into products, a suggestion made by us earlier in connection with the reactions of F^- and alkyl acetates.[13] This scheme could be tested on a quantitative basis if the different energies were known by using RRKM theory for the intermediates as proposed by Brauman.[20] Unfortunately, no numbers are available for the energetics of the different steps and no geometric parameters are known for the critical configuration.

The variation in the product distribution observed in methyl esters is likely to originate from variation in efficiencies of the S_N2 process. Since the critical step in the $B_{AC}2$ mechanism entails an intramolecular proton assisted displacement of CH_3OH in all cases, it is doubtful that large differences can result as a function of the R group. On the other hand, the results of Brauman[20] show that the S_N2 reactions are very sensitive to the leaving group and the incoming nucleophile. The fact that the S_N2 increasing participation parallels our rough measurements of reaction efficiencies seems to support our contention that changes in the branching ratios for methyl esters is primarily due to changes in the S_N2 process.

The role of the exothermicity in the branching ratio of the methyl esters is unclear. The values range from 45 kcal mol^{-1} for R = H to 67 kcal mol^{-1} for R = CF_3.[33] For the least favorable S_N2 substrate, $C_6H_5COOCH_3$, the exothermicity is 51 kcal mol^{-1}.[34]

It is obvious from the scheme proposed for the gas-phase hydrolysis reaction that any feature in the energy hypersurface that will lower E_a or E_b, or open up a new pathway, will increase the efficiency of the overall reaction. Ethyl esters are presumed to do this by opening the elimination channel (eq 2c).

Our original proposal to account for these elimination reactions in esters involves a cyclic mechanism as in eq 1.

$$^*OH^- + RCOOC_2H_5 \longrightarrow$$

$$\longrightarrow RCOO^- + C_2H_4 + H_2^*O$$

While this mechanism is attractive in principle, it requires that the reaction proceeds prior to the formation of a truly bound tetrahedral species. A long-lived intermediate in this case would be expected to equilibrate rapidly the labeled oxygen and the original carbonyl oxygen leading to at best 50% unlabeled $RCOO^-$ by this mechanism. In the approach shown above, it could be argued that the driving force provided by the strong incipient OH bond of the nascent water molecule may preclude the formation of a true tetrahedral intermediate. Likewise, the degree of effectiveness of the R groups to promote reaction 2c, which does not correlate with exothermicity, can be rationalized by the ease with which the proposed cyclic configuration is assumed as a function of the geometric requirements of R. It should be added that reactions which proceed from nonequilibrated positions have already been reported in ionic reactions of esters.[10]

An alternative to the elimination reaction is the mechanism proposed by Beauchamp and co-workers[35,36] in their studies of strong gas-phase bases and haloethanes.

$$^*OH^- + RCOOC_2H_5 \longrightarrow$$

$$\longrightarrow H_2^*O + C_2H_4 + RCOO^-$$

This mechanism was originally rejected by us[12,13] because reactions with F^- do not lead to the formation of associated species, $RCOOHF^-$, which were expected to be the most favored product ion for the cases where the exothermicity is less than the $[RCOO^-\cdots HF]$ bond energy. In the case of the hydroxide ion reactions, no $[RCOOHOH]^-$ ions were ever observed, but given the large exothermicities for the OH^- reactions, it is reasonable to expect that any associated species would dissociate into $RCOO^-$ and H_2O. Thus, this line of reasoning would seem to account for the overall reaction, although it is unclear why different R groups would have such a pronounced effect in enhancing the elimination reaction by this mechanism.

It is nevertheless clear that because of the nature of the experiments it is not possible to determine how much of the reaction yielding unlabeled $RCOO^-$ is due to the elimination channel and how much to the S_N2 pathway.

An ultimate comparison between gas-phase and solution hydrolysis allows us to conclude that it is the large differential role of solvation for the transition states in solution (which now lie well above the energy of the solvated reactants) which must be held responsible for the preference of the $B_{AC}2$ mechanism in solution.

Other Nucleophiles. The reactivity of NH_2^-, alkoxides, and F^- with esters can be discussed in general according to the qualitative scheme presented for the hydrolysis reactions. However, a comparison of the reactivity of the carbonyl carbon vs. S_N2 reactions is complicated by the fact that the S_N2 reaction is considerably more exothermic, whereas displacement at the carbonyl may be in some cases endothermic. In general, the S_N2 mechanism predominates as pointed out by Comisarow,[14] i.e.

The noticeable exception for S_N2 preference is the case of alkyl pivalates, which were found to favor very strongly the $B_{AC}2$ mechanism with hydroxide ions. Reactions 7 and 8 with

NH_2^- as the reagent ion can be visualized as proceeding through a tetrahedral intermediate. Likewise, reactions with

$$NH_2^- + (CH_3)_3CCOOCH_3$$

$$\longrightarrow \left[(CH_3)_3C-\underset{\underset{NH_2}{|}}{\overset{\overset{O^-}{|}}{C}}-OCH_3 \right] \nearrow \begin{array}{l} CH_3O^- + (CH_3)_3CCONH_2 \\ \\ \searrow (CH_3)_3CCONH^- + CH_3OH \end{array}$$

alkoxide ions show that even for thermoneutral reactions like 11 when $R'' = CD_3$ and $R' = CH_3$, the $B_{AC}2$ mechanism is favored. The reason for this behavior is not well understood in light of the results of Comisarow with methyl benzoate[14] which showed only S_N2 reactivity with methoxide while the $B_{AC}2$ process is highly favored for hydroxide ion. It is nevertheless important to emphasize the fast nature of the reaction with alkyl pivalates to show that unlike the solution reaction there is a negligible steric effect for the $B_{AC}2$ process. This observation lends further support to our scheme which states that the efficiency of the reaction will be determined by the ease with which the tetrahedral intermediate evolves into the products. The steric effect of the *tert*-butyl group in this step will be considerably minimized.

The apparent acceleration, or increase, in reaction 9 in ethyl pivalate suggests again that the elimination mechanism is at work driven by the formation of the strong NH bond of ammonia.

The case of F^- has been previously discussed at length.[12,13,20] For most alkyl esters, displacement reactions at the carbonyl center are energetically prohibited, except when proton-assisted displacement of the alkoxy group renders the process exothermic. For methyl acetate, the reaction via the carbonyl carbon is four times faster than the S_N2 reaction.

$$F^- + CH_3COOCH_3 \begin{array}{l} \nearrow \left[\underset{CH_3}{\overset{O^-}{\diagdown}} \underset{F}{\overset{OCH_3}{C}} \right] \longrightarrow CH_2CFO^- + CH_3OH \\ \\ \searrow [F^- \cdots CH_3OOCCH_3] \\ \qquad\qquad\qquad \longrightarrow CH_3COO^- + CH_3F \end{array}$$

We can summarize the results of this investigation by emphasizing the richness of the chemical reactivity of the esters in the gas phase, and the importance of energy paths of the intermediates in dictating the outcome of the reaction. It is particularly striking that substituents affect a given gas-phase reaction not only in small rate changes, by solution standards, but by opening new reactive channels.[37]

References and Notes

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