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Gas Phase Nucleophilic Displacement Reactions of Negative Ions with Carbonyl Compounds

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Abstract: The rates of a number of nucleophilic displacement reactions $X^- + RCOY \rightarrow Y^- + RCOX$ have been studied with pulsed ion cyclotron resonance spectroscopy, where X = F, Cl, CH_3O, CN, SH; R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, C_6H_5, CF_3; Y = Cl, Br. The results suggest that the potential surfaces contain at least two minima separated by a barrier. The kinetic model is analyzed using RRKM theory, which provides an estimate of the barrier height. The estimated stability of the "tetrahedral intermediate" is examined critically in terms of ions of comparable structure.

Introduction

The carbonyl group plays a central role in chemistry because of its participation in a wide variety of reactions of chemical and biochemical importance.[1] Thus, over the years, there has been considerable activity in the mechanistic study of reactions of carbonyl groups. Of the many reactions usually undergone by carbonyl substrates, nucleophilic displacements have been among the most extensively investigated, especially because of their relevance to the enzymatic catalysis of reactions of carboxylic acid derivatives.[2]

Most of these studies have been in solution with the attendant complications of the solvent system and our work was motivated by the thought that a systematic study of these reactions under solvent-free conditions would improve our understanding of the intrinsic factors controlling the reactivity of carbonyl substrates. We have therefore undertaken a detailed study of gas phase ionic nucleophilic displacement reactions at carbonyl centers using ion cyclotron resonance (ICR) spectroscopy.

There have been studies by other workers on some aspects of the reactions of ionic nucleophiles with carbonyl substrates in the gas phase. For example, Bowie and co-workers have reported the formation of adducts of acetic and trifluoroacetic anhydrides which are suggested to be collisionally stabilized tetrahedral adducts.[3] Riveros and co-workers have investigated reactions of ionic nucleophiles with some carbonyl substrates and found that other pathways in addition to conventional nucleophilic displacement at the carbonyl center are important in many cases.[4] Comisarow has also shown[5] that nucleophilic attack of CD_3O^- on $CF_3CO_2CH_3$ and $C_6H_5CO_2CH_3$ in the gas phase leads to displacement of $CF_3CO_2^-$ and $C_6H_5CO_2^-$ rather than CH_3O^-.

In a previous paper on this subject, we focused our attention on the formation and detection of adducts of nucleophiles with acyl halides.[6] In that paper, we showed that at least in one case the addition complex has structurally equivalent halides, which suggests a tetrahedral structure. Thermochemical estimates which are reported in this paper show, however, that some acyl halide addition complexes must have structures other than tetrahedral—presumably loose association complexes. In this paper. we also report on our kinetic and mechanistic studies of reactions of ionic nucleophiles toward carbonyl substrates in the gas phase. Variations in the nucleophile (X^-), leaving group (Y^-), and alkyl substrate (R) are found to affect the rate constants in a manner which is not consistent with the single minimum surface postulated from solution and theoretical studies. The similarities and differences in gas-phase structure-reactivity behavior from solution behavior are discussed.

Experimental Section

Instrumentation. A Varian V-5900 drift mode ion cyclotron resonance spectrometer was used for the nonkinetic experiments reported in this work.[7] The auxiliary equipment has been described previously[8] and typical operating parameters are as described earlier.[6] For the nonkinetic and some of the kinetic experiments, the pulsed double resonance and ion ejection techniques[9] were used either to confirm a particular reaction or to eliminate one reaction while monitoring another.

The kinetic experiments were done using a pulsed ion cyclotron resonance spectrometer.[10] Marginal oscillator frequencies of 153.5

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and 307 kHz were used. Primary ions were formed by a short pulse (typically 2-5 ms) of an electron beam and then trapped for as long as 2 s in the trapped ion analyzer cell. Typical operating parameters were 1.5-2.0 V for the trapping plate and 1.2-1.5 V for the upper and lower plates of the ICR cell. Pressures were measured with a Varian Ionization gage (Model 971-0014) which was then calibrated against an MKS Baratron capacitance manometer (Type 90H-1E Head) in the range 10^{-5}-10^{-3} Torr for each neutral sample. Typical rate constant measurements were performed in the range 10^{-6}-10^{-5} Torr over a period of 100-200 ms. With our apparatus, the thermal rate constant of the reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ was measured as $1.12 \pm 0.14 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, in good agreement with the average literature value[11] of $1.11 \pm 0.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

Materials. Acetyl chloride, acetyl bromide, propionyl chloride, and isobutyroyl chloride were obtained commercially (from MCB) and distilled at atmospheric pressure. Benzoyl chloride (Allied) was distilled at reduced pressure. Trifluoroacetyl chloride (PCR), acetyl fluoride (PCR), trifluoroacetic anhydride (Aldrich), sulfuryl fluoride (Matheson), hydrogen cyanide (Fumic, Inc.), hydrogen sulfide (Matheson), chloroform (MCB), and carbon tetrachloride (MCB) were all used as received without further purification Dimethyl peroxide,[12] pivaloyl chloride,[13] and trifluoroacetyl bromide[14] were prepared by literature methods. Nitrogen trifluoride was obtained from Dr. S. K. Brauman at SRI International and also from Mr. V. Hassan of NASA Ames Research Center. All samples were prepared on a vacuum line and degassed by several freeze-pump-thaw cycles prior to being introduced into the ICR foreline.

Primary ions were formed from the following sources. The approximate electron energy (absolute value of filament voltage minus trapping voltage) is indicated in electron volts for each compound: F^- from NF_3 (0.1-1.5) and SO_2F_2 (2.5-3.0); Cl^- from $CHCl_3$, CCl_4, or CH_3COCl (0.0-1.0); CH_3O^- from CH_3OOCH_3 (0.5-2.0); CN^- from HCN (2.0-4.0); SH^- from H_2S (3.0-4.0). In addition, CN^- and SH^- were formed by proton abstraction via F^- from HCN and H_2S, respectively.

Results

Most of the acyl halides used in this study form halide ions by electron impact during the grid pulse.

$$RCOY + e^- \rightarrow RCO + Y^-$$

This process is usually more facile than the formation of the reactant ions and resulted in a large buildup of negative ions, creating a space charge problem in the system. To alleviate this, we continuously ejected the halide ions of the neutral gas during the entire reaction sequence while monitoring the decay of the reactant ion. In order to monitor the actual growth of the halide ions Y^- resulting from the reaction, the halide ions formed during the grid pulse were ejected from the cell shortly after their formation. The subsequent growth curve of the halide ion was then monitored.

In the prototype ion-molecule reaction $X^- + RCOY \rightarrow Y^- + RCOX$, the neutral gas RCOY is present at a much larger concentration than the ions X^- and Y^- so the decay of X^- and the growth of Y^- follow pseudo-first-order kinetics.

$$[X^-]_t = [X^-]_{t=0}e^{-k't} \text{ where } k' = k[RCOY]$$

$$[Y^-]_t = [Y^-]_{t=0} + [X^-]_0[1 - e^{-k't}]$$

Pseudo-first-order rate constants were obtained by a linear least-squares analysis of the decay and growth curves of the reactant and product ions, respectively. For each spectrum, the ion-molecule rate constant was then calculated by dividing the pseudo-first-order rate constant by the pressure of the neutral gas.

Since there are relatively few collisions of ions with the bath gas in low-pressure ICR experiments, questions have been raised as to whether ICR rate constants are actually "thermal".[15] Some precautions and checks pertinent to this question were made. For some reactions of F^- reported in Table I, two different sources of F^- (NF_3 and SO_2F_2) were used and there was no noticeable difference in the rates. Rate constants for reactions involving CN^- and SH^-, which were produced by dissociative electron capture from HCN and H_2S, respectively, were not different from the same reactions of CN^- and SH^- produced by proton abstraction via F^- from HCN and H_2S, respectively. All usable data followed exponential behavior showing that the rate constants were independent of ion residence times and thus independent of the number of collisions.

The results of the rate measurements are summarized in Table I along with the corresponding reaction efficiencies and heats of reaction. The error limits on the rate constants are standard deviations for at least ten experiments performed at different neutral pressures and on at least two different days. The absolute accuracy of each rate constant is probably not better than ±20%, this being the estimated accuracy of the Baratron capacitance manometer readings below 10^{-3} Torr. However, the rate differences between pairs of typically fast and slow reactions which have almost equal collision frequencies (e.g., CH_3O^-/CH_3COCl and Cl^-/CH_3COCl) are well outside the limits of experimental error. Thus the reported rate constants with the error limits adequately reflect the relative rates of the reactions.

As shown in Table I, two product ions, $XHCl^-$ and Cl^-, were observed for some reactions of nucleophiles X^- with CH_3COCl. The reported numbers represent the total rate constant for decay of X^-. Analysis of the product ion intensities at short times showed that the contribution of the pathway for formation of $XHCl^-$ did not contribute more than 15% to the overall rate constant. For those reactions where two or more different neutral products are possible for the same product ion, neutral detection experiments[17] were performed, but we were not able to obtain consistent enough results to make any definite statements about the identity of the neutrals.

Nonkinetic Experiments. F^-/CH_3COF. In addition to the reactant ion F^-, negative ions of *m/e* 39 (FHF^-), 61 (CH_2COF^-), 103 ($FCOCHCOCH_3^-$), and 123 ($FCOCH_2CF(CH_3)O^-$) were observed. The following pathways were established by double resonance experiments.

$$F^- + CH_3COF \rightarrow FHF^- + CH_2CO$$

$$\rightarrow CH_2COF^- + HF$$

CH_3O^-/CH_3COF. The only ions formed were *m/e* 61 (CH_2COF^-) and 103. Ions of *m/e* 19 (F^-), 51 (CH_3OHF^-), and 123 were not observed.

$$CH_3O^- + CH_3COF \rightarrow CH_2COF^- + CH_3OH$$

$$\nrightarrow CH_3OHF^- + CH_2CO$$

$$\nrightarrow F^- + CH_3COOCH_3$$

CN^-/CH_3COF. For CN^- formed by dissociative electron capture from HCN, no product ions were observed. CH_2COF^-, $CNHF^-$, and F^- could not be observed.

$$HCN + e^- \rightarrow CN^- + H$$

$$CN^- + CH_3COF \nrightarrow CH_2COF^- + HCN$$

$$\nrightarrow CNHF^- + CH_2CO$$

$$\nrightarrow F^- + CH_3COCN$$

However, in a mixture of NF_3, HCN, and CH_3COF, double-resonance experiments established the following pathways.

$$F^- + HCN \rightarrow CN^- + HF$$

$$F^- + CH_3COF \rightarrow CH_2COF^- + HF$$

$$CH_2COF^- + HCN \rightarrow CNHF^- + CH_2CO$$

$$\not\rightleftharpoons CN^- + CH_3COF$$

SH^-/CH_3COF. No product ions were observed in the reaction of SH^- with CH_3COF.

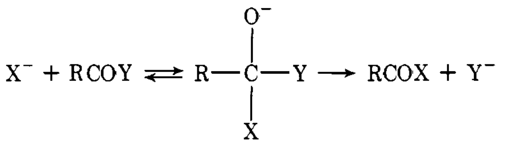
Table I. Rate Constants, Reaction Efficiencies, and Heats of Reaction of Ionic Nucleophilic Displacements at Carbonyl Centers

reaction	rate constant, 10^{-10} cm^3 molecule^{-1} s^{-1}	reaction efficiency[a]	$\Delta H°$, kcal/mol[b]
(1) $F^- + CH_3COCl \rightarrow FHCl^- + CH_2CO$			−27.7
$\rightarrow Cl^- + CH_3COF$ and/or	7.31 ± 0.30	0.25	−39.4
$\rightarrow Cl^- + CH_2CO + HF$			−15.1
(2) $^{37}Cl^- + CH_3CO^{35}Cl \rightarrow {}^{35}Cl^- + CH_3CO^{37}Cl$	1.19 ± 0.12	0.05	0.0
(3) $CH_3O^- + CH_3COCl \rightarrow Cl^- + CH_3COOCH_3$			−55.0
and/or	6.46 ± 0.39	0.26	
$Cl^- + CH_2CO + CH_3OH$			−22.7
(4) $CN^- + CH_3COCl \rightarrow CNHCl^- + CH_2CO$	2.38 ± 0.24	0.09	
$\rightarrow Cl^- + CH_3COCN$			
(5) $SH^- + CH_3COCl \rightarrow SH_2Cl^- + CH_2CO$	2.49 ± 0.08	0.10	
$\rightarrow Cl^- + CH_3COSH$			−17.5
(6) $F^- + CH_3COBr \rightarrow Br^- + CH_3COF$			−50.3
and/or	9.53 ± 0.61	0.33	
$Br^- + CH_2CO + HF$			−25.7
(7) $Cl^- + CH_3COBr \rightarrow Br^- + CH_3COCl$	2.34 ± 0.31	0.10	−9.9
(8) $CH_3O^- + CH_3COBr \rightarrow Br^- + CH_3COOCH_3$			−64.9
and/or	7.46 ± 0.7	0.32	
$Br^- + CH_2CO + CH_3OH$			−32.6
(9) $CN^- + CH_3COBr \rightarrow Br^- + CH_3COCN$			−4.0
and/or	2.75 ± 0.3	0.11	
$CH_2CO + HCN$			−27.4
(10) $SH^- + CH_3COBr \rightarrow Br^- + CH_3COSH$			
and/or	2.64 ± 0.3	0.12	−4.2
$Br^- + CH_2CO + H_2S$			
(11) $F^- + CH_3CH_2COCl \rightarrow FHCl^- + CH_3CHCO$			−30.5
$\rightarrow Cl^- + CH_3CH_2COF$	9.03 ± 1.14	0.29	−39.4
and/or			
$Cl^- + CH_3CHCO + HF$			−17.6
(12) $^{37}Cl^- + CH_3CH_2CO^{35}Cl \rightarrow {}^{35}Cl^- + CH_3CH_2CO^{37}Cl$	0.82 ± 0.15	0.034	0
(13) $F^- + (CH_3)_2CHCOCl \rightarrow FHCl^- + (CH_3)_2CCO$			−31.8
$\rightarrow Cl^- + (CH_3)_2CHCOF$	5.34 ± 0.52	0.17	−39.4
and/or			
$(CH_3)_2CCO + HF$			−18.9
(14) $^{37}Cl^- + (CH_3)_2CHCO^{35}Cl \rightarrow {}^{35}Cl^- + (CH_3)_2CHCO^{37}Cl$	0.65 ± 0.01	0.027	0.0
(15) $F^- + (CH_3)_3CCOCl \rightarrow Cl^- + (CH_3)_3CCOF$	4.88 ± 0.13	0.15	−39.4
(16) $SH^- + (CH_3)_3CCOCl \rightarrow Cl^- + (CH_3)_3CCOSH$	1.58 ± 0.23	0.06	−17.5
(17) $^{37}Cl^- + (CH_3)_3CCO^{35}Cl \rightarrow {}^{35}Cl^- + (CH_3)_3CCO^{37}Cl$	0.68 ± 0.02	0.028	0.0
(18) $F^- + C_6H_5COCl \rightarrow Cl^- + C_6H_5COF$	5.49 ± 0.21	0.14	20.0
(19) $^{37}Cl^- + C_6H_5CO^{35}Cl \rightarrow {}^{35}Cl^- + C_6H_5CO^{37}Cl$	0.61 ± 0.09	0.02	0
(20) $F^- + CF_3COCl \rightarrow Cl^- + CF_3COF$	4.19 ± 0.63	0.23	−39.4
(21) $^{37}Cl^- + CF_3CO^{35}Cl \rightarrow {}^{35}Cl^- + CF_3CO^{37}Cl$	1.77 ± 0.22	0.13	0
(22) $CH_3O^- + CF_3COCl \rightarrow Cl^- + CF_3COOCH_3$	3.15 ± 0.25	0.21	−55.0
(23) $CN^- + CF_3COCl \rightarrow Cl^- + CF_3COCN$	2.47 ± 0.17	0.15	<0.0
(24) $SH^- + CF_3COCl \rightarrow Cl^- + CF_3COSH$	2.48 ± 0.18	0.14	−17.5
(25) $F^- + CF_3COBr \rightarrow Br^- + CF_3COF$	3.81 ± 0.36	0.18	−50.3
(26) $Cl^- + CF_3COBr \rightarrow Br^- + CF_3COCl$	2.02 ± 0.06	0.12	−9.9
(27) $CH_3O^- + CF_3COBr \rightarrow Br^- + CF_3COOCH_3$	6.34 ± 0.50	0.37	−64.9
(28) $CH_3O^- + CF_3COF \rightarrow F^- + CF_3COOCH_3$	<0.01		−19.9

[a] This is the fraction of collisions which result in reaction, $k/k_{\text{collision}}$. The collision rate constants were calculated by the average dipole orientation theory (ADO) of Bowers.[16] [b] Gas-phase thermochemical data for the ions and neutral compounds used here were taken from the following sources. (1) heats of formation of CH_3COF, CH_3COCl, CH_3COBr, CH_2CO, CH_3COOCH_3, CH_3OH, H_2S, HCN, and HF from S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976. (2) Heats of formation of CH_3CH_2COCl, CH_3CH_2COF, CH_3CHCO, $(CH_3)_3CHCOCl$, $(CH_3)_2CCO$, $(CH_3)_3CCOCl$, $(CH_3)_3CCOF$, CF_3COCl, CF_3COF, CF_3COOCH_3, and $CF_3COOCOCF_3$ were calculated by Benson's group additivity method. See preceding reference. (3) Heats of formation of C_6H_5COCl and C_6H_5COF were taken from "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26**, 260 (1969). (4) Heat of formation of CH_3COSH from S. Sunner, *Acta Chem. Scand.*, **9**, 847 (1955). (5) Heats of formation of F^- and CN^- are from "JANAF Thermochemical Tables," 1974 Supplement, *J. Phys ·Chem. Ref. Data,* **3**, 311 (1974), Cl^-, Br^-, and HS^- from K. W. Egger and A. T. Cocks, *Helv. Chim. Acta,* **56,** 1516 (1973); $D°(F^- \cdot\cdot HCl)$ = 50 kcal/mol from R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93,** 7139 (1971).

Discussion

Nucleophilic displacement reactions in solution are generally believed to proceed via an addition-elimination mechanism with formation of a tetrahedral intermediate which subsequently breaks down to products or returns to reactants[2] (eq 1). This mechanism is consistent with the thermodynamic stability of many carbonyl addition complexes with respect to the nucleophile and carbonyl compound.[18] Until recent years, the most convincing evidence for the presence of tetrahedral intermediates was that of Bender.[19] In the alkaline hydrolysis of ethyl benzoate using $H_2{}^{18}O$, he detected some ^{18}O in the unreacted ester and found that the rates of isotopic exchange and hydrolysis were comparable. Kinetic evidence that an in-



$$X^- + RCOY \rightleftharpoons R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}-Y \longrightarrow RCOX + Y^- \qquad (1)$$

termediate actually lies on the reaction path for carboxylic ester hydrolysis was presented by Johnson.[20] More recently, with the aid of stopped-flow NMR, Cocivera and co-workers[21] have monitored the formation and breakdown of tetrahedral intermediates in nucleophilic reactions of aldehydes, ketones, and esters. These and other results[22] have led to the general belief that bimolecular nucleophilic displacement reactions at carbonyl centers in solution proceed via an addition–elimination mechanism.

Theoretical Studies. There have been a few theoretical studies of nucleophilic displacement at carbonyl centers. Attention has generally been focused on the approach of the nucleophile toward the carbonyl substrate. All studies reported thus far predict an attractive surface for all nucleophile–carbon distances greater than the equilibrium value, with no well-defined transition states between reactants and the tetrahedral adduct.[23,26] Guthrie has combined experimental results with group additivity relationships to evaluate the free-energy variations along the reaction coordinate for several carbonyl hydration processes in solution.[27] In this case, he found barriers for both formation and breakdown of the tetrahedral intermediates.

Gas-Phase Studies. The gas-phase reactions of ionic nucleophiles with CH_3COF, CH_3COCl, CH_3COBr, and acyl halides having β hydrogen typify the versatility of carbonyl derivatives. These reactions also bring out the important question of competition between different channels in reactions of ionic nucleophiles with neutral molecules. The reactions observed can be classified as (a) proton transfer, (b) base-induced complexation, (c) base-induced elimination, and (d) nucleophilic displacement.

$$\begin{array}{lll}
X^- + CH_3COY & \rightarrow CH_2COY^- + HX & \text{proton transfer} \\
 & \rightarrow XHY^- + CH_2CO & \text{base-induced complexation} \\
 & \rightarrow Y^- + HX + CH_2CO & \text{base-induced elimination} \\
 & \rightarrow Y^- + CH_3COX & \text{nucleophilic displacement}
\end{array}$$

The proton transfer, base-induced elimination, and complexation products can be accommodated by a mechanism similar to that proposed for the fluoroethanes by Beauchamp.[28] With CH_3COF where the β hydrogen is expected to be very acidic, only CH_2COF^- and FHF^- products were observed. With CH_3COCl, some $XHCl^-$ was formed in addition to Cl^-, but with CH_3COBr, where the β hydrogen is expected to be least acidic and nucleophilic displacement most exothermic, only Br^- was observed.

The result of the reaction of CH_3O^- with CH_3COF (which has previously been reported by José and Riveros[4c]), where three channels of almost equal exothermicities are available but the reaction proceeds via one of these channels exclusive of the other two, has an important bearing on the nature of the potential surface for each of these channels.

$$\begin{array}{ll}
CH_3O^- + CH_3COF & \Delta H = -18.4 \pm 2.1 \\
\quad \rightarrow CH_2COF^- + CH_3OH & \text{kcal/mol}^{29} \\
\quad \nrightarrow CH_3OHF^- + CH_2CO & \Delta H = -20.3 \text{ kcal/mol} \\
\quad \nrightarrow F^- + CH_3COOCH_3 & \Delta H = -19.9 \text{ kcal/mol}
\end{array}$$

Observations such as these in the case of alkyl fluorides have led Beauchamp to postulate that a precondition for nucleophilic displacement in the gas phase is nonavailability of exothermic proton transfer channels.[30] However, a closer look at the intrinsic factors leading to our observations will improve our understanding of this phenomenon. The total dominance of proton transfer, exclusive of base-induced complexation and nucleophilic displacement channels, suggests the intervention of significant barriers on the potential surfaces of the two latter channels. The nucleophilic displacement reactions investigated by Beauchamp in which proton transfer overshadowed the nucleophilic displacement channel are typical cases of nucleophilic displacement of sp^3 carbon centers. In such cases, the intervention of barriers has been well documented both theoretically and experimentally, even in cases where there are no other competitive channels.[31] Thus it is easy to see why simple proton transfer reactions (many of which have no apparent barriers on their potential surface) completely dominate the ion–molecule encounter in those cases. However, implication of a barrier on the path for nucleophilic displacement at a carbonyl center is particularly interesting because no such barriers have been suggested in theoretical studies. This point will be explored in later discussion.

Structure–Reactivity. In our structure-reactivity analysis of nucleophilic displacements at carbonyl centers in the gas phase, we shall be comparing reaction efficiencies instead of absolute reaction rate constants, the former being the fraction of collisions which result in reaction; this is the important factor in relative reactivity of molecules of different structures.

Variations in the R Group. In comparing relative rates as a function of chain length and steric bulk of the alkyl group, relative efficiencies are in the order of $CH_3COCl > CH_3CH_2COCl > (CH_3)_2CHCOCl \sim (CH_3)_3CCOCl$ for the thermoneutral isotope exchange reactions: $^{37}Cl^- + RCO^{35}Cl \rightarrow {}^{35}Cl^- + RCO^{37}Cl$, although the differences are quite small. This is the only reaction channel available for production of Cl^-. In 1 M H_2O in dioxane at 25 °C, Weller[32] and also Ugi and Beck[33] found the same order for the relative rates of hydrolysis of these compounds in solution. Thus, qualitatively the rates diminish with increasing chain length and steric bulk of the alkyl group in the same manner as in solution. Similarly the results of electronic variations in the acyl portion of the neutral substrate are in agreement with solution behavior, the following order being observed for the relative reaction efficiencies of the thermoneutral isotope exchange reactions: $CF_3COCl > CH_3COCl > C_6H_5COCl$.

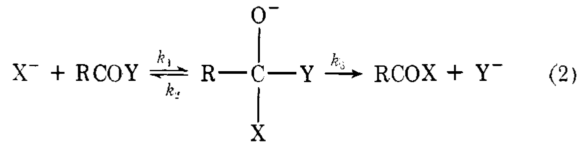
Leaving-Group Abilities. A meaningful discussion of leaving-group ability (LGA) can be made only in cases where we are certain that nucleophilic displacement alone is occurring. This is best exemplified by CF_3COF, CF_3COCl, and CF_3COBr, for which elimination is precluded. Of these three, F^- is clearly the poorest leaving group, irrespective of the attacking nucleophile. However, the LGA order is $Br^- > Cl^- > F^-$ with CH_3O^- as the nucleophile but $Cl^- > Br^- > F^-$ with F^- as the nucleophile. This reversal with F^- and CH_3O^- as nucleophiles was also found in nucleophilic displacement reactions of alkyl halides.[31] It resembles the effects in solution seen earlier by Jorgensen,[34] Hine,[35] and Bunnett[36] and later related to the hard and soft acids and bases (HSAB) principle by Pearson and Songstad.[37] If only the HSAB principle were operating, one might have expected the chloride isotope exchange reaction of CF_3COCl to be faster than Cl^- displacement from CF_3COCl by CH_3O^-. However, CH_3O^- displaces Cl^- faster than Cl^- is displaced by another Cl^- isotope. Thus, from our results, exothermicity appears to be the dominant factor controlling LGA. It is only when two reactions of very high or very low exothermicity are considered that secondary factors take over. For most nucleophiles in the gas phase, the LGA is in the order $Br \geq Cl > F$, which is the same order as in solution.[37] This is not surprising since the solvation of the leaving group does not affect the rate of displacement. The critical factor is the solvation of the nucleophile and transition state.

Nucleophilicity. For reactions with acyl halides, we find that nucleophilicity is in the order $CH_3O^- \geq F^- > CN^- \sim SH^- > Cl^-$. This closely parallels the exothermicities of the reactions involved except in some cases where $F^- \geq CH_3O^-$ despite the higher exothermicity of the CH_3O^- reactions. The dependence of nucleophilicity on exothermicity is in agreement with the Bell-Evans-Polanyi relationship.[39]

The order of nucleophilicities found here also parallels the basicities of these negative ions in the gas phase. This behavior is essentially the same as that observed in protic solvents[40] ($OH^- > CN^- > SH^- > F^- > Cl^- > Br^- > I^-$) where there is, again, a correspondence between nucleophilicity and basicity. The similarity between protic solvent and gas-phase reactivity of acyl halides provides an interesting contrast with the alkyl halides, which exhibit many changes even between protic and aprotic solvents.[41,42] Why are alkyl halide reactions so susceptible to solvent change while those of acyl substrates are not? As suggested by Dewar and Dougherty,[43] the importance of solvation depends on the strength of attachment of solvent groups to the nucleophiles. In reactions with alkyl halides, the alkyl group, which is the center of attack, is very weakly polar. Thus the strength of attachment of the nucleophile with the alkyl group is considerably smaller than the nucleophile-solvent bond strength. Consequently, the nucleophile is strongly attached to the solvent and a large desolvation energy is responsible for a major part of the activation energy of S_N2 reactions. The transition state for addition to carbonyl groups, however, must have much of the character of an alkoxide ion. Consequently the transition state responds to solvation in a manner similar to the ionic reactant, and thus the effect of solvent change on relative reactivity is minimal.

Qualitative Model

Nucleophilic displacements at carbonyl centers, while faster in solution than the corresponding alkyl halide displacements in solution, are not diffusion controlled. As in the case of alkyl halides, the major factor responsible for the slowness of the solution rates of acyl halide nucleophilic displacements is solvation of the attacking nucleophile. Even in the gas phase, a majority of alkyl halide displacements are still significantly slower than their collision frequencies. The origin of this slowness has been postulated to be due to a central barrier which exists between the initial collision complex and the final complex which dissociates to the products.[31] This experimental finding of slow S_N2 reaction at sp^3 centers is consistent with the central barrier predicted by earlier and current theoretical studies.[44] For acyl substrates, however, all previous theoretical studies point to the formation of a tetrahedral intermediate with no barrier to its formation or decomposition except in cases where the intermediate rearranges to some other structure.[23-26] Thus the current theoretical picture of acyl substrate nucleophilic displacements is eq 2, with a potential surface



$$X^- + RCOY \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}-Y \xrightarrow{k_3} RCOX + Y^- \quad (2)$$

having a single minimum well (Figure 1). The overall rate constant for this type of potential surface is

$$k_{obsd} = k_1 k_3/(k_2 + k_3)$$

For the symmetrical isotope exchange reactions, e.g., $^{37}Cl^- + CH_3CO^{35}Cl \rightarrow {}^{35}Cl^- + CH_3CO^{37}Cl$, where $k_2 = k_3$, $k_{obsd} = k_1/2$. For the exothermic reactions $k_3 \gg k_2$, in which case $k_{obsd} \approx k_1$.

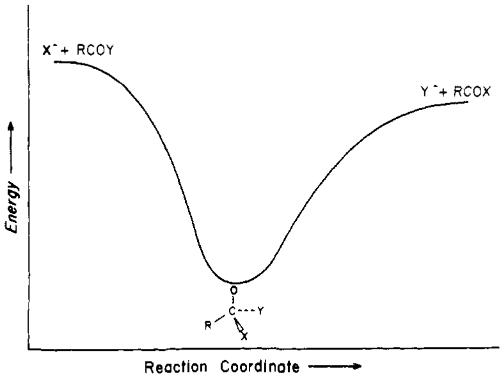


Figure 1. Typical "theoretical" potential surface for nucleophilic displacement at carbonyl centers.

However, our results show that even the fastest exothermic reactions are still at least three times slower than their respective collision frequencies and some reactions are as slow as 12% of the collision frequency. The thermoneutral isotope exchange reactions, which would be expected to be constant and equal to one-half of the collision frequency, are not only slower than the predicted value, but vary considerably with the electronic nature of the alkyl group. These results suggest the intervention of a barrier on the potential surface for nucleophilic displacements at carbonyl centers, contrary to the widely believed single minimum picture. The attractive ion-dipole interactions involved in an ion-molecule encounter are strong and long range enough to overcome any repulsive interactions in the approach of the ion toward the neutral molecule. Hence we do not expect a barrier in the formation of the initial ion-molecule collision complex. The derivation of the rate expression above assumes that this complex is the tetrahedral intermediate. However, the results of some reactions of nucleophiles with carbonyl substrates reported here and elsewhere[4,5,31] where alternate pathways compete with, and in some cases occur to the total exclusion of nucleophilic displacement at the carbonyl center strongly suggest that there is more to a nucleophile-carbonyl substrate collision than formation of a tetrahedral intermediate. For example, CH_3O^- exclusively undergoes proton transfer with CH_3COF instead of F^- displacement, even though the exothermicities of both channels are almost the same. Similarly, the reactions of OH^- and CD_3O^- with $CF_3CO_2CH_3$ lead exclusively to $CF_3CO_2^-$ instead of CH_3O^- displacement.[5,31] If the the tetrahedral intermediate complex were more stable than the collision complexes for these other pathways, one might have expected displacement of F^- and CH_3O^- to occur to a significant extent.

These findings are corroborated by our thermochemical analysis of some acyl chloride adducts formed in the gas phase. From the reversible chloride transfer between $CH_3CCl_2O^-$ and CH_3BrCl^- formed in our experiments[45] and from Dougherty's value for the heat of association of Cl^- with CH_3Br,[46] we estimate the heat of formation of $CH_3COCl_2^-$ as $\Delta H_f° = -124 \pm 2$ kcal/mol. Group additivity estimates[47] of $\Delta H_f°$ for tetrahedral CH_3CCl_2OH give a value[48] for $\Delta H_f°$ of tetrahedral CH_3CCl_2O radical of -28 kcal/mol. Thus if we assume that $CH_3CCl_2O^-$ formed in our experiments has a tetrahedral structure, the electron affinity of tetrahedral CH_3CCl_2O radical would have to be 96 kcal/mol. This extremely high electron affinity (compared to a value[49] of 50 kcal/mol for tetrahedral CF_3CH_2O) for an alkoxy radical makes us suspect that $CH_3CCl_2O^-$ formed in our experiments is more likely to be a loose ion-molecule complex. In agreement with this premise, the chloride binding energies of the acyl chloride adducts[50] (~11 kcal/mol for $CH_3CCl_2O^-$ and ~15 kcal/mol for $CF_3CCl_2O^-$) are in the same range as those obtained for other loose ion-molecule complexes as found by Kebarle[51] and also Dougherty.[46]

The foregoing suggests that there are a wide variety of nucleophile-carbonyl substrate collision complexes which may be more stable than the corresponding tetrahedral adduct, in contrast to solution behavior. This result is quite reasonable

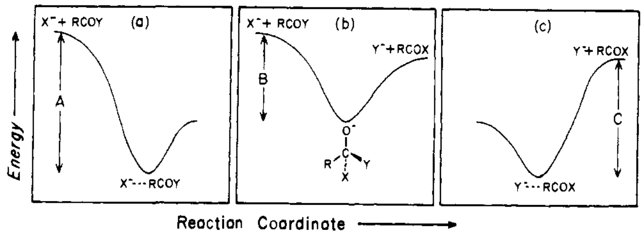


Figure 2. Reaction coordinate diagrams depicting the origin of the barrier in nucleophilic displacement reactions at carbonyl centers.

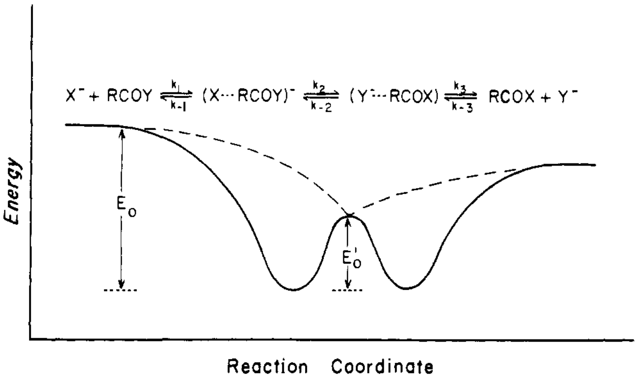


Figure 3. Double minimum well picture of nucleophilic displacement at a carbonyl center.

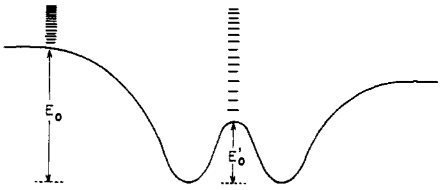


Figure 4. Reaction coordinate diagram with pictorial energy level spacings of the two transition states.

when we note that the tetrahedral ion is the most favorably solvated structure of the complex—a factor of no consequence in the gas phase.

We suggest that there is a straightforward mechanism by which a loose nucleophile-carbonyl substrate complex which is more stable than the tetrahedral intermediate can cause a retardation of the rate of nucleophilic displacement at the carbonyl center. This is illustrated by the reaction coordinate diagrams in Figure 2. The potential surface for nucleophilic displacement at the carbonyl center in the absence of other reactive or nonreactive channels is shown in the middle. The partial reaction coordinate diagrams shown on the left and right are for formation and breakdown of loose ion-molecule complexes, which are more stable than the tetrahedral intermediate with respect to the reactants, A, C > B. Superposition of the three diagrams then produces a double minimum well (Figure 3). In Figure 3, the dotted curve depicts the potential surface for carbonyl nucleophilic displacement in the absence of these other more stable complexes. The tetrahedral structure now becomes a saddle point (or possibly a local minimum) connecting the two lower minima. For convenience, it can be treated as a transition state for exchange between those complexes. Thus, a barrier has been introduced into the displacement reaction by the intervention of some stable complexes which are not of direct relevance to the reaction. Dynamically, collision of X^- with RCOY forms the stable complex X^----RCOY, which then has to overcome a barrier prior to formation of products. The other loose complex on the right-hand side of the tetrahedral structure is necessary for microscopic reversibility. Thus the tetrahedral "intermediate" appears as a transition state between the two loose complexes. An explanation for slow reactions on this type of surface has been given earlier.[31] While the forward reaction k_2 is favored energetically, the back reaction k_{-1} is greatly favored by entropy. At the given total energy, the density of states for the back reaction k_{-1} is greater than that for the forward reaction k_2 (Figure 4). That is, the entropic factor favoring the back reaction more than compensates for the energetic factor which favors the forward direction. The ratio of rates in the two channels depends only on the heights of the two transition states and the energy of the system. The depth of the well has no consequence provided that it lies below the two saddle points. Its depth only controls the absolute rate in each channel.

There are other possible explanations for these slow rates, including more complex surfaces or dynamics controlled by factors other than statistical reaction rate theory (direct reactions). However, there are good reasons[31] for choosing our model for a working hypothesis. First, the reactions are carried out at thermal energies. Second, the molecules are large, with many internal degrees of freedom. Third, within the constraints of a statistical model this is the simplest mechanism which can work. Fourth, the qualitative behavior of these slow reactions agrees with the prediction of the model. Fifth, it is possible to make quantitative predictions, and ultimately these can be subjected to experimental tests. Sixth, the model is physically reasonable, whereas any alternative would be completely ad hoc at the present time. Consequently, we believe that this model is likely to be correct, and we now try to gain further insight into the nature of the reaction by using the model in a calculation of reaction efficiencies as a function of the central barrier height.

Quantitative Model

In order to calculate the reaction efficiency, we need a rate expression which fits our proposed double-minimum potential well model.

$$X^- + RCOY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^-\text{---}RCOY \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Y^-\text{---}RCOX \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RCOX + Y^- \quad (3)$$

Under the conditions of our experiments, the neutral product of the forward reaction, RCOX, is present in such low concentrations that k_{-3} can be neglected. With this consideration, the generalized rate constant for (3) is

$$k_{\text{obsd}} = \frac{k_1 k_2}{(k_{-1} + k_2) + (k_{-2}k_{-1})/k_3}$$

For the symmetrical isotope exchange reactions, $k_{-1} = k_3$ and $k_2 = k_{-2}$:

$$k_{\text{obsd}} = k_1 k_2/(k_{-1} + 2k_2) \quad (4)$$

For the exothermic reactions, $k_3 > k_{-1}$ because both channels are entropically similar while the k_3 channel is energetically favored. Physically, this means that once the complex Y^----RCOX is formed, it almost always goes on to products. Consequently, k_{-2} is negligible compared to k_3, and in this case

$$k_{\text{obsd}} = k_1 k_2/(k_{-1} + k_2) \quad (5)$$

Following our earlier procedure[31] for S_N2 reactions at sp^3 centers, the RRKM method[52] is used to calculate k_2/k_{-1} as a function of internal energies. The criteria and evidence for the applicability of this statistical theory to the reactions discussed here are the same as outlined for the S_N2 reactions.[31]

Method

In RRKM formulation, the microcanonical rate constant $k(E)$ for unimolecular decomposition of a species with internal energy E is given by[52a]

$$k(E) = \frac{G(E - E_0)}{hN(E)} \qquad (E \geq E_0) \tag{6}$$

$G(E - E_0)$ is the sum of vibrational and internal rotational quantum states of the transition state up to energy $E - E_0$. $N(E)$ is the density of states for the intermediate complex which in this case is X^----RCOY. For a channel whose transition state has a smaller moment of inertia than that of the intermediate, a correction ΔE_{rot} must be made in the expression to account for the energy that would be constrained in external rotations in order to conserve angular momentum.[53] The rate constant expression in such cases is given by

$$k'(E) = G'(E - E_0' - \Delta E_{\mathrm{rot}})/hN(E) \tag{7}$$

The correction factor ΔE_{rot} is taken to be[54]

$$\Delta E_{\mathrm{rot}} = (1 - I'/I)kT \tag{8}$$

where I' and I are the external moments of inertia for the transition state and the intermediate.

The fraction of complexes in the energy range E to $E + \delta E$ partitioning into products is equal to $\{k_2(E)/[k_{-1}(E) + ak_2(E)]\}F(E)\delta E$ where $F(E)$ is the energy distribution function and $a = 2$ or 1 for the thermoneutral or exothermic cases, respectively. The structure of the intermediate need not be specified, and we can write the overall fraction partitioning into the product channel as

$$\text{efficiency} = \int_{E_0}^{\infty} \frac{G'(E - E_0' - \Delta E_{\mathrm{rot}})}{G(E - E_0) + aG'(E - E_0' - \Delta E_{\mathrm{rot}})} \times F(E)\,\mathrm{d}E \tag{9}$$

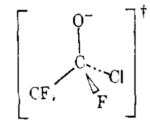
where G' is the k_2 channel, G the k_{-1} channel, and ΔE_{rot} is the difference in rotational energy in the two transition states. For this type of chemical activation, the distribution function is given by[55]

$$F(E) = \frac{G(E - E_0)\exp(-E/kT)}{\int_{E_0}^{\infty} G(E - E_0)\exp(-E/kT)\,\mathrm{d}E} \tag{10}$$

The sums of states in eq 9 were evaluated by a direct count of vibrational states using seven frequency groups and a classical count of internal rotational states.[56] The integrals were evaluated numerically.

1. F^- + CF_3COCl. The two sets of parameters required to calculate the sums of states of the transition states are the vibrational frequencies and moments of inertia of the internal rotors. The ratio of the external moments of inertia are required for the correction factor ΔE_{rot}. Thus we have to develop models for the two transition states involved. Henceforth, we shall refer to the transition state for k_{-1} as A and that for k_2 as B. For transition state A, the Gorin model is used.[57] This model treats F^- and CF_3COCl as essentially noninteracting particles. The model has been shown to work well for unimolecular decomposition reactions of ions whose reverse reaction has no barrier to recombination, e.g., proton-bound dimers.[58] The external moment of inertia for transition state A was calculated by treating F^- and CF_3COCl as point masses at an interatomic distance of r_m. An expression for r_m is given by Waage and Rabinovitch[53] and for these ion–molecule reactions the Langevin-polarization potential is assumed. For this eight-atom "molecule" there are 18 degrees of freedom. At this large separation of the two species, the vibrational frequencies of CF_3COCl remain unchanged so there are only three more internal degrees of freedom to account for. These are the two-dimensional internal rotor which corresponds to tumbling of CF_3COCl (Gorin model) and the reaction coordinate.

Table II. Parameters Used in the Calculations[a] of Reaction Efficiencies for $F^- + CF_3COCl \rightarrow Cl^- + CF_3COF$

	transition state A	transition state B
	$[F^- \text{-----} CF_3COCl]^\dagger$	
ν_i[b]	1811 (1)	1329 (2)
	1242 (3)	1219 (3)
	791 (3)	864 (2)
	536 (3)	600 (3)
	361 (2)	359 (4)
	215 (2)	203 (2)
	40 (1)	70 (1)
I_i,[b] σ_i	251.9, 1 (2)	
I_A/I_B[b]	3.47	

[a] Degeneracies are in parentheses. Frequencies ν_i are in cm^{-1}, moment of inertia in amu $Å^2$, and σ_i is the symmetry number for the internal rotor of transition state A. [b] CF_3COCl frequencies and moments of inertia were taken from C. V. Berney, *Spectrochim. Acta, Part A*, **20**, 1437 (1964). [c] CF_3CF_2Cl frequencies and moments of inertia were taken from F. B. Brown, A. D. H. Clague, N. D. Heitkamp, D. F. Koster, and A. Danti, *J. Mol. Spectrosc.*, **24**, 163 (1967).

Transition state B is tetrahedral CF_3COClF^-. This too is an eight-atom structure with 18 internal degrees of freedom. Since tetrahedral CF_3COClF^- has never been spectroscopically examined, it was treated as the isoelectronic tetrahedral CF_3CF_2Cl using the vibrational frequencies of CF_3CF_2Cl except that the C–O stretching frequency of an alcohol (1300 cm^{-1}) was substituted for one of the CF_2 stretching frequencies. The external moment of inertia was approximated by the experimentally determined principal moments of inertia of CF_3CF_2Cl. The parameters for the calculation are given in Table II.

2. Cl^- + CH_3COCl. The parameters for the two transition states were chosen in an analogous fashion with those of F^- + CF_3COCl. CH_3CFCl_2 was used as a model for transition state B. The parameters for the calculation are reproduced in Table III. With the same procedure, calculations were also done for F^- + CH_3COCl, Cl^- + CF_3COCl, and CH_3O^- + CH_3COF.

Calculations. The results of our calculations are shown in Tables IV and V and graphically illustrated in Figure 5.

Barriers which are well below the potential energy of the reactants still slow down the reactions considerably. For F^- + CF_3COCl, the product channel is favored over the reactant channel at high relative barrier heights ($E_0 - E_0' > 10$ kcal/mol) but this trend reverses rather sharply at low relative barrier heights. The relative barrier height $E_0 - E_0'$ which corresponds to the experimental reaction efficiency for the reaction $F^- + CF_3COCl \rightarrow Cl^- + CF_3COF$ is 8 kcal/mol. The efficiency is independent of the well depth, but, if we assume a well depth E_0 of 15 kcal/mol for the formation of $[F^-CF_3COCl]$ (it is ca. 15 kcal/mol for $[Cl^-CF_3COCl]$),[50] this corresponds to a central barrier of about 7 kcal/mol. The reaction of Cl^- + CH_3COCl has $E_0 - E_0'$ of 7 kcal/mol, which corresponds to a central barrier height of about 4 kcal/mol.

These calculations are insensitive to minor variations on the nucleophile and/or neutral substrate but very sensitive to

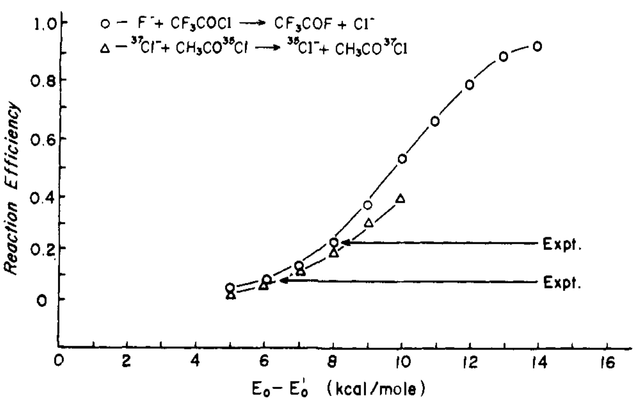
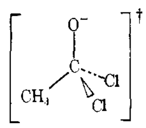


Figure 5. RRKM calculated reaction efficiencies as a function of barrier height ($E_0 - E_0'$). The arrows indicate the position of the experimental reaction efficiencies.

Table III. Parameters Used in the Calculation[a] of Reaction Efficiencies for $^{37}Cl^- + CH_3CO^{35}Cl \rightarrow {}^{35}Cl^- + CH_3CO^{37}Cl$

	transition state A	transition state B
	$[Cl^- \cdots\cdots CH_3COCl]^\dagger$	
ν_i[b]	2997 (3)	3000 (3)
	1822 (1)	1442 (2)
	1411 (3)	1342 (2)
	1030 (3)	1143 (2)
	559 (2)	744 (2)
	390 (2)	401 (3)
	238 (1)	259 (3)
I_i,[c] σ_i	91.20, 1 (2)	
I_A/I_B	7.44	

[a] Degeneracies are in parentheses. Frequencies (ν_i) are in cm^{-1}, moment of inertia (I_i) is in amu Å^2 and σ_i is the symmetry number for the internal rotor. [b] CH_3COCl frequencies were taken from J. A. Ramsey and J. A. Ladd, *J. Chem. Soc. B,* 118 (1968). CH_3CFCl_2 frequencies were taken from D. C. Smith, G. M. Brown, J. R. Nielsen, R. M. Smith, and C. Y. Liang, *J. Chem. Phys.*, **20,** 473 (1952). [c] Principal moments of inertia of CH_3COCl were from K. M. Sinnott, *J. Chem. Phys.*, **34,** 851 (1961).

changes which affect the vibrational-rotational degrees of freedom in the two transition states involved. For example, substitution of Cl^- for F^- or CF_3COCl for CH_3COCl introduces no significant changes in the qualitative behavior of efficiency as a function of $E_0 - E_0'$.

However, in comparing monatomic and polyatomic nucleophiles (e.g., F^- and CH_3O^-) we note that comparable barriers, when low, are predicted to result in much lower efficiencies for the polyatomic nucleophiles. This is a consequence of a loss of free rotation on going to transition state B compared with transition state A. Because CH_3O^- is polyatomic, it has rotational degrees of freedom, some of which are lost by conversion to vibrational degrees of freedom in transition state B. Consequently the reactant channel A is so much more favored entropically than the product channel B that even a very small barrier causes almost total domination of the reactant channel over the product channel.

These calculations may not predict *exact* absolute values of the central barrier heights, but they do, however, enable us to explain quantitatively how a central barrier that is well below the potential surface of the reactants can still lead to low reaction efficiencies. Minor structural changes in the nucleophile and carbonyl substrate do not cause significant changes in the results, in agreement with previous RRKM calculations.[52]

Table IV. Calculated Efficiency for $F^- + CF_3COCl \rightarrow Cl^- + CF_3COF$ as a Function of the Relative Barrier Heights ($E_0 - E_0'$)

$E_0 - E_0'$	efficiency[a]	$E_0 - E_0'$	efficiency[a]
15.0	0.92	9.0	0.36
14.0	0.87	8.0	0.23
13.0	0.81	7.0	0.12
12.0	0.73	6.0	0.06
11.0	0.62	5.0	0.02
10.0	0.49		

[a] Assumes efficiency = $k_2/(k_{-1} + k_2)$.

Table V. Calculated Efficiency for $Cl^- + CH_3COCl \rightarrow Cl^- + CH_3COCl$ as a Function of Relative Barrier Heights ($E_0 - E_0'$)

$E_0 - E_0'$	efficiency[a]	$E_0 - E_0'$	efficiency[a]
10.0	0.30	7.0	0.06
9.0	0.21	6.0	0.03
8.0	0.13	5.0	0.01

[a] Assumes efficiency = $k_2/(k_{-1} + 2k_2)$.

Since the tetrahedral structure is assumed to be transition state B, the difference in barrier heights $E_0 - E_0'$ which corresponds to experimental reaction efficiencies allows us to make rough estimates of the relative stabilities of these tetrahedral complexes with respect to the reactants. While such values are not exact, they provide a reference point with which we can compare values of the stabilities of tetrahedral complexes estimated by other methods. This also allows us to determine the relative solvation of the tetrahedral complexes compared to the reactants in cases where the thermochemical values in solution are known.

"Tetrahedral Intermediates" Revisited. In our calculation for $F^- + CF_3COCl$, the difference in barrier height corresponding to the experimental rate constant is 8 kcal/mol. This implies that the tetrahedral adduct is about 8 kcal/mol more stable than the reactants. From the $\Delta H_f°$ of F^- (−60 kcal/mol)[59] and CF_3COCl (−215.24 kcal/mol),[60] we obtain a $\Delta H_f°$ of −283 kcal/mol for the tetrahedral adduct. Group additivity[47] allows an estimate of the $\Delta H_f°$ of the alcohol of this tetrahedral adduct (−266.32 kcal/mol). From this value and assuming an O-H bond dissociation energy of ca. 104 kcal/mol for this alcohol, we obtain a $\Delta H_f°$ of −214.32 kcal/mol for tetrahedral CF_3CClFO radical. We thus obtain an electron affinity of ~69 kcal/mol for CF_3CClFO radical. When compared to a value of 50.5 kcal/mol obtained for CF_3CH_2O by Beauchamp from the acidities of fluorinated alcohols,[49] the electron affinity obtained here appears plausible. The experimental reaction efficiency for $Cl^- + CH_3COCl$ corresponds to a transition state which lies ~7 kcal/mol below the energy of the reactants and thus[61] has a $H_f°$ of −120 kcal/mol. Assuming a tetrahedral structure and following a similar procedure as above we obtain an electron affinity of 92 kcal/mol for tetrahedral CH_3CCl_2O radical. This value appears very high for an alkoxy radical.[62]

There are three possible explanation for this discrepancy. (1) The O-H bond strength of 104 kcal/mol that we have assumed for the disubstituted (α carbon) alcohols may be considerably smaller than the true value. (2) The electron affinity is, in fact, unusually high. (3) The tetrahedral adducts for these symmetrical reactions may be too high in energy to intervene in the mechanism for nucleophilic displacement. If this is so, we would have to look for an alternative structure for the transition state in these reactions.

The first alternative is that the O-H bond dissociation energy in tetrahedral CH_3CCl_2OH is unusually small. Its value would have to be less than the normal RO-H bond dissociation energy by about 25 kcal/mol in order to give a reasonable electron affinity (say 67 kcal/mol) for CH_3CCl_2O. We find no evidence in the literature where substitution of electronegative substituents on an alcohol causes such a large decrease in its O-H bond strength.

The second alternative is that the electron affinity of tetrahedral CH_3CCl_2O is unusually high. This might arise from extensive delocalization onto the halogens, via, say, hyperconjugation. However, although fluorine hyperconjugation is often invoked,[63] there seems to be less precedent for Cl hyperconjugation. Inductively, substitution of CF_3 for CH_3 only raises the electron affinity[64] of CH_3COCH_2 from 40.6 to 59.5 kcal/mol (CF_3COCH_2). Thus it would be surprising for the electron affinity to increase from ~40 kcal/mol in CH_3CH_2O to 92 kcal/mol in tetrahedral CH_3CCl_2O.

The third alternative is that the transition state has something other than a tetrahedral structure in the thermoneutral acyl nucleophilic displacement reactions. Such possibilities are limited because these are symmetrical reactions which suggest symmetrical or a pair of near symmetrical transition states. The obvious symmetrical structure is planar, with the π bond of the carbonyl group retained, as suggested by Dewar.[65]

The electronic structure of such a species is interesting in that its π system is isoelectronic with that of a trimethylenemethane containing six π electrons. Thus we would expect it to have considerable π stabilization since the HOMO should be only slightly antibonding.

At this point we cannot directly answer the problem of the extremely high stability which tetrahedral structures of some nucleophile-carbonyl substrate adducts must have in order to be energetically accessible on the potential surface for nucleophilic displacement at carbonyl centers. More detailed theoretical studies on the stabilities of these structures would be helpful in finding an answer to this problem.

Conclusion

In this work, the kinetics and mechanisms of the gas-phase reactions of ionic nucleophiles toward carbonyl substrates were investigated.

Gas-phase ionic nucleophilicities toward carbonyl centers are found to be in the order $CH_3O^- \geq F^- > CN^- > SH^- > Cl^-$, which is the same as the gas-phase basicity order of the nucleophiles. The leaving-group abilities, $Br^- \geq Cl^- > F^-$, are in the same order as in solution. Nucleophilic displacement at carbonyl centers is favored by electron-withdrawing groups on the alkyl group of the carbonyl substrate but slightly retarded by increasing chain length and steric bulk of the alkyl group. The closer similarities between solution and gas-phase behavior of carbonyl systems than for reactions at sp^3 carbon centers are discussed in terms of the competition between nucleophile-solvent and nucleophile-substrate interactions in the two systems.

Quantitatively, the rates of ionic nucleophilic displacement at carbonyl centers are many orders of magnitude faster in the gas phase than in solution. However, these gas-phase rates are slower than expected for reactions occurring via a single minimum potential well, which is the currently accepted theoretical model. Our results are consistent with a double-minimum potential surface with loose association complexes of nucleophile and carbonyl substrate in the minima and a tetrahedral structure at a saddle point on the barrier between the two wells. Thermochemical estimates of energies of the tetrahedral structures were made. In the case of thermoneutral isotope exchange reactions, these estimates place the tetrahedral structure at an energy too high to account for the rates of the reactions suggesting that either these estimates are incorrect or that the mechanism does not proceed through these structures.

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An Experimental Study of the Gas-Phase Kinetics of Reactions with Hydrated H_3O^+ Ions (n = 1–3) at 298 K

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Abstract: Flowing afterglow experiments are reported which follow the influence of stepwise hydration on the kinetics of proton transfer from the hydronium ion to H_2S, CH_2O, $HCOOH$, CH_3OH, CH_3CHO, C_2H_5OH, CH_3COOH, $HCOOCH_3$, $(CH_3)_2O$, $(CH_3)_2CO$, and NH_3 at 298 ± 2 K. Rate constants have been measured for the reactions of these molecules with $H_3O^+{\cdot}H_2O$, $H_3O^+{\cdot}(H_2O)_2$, and $H_3O^+{\cdot}(H_2O)_3$. The reactions were observed to proceed according to the general equation $H_3O^+{\cdot}(H_2O)_n + B \rightarrow BH^+{\cdot}(H_2O)_m + (n - m + 1)H_2O$ with $0 \leqslant m \leqslant n$, albeit product distributions could not be unraveled. Comparisons are made with the rate constants for the "nude" reactions involving H_3O^+. The reversal in the relative basicity of H_2O and H_2S upon hydration which can be deduced from known energetics of solvation is manifested by a sharp drop (by $\gtrsim 10^3$) in the observed reaction rate constant for n = 1, 2, and 3. For B = CH_2O, equilibrium-constant measurements are reported which indicate a trend toward the equalization of the basicities of H_2O and CH_2O upon hydration with up to three water molecules. All of the hydrated H_3O^+ ions are observed to react rapidly and irreversibly with the remaining, somewhat stronger, oxygen bases with $k \geqslant 10^{-9}$ cm^3 molecule^{-1} s^{-1} and decreasing slightly and monotonically with increasing hydration. Comparisons with calculated capture rate constants indicate that these reactions proceed with approximately unit probability. The intriguing possibility of generating polymeric water molecules from the reactions investigated is discussed briefly.

Introduction

Hydrated H_3O^+ ions containing large numbers of water molecules can be generated in the gas phase through the sequential action of termolecular association or "clustering" reactions of the type

$$H_3O^+{\cdot}(H_2O)_n + H_2O + M \rightarrow H_3O^+{\cdot}(H_2O)_{n+1} + M \quad (1)$$

where M is an inert third body which serves to deactivate the hydrated H_3O^+ ion. For example, Kebarle and co-workers[1] were able to observe hydrates up to n = 7 in irradiated water vapor at pressures from 0.1 to 6 Torr and temperatures from 288 to 873 K, and also to measure the equilibrium constant for each of the steps involved in the buildup of $H_3O^+{\cdot}(H_2O)_7$ from H_3O^+. Indeed, gas-phase observations have been reported of cluster ions with water contents as large as n = 27, from which it has been inferred that hydrated H_3O^+ ions may grow directly and continually in the gas phase from the "nude" hydronium ion to charged droplets.[2] The availability of these ions in the gas phase has led to the exciting prospect of actually monitoring their reactions as a function of stepwise hydration and in the absence of interference from the bulk solvent effects present when such species react in solution. Concomitant information about the reaction of H_3O^+ then allows the extrapolation of the fine structure effect of hydration from the extreme of the intrinsic reaction to extents of hydration at which the distinction between the gas phase and solution begins to dissolve. We have recently reported such a study for reactions involving the isoelectronic counterparts associated with OH^-, vis., $OH^-{\cdot}(H_2O)_n$, and methanol, in which we followed the transition in the relative acidity of water and methanol from the gas phase to solution.[3]

The present study is concerned with the influence of the stepwise hydration on the kinetics of proton transfer from H_3O^+ to a variety of molecules, i.e., with reactions which may be represented by the general equation

$$H_3O^+{\cdot}(H_2O)_n + B \rightarrow BH^+{\cdot}(H_2O)_m + (n - m + 1)H_2O \quad (2)$$

where m may conceivably have any value between 0 and n with the water being produced as individual molecules, dimers, or

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