Intermediates and Potential Energy Surfaces in Thermoneutral Carbonyl Addition–Elimination Reactions

James L. Wilbur[†] **and John I. Brauman***

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received August 16, 1993[⊗]

Abstract: The experimental determination of the potential energy surface for gas-phase carbonyl addition–elimination reactions has been approached through the synthesis, isolation, and characterization of intermediates in four thermoneutral displacement reactions at carbonyl centers. The structure and reactivity of the putative intermediates were determined by both chemical and photochemical methods. For the reaction of $Cl^- + CH_3OCOCl$, the intermediates are shown conclusively to be unsymmetrical ion–molecule complexes, and the possibility of a stable, covalent tetrahedral adduct is ruled out. Infrared photoactivation of the intermediates results in unimolecular decomposition via an exothermic S_N2 substitution channel at the ester position. For the reaction of Cl^- with acetyl chloride, trimethylacetyl chloride, and trifluoroacetyl chloride, the tetrahedral species (intermediate or transition state) is observed to be energetically accessible under the experimental conditions. It is not possible, however, to determine unambiguously the structure(s) of the lowest energy species. The binding energies of the complexes and the existing kinetic and theoretical data, however, suggest that an electrostatic complex is most probable.

I. Introduction

Displacement reactions at carbonyl centers have been widely studied, both in solution and in the gas phase. These reactions are of particular interest given their widespread use in synthetic chemistry and their relevance to biological problems. Moreover, they represent a fundamental class of reactions that are sufficiently simple to offer the promise of a detailed understanding of their properties.

The mechanistic details of the rich chemistry observed in acyl-transfer reactions in solution are contained in numerous excellent reviews.[1,2] Early experiments by Bender[3] involving the hydrolysis of esters suggested that carbonyl addition–elimination reactions proceed through a covalently bound tetrahedral intermediate. Subsequent studies, which employed spectroscopic methods[4] as well as kinetic studies[5,6] and breaks in pH rate profiles,[7–9] were also consistent with this proposal.

The properties of carbonyl addition–elimination reactions in the gas phase have also been studied. By analogy to solution-phase results, early models for gas-phase carbonyl addition–elimination reactions suggested a single-minimum potential energy surface (Figure 1), in which a stable, covalently bound tetrahedral intermediate is the global minimum. Kinetic experiments by Asubiojo and Brauman,[10] however, found that the observed rates for a series of acyl-transfer reactions were significantly slower than the predicted collision rate, indicating a bottleneck to reaction. This observation could not be rationalized by a single-minimum potential energy surface, which lacks an enthalpic barrier to product formation. The authors postulated that the potential energy surface for the reaction was best described as a double minimum surface (Figure 2), where the minima are unsymmetrical complexes in which the ionic species is electrostatically bound by the (induced) dipole of the neutral molecule. The double-minimum model has also been applied to other classes of gas-phase ion–molecule reactions such as nucleophilic substitution and electron transfer and has been widely used to interpret the behavior of many gas-phase carbonyl addition–elimination reactions.

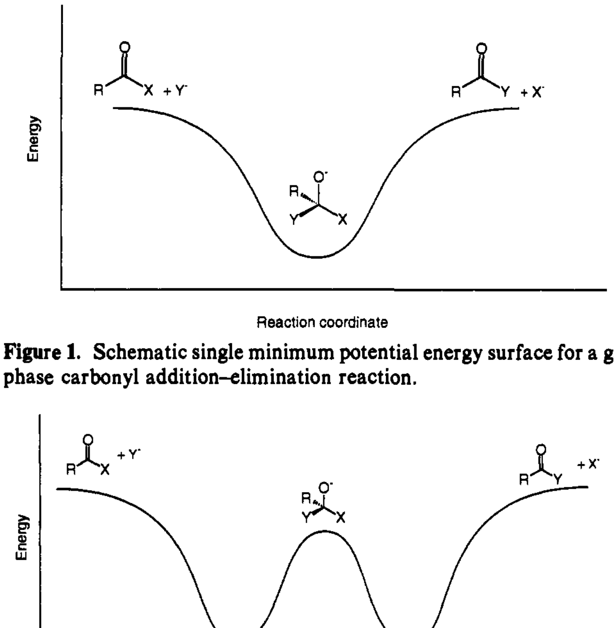


Figure 1. Schematic single minimum potential energy surface for a gas-phase carbonyl addition–elimination reaction.

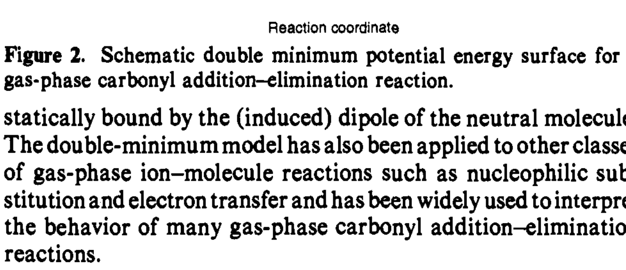


Figure 2. Schematic double minimum potential energy surface for a gas-phase carbonyl addition–elimination reaction.

Despite the success of the double minimum surface as a model for understanding gas-phase carbonyl reactions, a definitive experiment that verifies the model and does not rely on inference is desirable. One possible approach is to create, isolate, and characterize directly species that are intermediates in carbonyl addition–elimination reactions. If a single minimum surface is the correct model, a stable tetrahedral intermediate should be

---

[†] Present address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1994.

(1) Bender, M. L. *Chem. Rev.* **1960**, *60*, 53.
(2) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; Dover: New York, 1987.
(3) Bender, M. L. *J. Am. Chem. Soc.* **1953**, *75*, 5986.
(4) Fraenkel, G.; Watson, D. *J. Am. Chem. Soc.* **1975**, *97*, 231.
(5) Johnson, S. L. *J. Am. Chem. Soc.* **1964**, *86*, 3819.
(6) Johnson, S. L. *Tetrahedron Lett.* **1964**, 1481.
(7) Zerner, B.; Bender, M. L. *J. Am. Chem. Soc.* **1961**, *83*, 2267.
(8) Hand, E. S.; Jencks, W. P. *J. Am. Chem. Soc.* **1962**, *84*, 3505.
(9) Fedor, L. R.; Bruice, T. C. *J. Am. Chem. Soc.* **1965**, *87*, 4138.
(10) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715.

0002-7863/94/1516-5839$04.50/0

found. In the case of a double minimum surface, however, unsymmetrical ion–dipole complexes are expected. In a previous study from our laboratory,[11] intermediates for the thermoneutral carbonyl displacement reaction shown in eq 1 were reported to possess the characteristics of an unsymmetrical ion–molecule complex. The observation of a stable intermediate that possessed

$$CF_3COCl + {}^*Cl^- \rightarrow CF_3CO^*Cl + Cl^- \qquad (1)$$

the characteristics of an ion–dipole complex and the nonobservation of a stable tetrahedral adduct were interpreted as direct evidence for a multiple-well potential energy surface. Subsequent studies using new instrumentation, however, that sought to extend this work, found that the original results presented above were not reproducible.[12] Although these results could not be reproduced, there was no evidence found that obviated the double well potential energy surface, and quantum mechanical calculations[13] and other kinetic experiments remained consistent with the model. Thus, other, more extensive studies, that are the topic of this paper, were performed.

In this paper, we reexamine the nature of the potential energy surface for acyl-transfer reactions. We report the synthesis, isolation, and characterization by both chemical and photochemical methods of species corresponding to intermediates in the displacement reaction shown in eq 1. We find that although the intermediates isolated have a binding energy similar to those of other known ion–molecule complexes,[14–17] there is no evidence that rules out the possibility of a covalent tetrahedral adduct as a stable intermediate. Similar results were obtained for the related thermoneutral carbonyl displacement reactions shown below (eq 2). Finally, we reexamine a second thermoneutral carbonyl

$$RCOCl + {}^*Cl^- \rightarrow RCO^*Cl + Cl^- \qquad (R = CH_3,\ t\text{-Bu}) \qquad (2)$$

$$CH_3OCOCl + {}^*Cl^- \rightarrow CH_3OCO^*Cl + Cl^- \qquad \text{(addition–elimination)} \quad (3)$$

$$MeOCOCl + {}^*Cl^- \rightarrow Me^*Cl + CO_2Cl^- \qquad (S_N2\ \text{displacement}) \quad (4)$$

displacement reaction, shown in eq 3. Reactive intermediates for this system, which also has a competing and exothermic channel for S_N2 substitution at the ester position (eq 4), have been synthesized, isolated, and characterized by both chemical and photochemical methods. These intermediates are shown conclusively to be unsymmetrical ion–molecule complexes, and the possibility that this is a stable, covalent tetrahedral adduct is ruled out. This finding is consistent with that reported previously.[11]

II. Experimental Section

Instrumentation. Experiments were performed with a Fourier transform IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer equipped with impulse excitation.[18] The ICR consisted of a 1- × 1- × 1.5-in. rectangular cell, constructed of polished 0.020-in. oxygen-free hard copper (OFHC) plates, in which all ion generation, reactions, and detection occurred. These plates were mounted on Vespel rods, which formed the structural frame for the cell. The frame and cell were encased in a stainless-steel high-vacuum can and placed between the poles of a Varian electromagnet operating between 0.8 and 1.2 T. The high-vacuum can was equipped with a KCl window, and the front plate of the cell had a 15/16-in. diameter hole covered with 95% transmitting copper micromesh (20 lines per inch) to allow light to enter the cell. A polished copper mirror in the rear of the cell refleted the incident light back through the cell and out the KCl window. Neutral samples were admitted to the high-vacuum can by means of Varian leak values. Pressures of the neutral species in the ICR cell were monitored with an ion gauge (Varian 844), which was calibrated against a capacitance manometer when accurate values of the pressure were needed. Typical operating pressures were between 10^{-8} and 10^{-6} Torr.

Primary ions were generated by electron impact on neutral precursors. Resistive heating of a rhenium filament mounted on a Macor support generated the electrons, which entered the cell through a 1/8-in. hole which was covered with a 60% transmitting gold micromesh. The kinetic energy of the incident electrons was controlled by varying the potential applied to the filament and the bias on the parallel trapping plates. Typical operating current and voltage for the filament were 2–3 A and 1–3 V, respectively (for the generation of negative ions).

The multimode output of a tunable Lumonics TEA 103-2 CO_2 pulsed laser was used for all IRMP activation experiments. The laser beam was focused, reduced to the desired spot size using an iris, and allowed to enter the ICR cell through the KCl window. After the beam passed through the ion cloud, a mirror in the back of the ICR cell reflected the pulse back through the ion cloud. The intensity of the laser pulse was attenuated by passing the beam through CaF_2 flats of varying thickness. Pulse energies were measured using a Scientech 365 power and energy meter with a Scientech 38-0102 volume-absorbing disk calorimeter. Dividing the energy by the measured area of the beam pulse provided the fluence of the incoming beam. This fluence was multiplied by 2 to determine the effective fluence. For the IRMP experiments, the 9.6-μm, P(18) branch was used, corresponding to a wavelength of 1048.66 cm^{-1} (3.0 kcal mol^{-1} $photon^{-1}$). The absorption rates for pulsed IRMP activation experiments[19] are estimated to be 10^4–10^6 photons s^{-1}.

The duty cycle for IRMP activation experiments involved generation of complex ions (see below), double resonance ejection of all ions other than the ion of interest, irradiation with light, and detection (1–3 ms after irradiation). A similar duty cycle was performed with the laser blocked (light off) and subtracted from the "light on" spectrum to correct for background peaks. For each data point, multiple scans (50–500) were averaged to obtain reproducible ion abundances, and multiple data points were averaged at each fluence.

Materials. The primary ion, Cl^- (m/z = 35, 37), was generated from $ClCO_2CH_3$ (5×10^{-7} to 8×10^{-7} Torr) and RCOCl (R = CF_3, CH_3, and *t*-Bu; 2×10^{-7} to 1×10^{-6} Torr) by dissociative electron attachment. All chemicals were obtained from Aldrich, used without further purification, and subjected to multiple freeze–pump–thaw cycles before introduction into the ICR.

Formation of Complex Ions. Stable adducts corresponding to intermediates in gas-phase bimolecular reactions are not typically observed under ICR operating conditions, because the excess energy present in the reaction complex causes the intermediate to either revert to reactants or fragment to products. The excess energy can be removed, for example, by third body collisions or radiative emission. In the low-pressure regime of an ICR (10^{-8} Torr), however, such processes do not normally occur with sufficient frequency to be experimentally useful. Thus, species corresponding to intermediates in the gas-phase carbonyl addition-elimination reactions, eqs 1–3, were synthesized using the method developed by McMahon and co-workers.[14–17,20] Chloride ion, generated via electron impact (eqs 5a,b), reacts with methyl chloroformate, $ClCO_2CH_3$, to give the chlorocarbonate anion (eq 5c), which then donates chloride ion to form the desired adduct (eq 5d). Adducts $M{\cdot}Cl^-$ created in this fashion could be trapped in the ICR cell for 1–2 s, which is typical for trapping times of stable ions in our ICR spectrometer.

$$ClCO_2CH_3 \xrightarrow{e^-} Cl^- + CO_2CH_3 \qquad (5a)$$

$$RCOCl \xrightarrow{e^-} Cl^- + RCO \qquad (5b)$$

$$Cl^- + ClCO_2CH_3 \rightarrow ClCO_2^- + CH_3Cl \qquad (5c)$$

$$ClCO_2^- + M \rightarrow M{\cdot}Cl^- + CO_2 \qquad (5d)$$

$$CF_3H{\cdot}Cl^- + RCOCl \rightleftharpoons CF_3H + RCOCl{\cdot}Cl^- \qquad (5e)$$

---

(11) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 589.
(12) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 7835.
(13) Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 3856.
(14) Larson, J. W.; McMahon, T. B. *Can. J. Chem.* **1984**, *62*, 675.
(15) Larson, J. W.; McMahon, T. B. *J. Phys. Chem.* **1984**, *88*, 1083.
(16) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 517.
(17) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.
(18) McIver, R. T., Jr.; Hunter, R. L.; Baykut, G. *Rev. Sci. Instrum.* **1989**, *60*, 400.
(19) Osterheld, T. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 7158.
(20) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*. 2944.

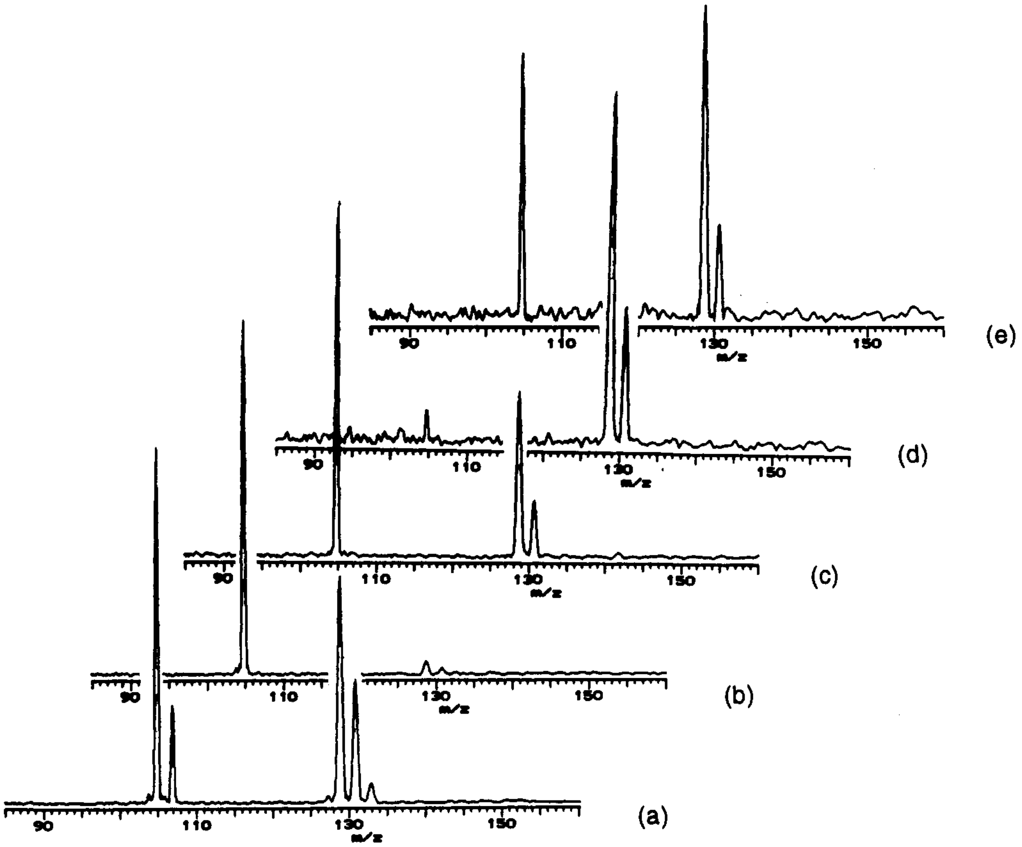


Figure 3. Data for chemical exchange studies. See text for details.

(M = chloride acceptor, e.g., CF_3COCl, CF_3H; R = CH_3O, CF_3, CH_3, *t*-Bu)

III. Results

The equilibrium shown in eq 5e was exploited to characterize the putative reaction intermediates structurally. We consider first the reaction of Cl^- with methyl chloroformate (eqs 3, 4). Complex ions of the form $[CH_3OCOCl_2]^-$, *m/z* 129, 131, and 133, which correspond to intermediates in the bimolecular reaction of Cl^- with methyl chloroformate (eqs 3, 4), and $CF_3H{\cdot}Cl^-$, *m/z* 105, 107, were synthesized as shown in eqs 5a–d. Figure 3a shows the resulting Fourier transform (FT) mass spectrum of these complex ions.[21] At approximately 400 ms following the electron beam pulse which generated the primary ions, all ions except $CF_3H{\cdot}{}^{35}Cl^-$ were ejected from the ICR cell (Figure 3b). $CF_3H{\cdot}{}^{35}Cl^-$ then transferred $^{35}Cl^-$ to neutral methyl chloroformate in the cell, forming $CH_3OCO^{35}Cl{\cdot}{}^{35}Cl^-$ and $CH_3OCO^{37}Cl{\cdot}{}^{35}Cl^-$. After equilibrium (eq 5e) was established (~300 ms), the ions were detected, yielding the mass spectrum in Figure 3c.

The nonobservation of $CF_3H{\cdot}{}^{37}Cl^-$ (*m/z* 107) and $CH_3OCO^{37}Cl{\cdot}{}^{37}Cl^-$ (*m/z* 133) indicates that only $^{35}Cl^-$ is transferred between the neutral molecules and that scrambling of the isotopic chlorines in $CH_3OCOCl_2^-$ does not occur.

To confirm that $CH_3OCOCl_2^-$ exchanges chloride back to CF_3H, the following reaction sequence was performed. At the same time delay that the mass spectrum shown in Figure 3c was recorded (~700 ms), all ions except the complex ions $CH_3OCO^{35}Cl{\cdot}{}^{35}Cl^-$ and $CH_3OCO^{37}Cl{\cdot}{}^{35}Cl^-$ were ejected from the cell (Figure 3d). Another delay period (~400 ms) was then used to allow Cl^- transfer, and the mass spectrum shown in Figure 3e was obtained. The presence of $CF_3H{\cdot}{}^{35}Cl^-$ (*m/z* 105) confirms that back transfer from $CH_3OCOCl_2^-$ complex ions is possible, while the nonobservation of $CF_3H{\cdot}{}^{37}Cl^-$ (*m/z* 107) and $CH_3OCO^{37}Cl{\cdot}{}^{37}Cl^-$ (*m/z* 133) confirms again that only $^{35}Cl^-$ is transferred between the neutrals. Thus, for the complex ion $CH_3OCOCl_2^-$, only the chloride which was transferred from $CF_3H{\cdot}Cl^-$ could be exchanged; the chloride which was originally covalently bound to the neutral CH_3OCOCl was never exchanged.

IRMP activation of the thermalized complex ion $CH_3OCOCl_2^-$ resulted in unimolecular dissociation of two products, Cl^- and $ClCO_2^-$. The branching ratio, which was observed to change with intensity, is presented in Table 1. IRMP activation of "labeled" $CH_3OCOCl_2^-$ complex ions (in which only $^{35}Cl^-$ had been transferred from $CF_3H{\cdot}{}^{35}Cl^-$) was also effected. The branching ratios and isotopic composition of the product ions, Cl^- and $ClCO_2^-$, are also shown in Table 1.

We consider next the thermoneutral acyl-exchange reaction of Cl^- with trifluoroacetyl chloride (eq 1). Stable adducts of the form $CF_3COCl_2^-$ (*m/z* 167, 169, 171) were synthesized as described above and subjected to a sequence of chloride-exchange reactions similar to those described above for methyl chloroformate. $CF_3H{\cdot}{}^{35}Cl^-$ was isolated and allowed to transfer $^{35}Cl^-$ to neutral CF_3COCl until equilibrium was reached. The formation

Table 1. Observed and Calculated Product Ratios for IRMP Activation of $CH_3OCOCl{\cdot}{}^{35}Cl^-$ Intermediates and the Bimolecular Reaction of Cl^- + CH_3OCOCl

	observed branching ratios			calculated ratios[a]	
	$\frac{ClCO_2^-}{(^{35}Cl^- + {}^{37}Cl^-)}$	$\frac{^{35}Cl^-}{^{37}Cl^-}$	$\frac{^{35}ClCO_2^-}{^{37}ClCO_2^-}$	$\frac{ClCO_2^-}{^{35}Cl^-}$	Φ[b]
IRMP activation					
low intensity[c]	4.5	3.1	3.0	>10	~90%
high intensity[d]	1.7	6.1	3.0	1.3	~56%
bimolecular reaction[e]	0.05				~5%

[a] Using Scheme 1 and the method outline in the Appendix. [b] Φ = efficiency = product formed/(product + reactant) = $ClCO_2^-/(ClCO_2^- + Cl^-)$. [c] Fluence = 1.1 – 1.3 J/cm^2, 9.6 μm, P(18) = 1048.66 cm^{-1}. [d] Fluence = 0.1 – 1.3 J/cm^2, 9.6 μm, P(18) = 1048.66 cm^{-1}. [e] Sec ref 14.

---

(21) It is important to note that the isotope ratios for the complex ions properly reflect the natural isotopic abundance of Cl^-, which is ^{35}Cl:^{37}Cl = 3:1.

of $CF_3CO^{35}Cl\cdot{}^{35}Cl^-$ and $CF_3CO^{37}Cl\cdot{}^{35}Cl^-$ ions was observed; however, at longer times, $CF_3H\cdot{}^{37}Cl^-$ (*m/z* 107) and $CF_3CO^{37}Cl\cdot{}^{37}Cl^-$ (*m/z* 171) were also observed. To confirm that the source of $CF_3H\cdot{}^{37}Cl^-$ was transfer of $^{37}Cl^-$ from $CF_3COCl_2^-$ adducts, the same sequence of reactions was carried out, but $CF_3COCl_2^-$ ions containing both $^{35}Cl^-$ and $^{37}Cl^-$ were continuously ejected. Under these conditions, neither $CF_3H\cdot{}^{37}Cl^-$ nor $CF_3CO^{37}Cl\cdot{}^{37}Cl^-$ was observed, even at long reaction delays. That complete scrambling of isotopes occurred was further supported by the observation that the relative intensities of the three isotopologs at *m/z* 167, 169, and 171 approached a ratio of 9:6:1, as would be expected for a compound containing two chlorines at their natural abundance. Finally, IRMP activation of $CF_3COCl\cdot{}^{35}Cl^-$ produced both $^{35}Cl^-$ and $^{37}Cl^-$ in a ratio of 3:1. Thus, the two chlorides in the adducts $CF_3COCl_2^-$ were not observed to retain their identity and in fact, were observed to become equivalent.

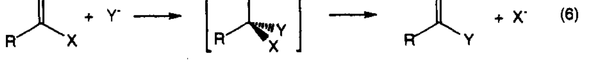
The same sequence of reactions was carried out using CH_3OH (instead of CF_3H) as the initial chloride donor/acceptor, with similar results.

Identical chloride-exchange experiments were also conducted for the reaction of Cl^- with both acetyl chloride and trimethylacetyl chloride (eq 2). In both cases, the chlorides in the adducts $RCOCl_2^-$ were observed to lose their identity.

Chloride binding energies for each of the carbonyl substrates were determined using the halide-exchange equilibrium shown in eq 5e. The chloride binding energies ($\Delta H°$) of CH_3COCl, $(CH_3)CCOCl$, and CF_3COCl ion were determined to be 14.5, 15.5, and 18 kcal mol^{-1}, respectively. The Cl^- binding energies of CH_3OCOCl and CF_3COCl have been measured by Larson and McMahon,[17] with values of 14.1 and 17.8 kcal mol^{-1}, respectively. CH_3COCl was determined relative to CH_3OCOCl, while $(CH_3)_3COCl$ was determined relative to both CH_3OCOCl and CF_3H. CF_3COCl was measured relative to CF_3H and SO_2.

IV. Discussion

Background. Displacement reaction of nucleophiles at carbonyl carbon has long been a topic of significant interest.[2] Synthetic transformations involving aldehydes, ketones, and carboxylic acid derivatives are well known, and many biological processes involve the carbonyl functional group. In solution, these reactions are thought to proceed through an addition–elimination mechanism[2,22–24] which involves a tetrahedral species as an intermediate (eq 6). Support for this mechanism is provided in part by the observation that tetrahedral addition products can be formed in solution. Stable tetrahedral adducts are well known in solution for aldehydes and ketones. For example, the hydrate of acetaldehyde in water exists in nearly equal amounts with the free aldehyde,[25] and chloral is known to make stable addition products with water and with alcohols.[26] Tetrahedral addition products for carboxylic acid derivatives, however, are formed much less readily, due in part to the resonance stabilization of the carbonyl group by the substituents (X, Y; eq 6). Nevertheless, in favorable cases adducts may form. For example, ethoxide ion adds to ethyl trifluoroacetate to form a stable addition product,[3] and other cyclic addition products are also known.[27] The involvement of tetrahedral addition products as intermediate species in carbonyl addition–elimination reactions has also been established.[1] Oxygen-18 labeling studies in the alkaline hydrolysis of esters[1,3,28] suggested that the reaction proceeded through a tetrahedral addition intermediate. Further ^{18}O labeling studies involving the alkaline hydrolysis of amides[7] and thioesters[8,9] also implicated a stable tetrahedral adduct. Kinetic evidence for tetrahedral intermediates has been provided.[5,6,29–31] and spectroscopic studies have also been reported.[4]



(6)

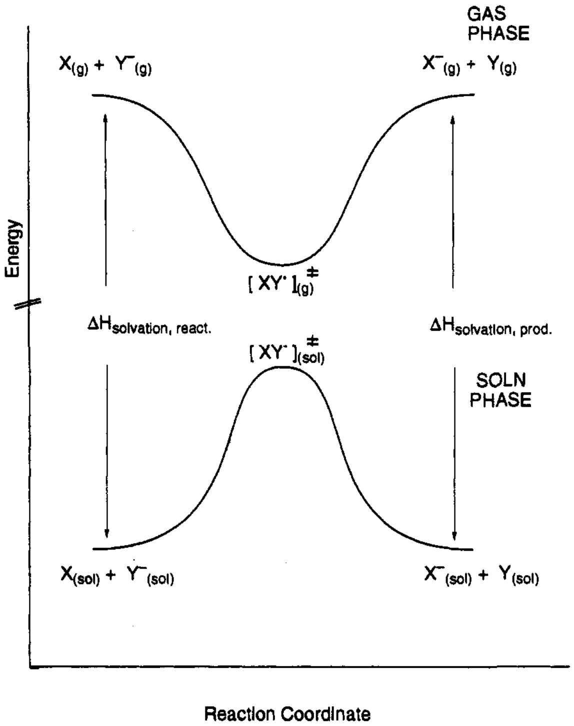


Figure 4. General solution and gas-phase potential energy surfaces.

The mechanism of gas-phase ion–molecule reactions at carbonyl centers and, in particular, the importance of tetrahedral species as intermediates are less clear. First, there are significant differences between solution-phase and gas-phase potential energy surfaces (Figure 4). The lower surface is typical for solution-phase reactions, where the solvated reactants and products are lower in energy than any loosely complexed species. The activation barriers which separate reactants and products arise from a combination of desolvation energies and any intrinsic barrier associated with formation of transition states and/or intermediate species. In the gas phase, however, bimolecular reactions take place in the absence of solvent, which dramatically changes the potential energy surface.[32] Association is energetically favorable due to electrostatic attractions between the ion and the dipole of the neutral molecule, and the reactants and products are often higher in energy than the associated species. Consequently, gas-phase potential energy surfaces appear to be "inverted" relative to solution-phase reactions (upper curve, Figure 4).

The single-minimum potential energy surface (Figure 1), in which a stable, covalently bound tetrahedral intermediate is the global minimum, has been suggested for gas-phase addition-elimination reactions. The simplicity of the model and its obvious connection to solution-phase results make it appealing. Such a potential energy surface, however, contains no enthalpic barrier to reaction. Thus, for exothermic reactions, formation of products should proceed at or very near the association rate.

Asubiojo and Brauman[10] observed that many displacement reactions at carbonyl centers produced products with rates that

---

(22) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1985.

(23) Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

(24) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1985; Vol. A.

(25) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1.

(26) Post, J. *J. Org. Chem.* **1941**, *6*, 830.

(27) Zaugg, H. E.; Papendick, V.; Michaels, R. J. *J. Am. Chem. Soc.* **1964**, *86*, 1399.

(28) Bender, M. L. *J. Am. Chem. Soc.* **1951**, *73*, 1626.

(29) Mader, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 3191.

(30) Schowen, R. L.; Jayaraman, H.; Kershner, L. *J. Am. Chem. Soc.* **1966**, *88*, 3373.

(31) Eriksson, S. O.; Holst, C. *Acta Chem. Scand.* **1966**, *20*, 1892.

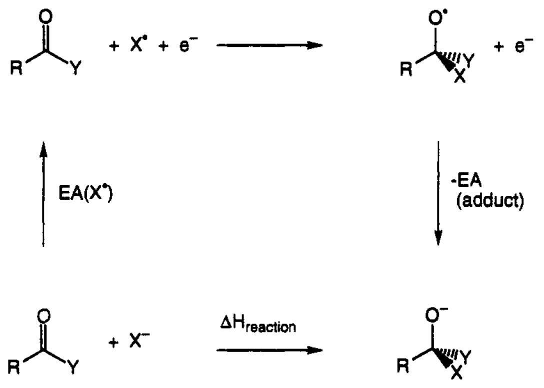
(32) Dewar, M. J. S.; Storch, D. M. *J. Chem. Soc., Chem. Commun.* **1985**, 94.

were much slower than the collision rate. Indeed, even highly exothermic reactions showed an efficiency[33] that was significantly less than unity, suggesting a bottleneck to reaction. The double-minimum surface shown in Figure 2 was proposed to explain these observations. In this model, the minima of the surface are unsymmetrical complexes in which the ionic species is electrostatically bound by the dipole of the neutral molecule. The tetrahedral adduct, which lies between the two "ion–dipole" complexes, is a transition state. In the bimolecular reaction, the ion–dipole complexes, once formed, can either cross the reaction barrier to form products or revert to reactants. Because the latter channel is entropically favored, the rates for dissociation (of the complex) to products and reactants can compete, even when the reaction barrier is below the entrance channel, and thus reduce the efficiency of product formation. Although the single and double minimum potential energy surfaces appear to be quite different, the double minimum surface can be thought of as originating from the single well potential when the loose electrostatic complexes have become more stable than the tetrahedral adduct. Thus, the two surfaces are related by the relative stabilities of the electrostatic complexes and the covalent tetrahedral adduct.

The stability of an ion–dipole complex in the gas phase is dependent on the electrostatic attraction between the ion and the dipole of the neutral molecule. For most carbonyl addition-elimination reactions, the binding energy is relatively constant, between 12 and 20 kcal mol^{-1}. The stability of tetrahedral addition products, however, may be more variable. In the absence of solvation, the enthalpy of addition depends most strongly on the properties of the nucleophile and the tetrahedral adduct. The thermochemical cycle shown in Figure 5 has been suggested previously[34,35] to illustrate how the difference in electron affinities between the attacking nucleophile and the tetrahedral adduct affects the overall enthalpy of adduct formation. If the difference between the reactants and products in the upper reaction (carbonyl + $X^\bullet$ vs neutral adduct) is small relative to the difference between the corresponding ionic reactants and products (a rough approximation), then the heat of reaction for formation of the anionic tetrahedral adduct reduces to the difference in the electron affinities of the nucleophile and adduct. In the case of a nucleophile with a very low electron affinity (e.g., CH_3^-), the tetrahedral adduct is expected to be very stable. In the opposite case, however, where the nucleophile has a very high electron affinity (e.g., Cl^-, CN^-), the relative stability of the tetrahedral addition product is expected to be low. When the electron affinity of the attacking nucleophile is between these two limiting cases, as with alkoxide ions, the energetics for formation of the tetrahedral adduct become less clear.

As predicted by the thermochemical cycle in Figure 5, tetrahedral adducts have been observed as stable species for alkyl anion and hydride nucleophiles. Bohme and co-workers formed tetrahedrally coordinated methoxide by the reaction of H^- with formaldehyde using a helium buffer gas to collisionally deactivate the addition complex.[36] McDonald and Chowdhury reported the formation of a stable product resulting from the condensation of CF_3^- and $(CF_3)_2CO$, and inferred a tetrahedral structure based on proton affinity bracketing experiments.[37] A tetrahedral structure has also been invoked for the carbonyl addition products of $O_2^{\bullet -}$ with ketones.[38]

Both tetrahedral adducts and ion–dipole complexes have been observed for the reaction of OH^- and alkoxides with carbonyl compounds. Bohme observed a stable adduct when OH^- reacted with formaldehyde in the presence of a helium buffer gas.[39] A tetrahedral structure was suggested and has also been implicated by theoretical calculations.[40,41] Bowie and Williams observed a stable addition product from the reaction of trifluoroacetate anion and perfluoroacetic anhydride, and suggested a tetrahedral structure based on its decomposition reactions.[42] Brauman and co-workers[35] found the most stable structure for a deprotonated cyclic hemiacetal anion to be tetrahedral. They also suggested that the addition product of CH_3O^- with benzaldehyde was tetrahedral. Nibbering and van der Wel,[43,44] however, concluded that ion–dipole complexes coexisted with the tetrahedral adduct for a series of reactions of methoxide with aldehydes and esters. Bowie and co-workers reacted aldehydes, ketones, and esters with alkoxide alcohol $[RO^- \cdots HOR]$[45] and F^- alcohol adducts $[F^- \cdots HOR]$[46] to form stable addition products. Ab initio calculations indicated that the addition products were best described as "solvated enolate" complexes.



Nucleophiles	EA
CH_3^-	2 kcal mol^{-1}
CH_3O^-	37 kcal mol^{-1}
Cl^-	83 kcal mol^{-1}

Figure 5. Thermochemical cycle for the estimation of relative stabilities of carbonyl adduct formation.

For weak nucleophiles with high electron affinities, ion–dipole complexes are predicted by the thermochemical cycle presented above. Experimentally, Larson and McMahon[14–17,20,47] have measured the complex binding energies for F^-, Cl^-, and CN^- with a series of neutral molecules, including simple aldehydes, esters, and ketones. In most cases, the Cl^- affinity was most consistent with an electrostatic complex. Ab initio studies by Bowie and co-workers on the reaction of F^- with acrolein found that an ion–dipole complex was comparable in stability to the tetrahedral addition compound. Howard and Kollman[48] performed ab initio calculations on the reaction of HS^- with formamide. They identified an ion–dipole complex on the reaction coordinate, but no stable tetrahedral structure was found. Theoretical studies by Yamabe and Minato[49] predicted an ion–dipole structure for

---

(33) The efficiency, $\Phi \equiv$ (number of collision producing products)/(total number of collisions).

(34) Baer, S. Ph.D. Thesis, Stanford University, Stanford, CA. 1990.

(35) Baer, S.; Brinkman, E. B.; Brauman, J. I. *J. Am. Chem. Soc.* **1991**, *113*, 805.

(36) Bohme, D. K.; Mackay, G. I.; Tanner, S. D. *J. Am. Chem. Soc.* **1980**, *102*, 407.

(37) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1983**, *105*, 7267.

(38) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123.

(39) Tanner, S. D.; Mackay, G. I.; Bohme, D. K. *Can. J. Chem.* **1981**, *59*, 1615.

(40) Williams, I. H.; Maggiora, G. M.; Schowen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 7831.

(41) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517.

(42) Bowie, J. H.; Williams, B. D. *Aust. J. Chem.* **1974**, *27*, 1923.

(43) Nibbering, N. M. M.; van der Wel, H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 479.

(44) Nibbering, N. M. M.; van der Wel, H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 491.

(45) Klass, G.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1982**, *35*, 2471.

(46) Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1983**, *36*, 289.

(47) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1987**, *109*, 6230.

(48) Howard, A. E.; Kollman, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 7195.

(49) Yamabe, S.; Minato, T. *J. Org. Chem.* **1983**, *48*, 2972.

the complex in the reaction of Cl^- with CH_3COCl. Blake and Jorgensen[13] have reported more recent calculations which predicted an ion–dipole complex for the reactions of Cl^- with $HCOCl$ and CH_3COCl. A double minimum surface was predicted for both of the bimolecular reactions.

Our experiments address the potential energy surface of addition–elimination reactions of Cl^- with acyl chlorides. Kinetics, thermochemical arguments, and theoretical predictions indicate that a double minimum surface may be present. Our experiments, by determining directly the structure of intermediate species, can provide more definitive evidence about the nature of the potential surface.

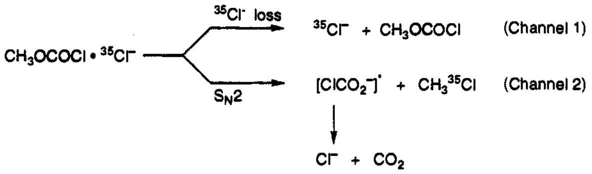
Reaction of Cl^- + CH_3OCOCl. The reaction of Cl^- with methyl chloroformate has two possible channels, a thermoneutral carbonyl displacement reaction (eq 3) and a competing exothermic S_N2 displacement reaction (producing $ClCO_2^-$) at the ester position (eq 4). The S_N2 reaction is observed[14] to proceed at room temperatures with a rate constant of 1×10^{-10} cm^3 molecule^{-1} s^{-1}, corresponding to an efficiency of approximately 5%. The bimolecular carbonyl addition–elimination reaction is not observed to compete with the S_N2 reaction, although observation of a slow ($\sim < 10^{-11}$ cm^3 molecule^{-1} s^{-1}) thermoneutral reaction at the carbonyl center would be obscured by decomposition of $ClCO_2^-$ produced via the substitution channel.[50] The observation that the S_N2 reaction proceeds at only 5% efficiency indicates the presence of a barrier to its product formation. Since the S_N2 reaction is the kinetically preferred channel, this implies the existence of a substantial barrier for the carbonyl addition-elimination channel.

Using the reaction sequence shown in eqs 5a–d, species corresponding to putative intermediates in the reaction of Cl^- + CH_3COCl were synthesized and isolated. Chloride-transfer experiments (Figure 3) indicated that the two chlorides in $CH_3OCOCl_2^-$ were distinguishable, that is, only the chloride that originally came from the external source, $CF_3H{\cdot}Cl^-$, could be exchanged. Thus, the two chlorides in the $CH_3OCOCl_2^-$ intermediate are not equivalent. This observation rules out the possibility that the observed intermediate is a covalent tetrahedral species in which both chlorines are equivalent. Further, the chloride binding energy[14,51] of CH_3OCOCl is 14.1 kcal mol^{-1}, comparable to those of other known ion–dipole complexes involving Cl^-. These observations indicate that the $CH_3OCOCl_2^-$ intermediate is best described as an ion–molecule complex in which the Cl^- ion is electrostatically bound to the dipole of the neutral CH_3OCOCl.

These results are consistent with a double well potential surface for the thermoneutral chloride-exchange reaction. The structures of the putative intermediates we have isolated are most consistent with an unsymmetrical ion–dipole complex, and there is no evidence that indicates the presence of a stable tetrahedral species. By symmetry, the presence of a second ion–dipole complex in the exit channel for the reaction is required. Interconversion of these two complexes presumably would occur through a tetrahedral species corresponding to the barrier separating the two complexes. Interconversion, however, does not occur, as shown by the chloride-transfer experiments, indicating that the tetrahedral structure is inaccessible. A triple-minimum surface where the tetrahedral species is a global minimum is not ruled out, provided there is a significant barrier between it and the ion–dipole complex.

Further structural details were obtained by infrared multiple photon (IRMP) activation[52,53] and subsequent unimolecular decomposition of the $CH_3OCOCl_2^-$ intermediate. Two products, $ClCO_2^-$ and Cl^-, result from unimolecular dissociation of the intermediate. IRMP activation was also carried out with isotopically labeled $CH_3OCOCl_2^-$, where the external Cl^- is $^{35}Cl^-$ and the chlorine covalently bound to the neutral is either $^{35}Cl^-$ or $^{37}Cl^-$. The branching ratios for formation of $ClCO_2^-$ and Cl^- and the isotopic distributions of these products, which are observed to change with intensity, are shown in Table 1.

Scheme 1



The ratio of products formed, $ClCO_2^-/Cl^-$, is 4.5 at low intensities, and decreases to 1.7 at high intensities. This observation is consistent with a lower energy threshold for formation of $ClCO_2^-$. Formation of $ClCO_2^-$, as with the bimolecular reaction (eq 4), results from dissociation via the S_N2 channel. Thus, when the $CH_3OCOCl_2^-$ intermediate is energized via IRMP activation, the lowest energy pathway observed is dissociation across the S_N2 barrier.

The observed isotope ratios for the $ClCO_2^-$ product can be used to extract structural information on the $CH_3OCOCl_2^-$ intermediate. The isotope ratio of $^{35}Cl^-$ to $^{37}Cl^-$ in the neutral CH_3OCOCl must be 3:1, the natural chloride isotope abundance. If the two chlorines in isotopically labeled $CH_3OCOCl{\cdot}{}^{35}Cl^-$ were to undergo exchange (i.e., become equivalent), then the relative abundance of $^{35}Cl^-$ at both chlorine sites would be enriched. In this case, the isotope ratio for $ClCO_2^-$ would be expected to approach 7:1. If the external $^{35}Cl^-$ does not scramble with the chlorine in the neutral CH_3OCOCl, an isotope ratio of 3:1 is expected for $ClCO_2^-$. The isotope ratio of the $ClCO_2^-$ ion, which results from dissociation of the isotopically labeled intermediate $CH_3OCOCl{\cdot}{}^{35}Cl^-$ via the S_N2 pathway, is 3:1 for all intensities. Thus, the external $^{35}Cl^-$ retains its identity and does not become equivalent with the other chlorine in the $CH_3OCOCl{\cdot}{}^{35}Cl^-$ intermediate under conditions of photoactivation.

Both $^{35}Cl^-$ and $^{37}Cl^-$ are observed, however, when $CH_3OCOCl{\cdot}{}^{35}Cl^-$ is dissociated via IRMP activation. Unimolecular dissociation of the noncovalent bond between the external $^{35}Cl^-$ and the neutral CH_3OCOCl is a plausible pathway for production of $^{35}Cl^-$. The source of $^{37}Cl^-$, however, is less obvious. We have previously shown, both by chemical-exchange experiments and under conditions of photoactivation, that the two chlorines in the $CH_3OCOCl{\cdot}{}^{35}Cl^-$ intermediate do not become equivalent, that is, scrambling of the external chloride is not observed. Thus, creation of an intermediate $CH_3OCOCl{\cdot}{}^{37}Cl^-$ via isomerization and subsequent decomposition to produce $^{37}Cl^-$ can be ruled out. An alternative pathway for Cl^- and CO_2 production is shown in Scheme 1. As stated previously, $^{35}Cl^-$ can be produced by cleavage of the electrostatic ion–dipole interaction in the $CH_3OCOCl{\cdot}{}^{35}Cl^-$ complex. Formation of $ClCO_2^-$ via the S_N2 channel is an exothermic process, and production of hot $ClCO_2^-$, which subsequently decomposes to produce Cl^- and CO_2, is possible. The Cl^- binding energy to CO_2 is weak[54] (8.0 kcal mol^{-1}), comparable to that of xenon[55] (7.5 kcal mol^{-1}). Thus, only a small amount of excitation of the $ClCO_2^-$ would be required for decomposition. Indeed, $ClCO_2^-$ is observed to decompose to Cl^-

---

(50) The thermoneutral chloride-exchange reaction could, in principle, be observed by use of the isotopic exchange reaction $^{35}Cl^- + CH_3CO^{37}Cl = {}^{37}Cl^- + CH_3CO^{35}Cl$. However, the product of the competing S_N2 reaction, $ClCO_2^-$, decomposes to Cl^- and CO_2 under the experimental conditions, thus preventing conclusive observation of the chloride-exchange reaction.

(51) Wilbur, J. L.; Brauman, J. I., unpublished result.

(52) Briefly, the intermediates are subjected to infrared radiation and energized by the absorption of multiple (5–10) photons. If the ions absorb sufficient energy to reach a dissociation threshold and the rate for dissociation competes with the rate of photon absorption, unimolecular decomposition will occur.

(53) Johnson, C. E.; Brauman, J. I. In *Techniques for the Study of Ion Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley: New York, 1988; Vol. XX.

(54) Keesee, R. G.; Lee, N.; Castleman, A. W. *J. Chem. Phys.* **1980**, *73*, 2195.

(55) Riveros, J. M.; Tiedeman, P. W.; Breda, A. C. *Chem. Phys. Lett.* **1973**, *20*, 345.

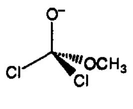
and CO_2 readily under ICR conditions (350 K, 10^{-6} Torr), presumably due to low-energy collisions (<10 kcal/mol) with neutrals.[51]

Assuming that Scheme 1 is operative, we can estimate the actual branching ratio for production of $ClCO_2^-$ and Cl^-. We have observed that $ClCO_2^-$ is produced with a 3:1 chloride isotopic abundance. Assuming the rates for dissociation of hot $ClCO_2^-$ to produce Cl^- and CO_2 are equal for both $^{35}Cl^-$ and $^{37}Cl^-$, this channel is expected to produce $^{35}Cl^-$ and $^{37}Cl^-$ in a ratio of 3:1. At low fluences, the ratio of $^{35}Cl^-$ to $^{37}Cl^-$ is 3:1. If $^{37}Cl^-$ originates exclusively from decomposition of hot $ClCO_2^-$, then at low fluences (by virtue of the 3:1 isotope ratio), essentially all $^{35}Cl^-$ must also come from this channel. Thus, at low fluences, no $^{35}Cl^-$ is produced by simple dissociation, and all $CH_3OCOCl{\cdot}{}^{35}Cl^-$ intermediates decompose via the S_N2 channel.

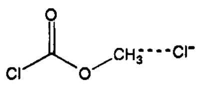
At high fluences, the ratio of $^{35}Cl^-$ to $^{37}Cl^-$ is 6:1. Here, $^{35}Cl^-$ is likely to originate from both channels shown in Scheme 1. It is possible to calculate (Appendix) the contribution of each channel to the experimentally observed product ratio and thus obtain the actual product branching ratios. At high fluences, we find that the $CH_3OCOCl{\cdot}{}^{35}Cl^-$ complex dissociates through both channels (S_N2 and $^{35}Cl^-$ loss) with a ratio of approximately 1.3:1, respectively. Decomposition via the higher energy, higher *A*-factor Cl^- loss channel is expected at the higher intensity (faster pumping rate). The calculated branching ratios for the two channels and the corresponding efficiencies are shown in Table 1. The observation that unimolecular dissociation occurs via both the Cl^- loss and the S_N2 channel indicates that the two channels are within[56] ~3–4 kcal mol^{-1} of each other, consistent with the low efficiency (~5%) observed in the bimolecular reaction.

The calculated efficiencies for the IRMP activation experiments are also shown in Table 1. It is interesting that the efficiencies observed for the IRMP experiments are significantly higher (~>90% at low intensity, ~50 % at high intensity) than that observed in the bimolecular reaction (~5%). A similar result was reported previously[57] for the S_N2 reaction of Cl^- with methyl trifluoroacetate and was attributed to differences in angular momentum and energy distributions for the bimolecular and unimolecular processes. Because of large impact parameters, the bimolecular reaction is characterized by orbital angular momentum not present in the photolysis experiments. The orbital angular momentum in the bimolecular reaction raises the average effective barrier, resulting in a change in the efficiency. In the S_N2 system previously mentioned, statistical reaction rate models indicated that these changes accounted for about 30% of the effects seen. Differences in energy distributions are also likely to be important. In the energization of the intermediate, there is an energy regime of width 3–4 kcal/mol in which an activated species has sufficient energy to cross the reaction barrier but not enough energy to access the entrance channel.[58] For species in this regime, formation of products is 100% efficient. In the case of the bimolecular reaction, the reactants have energy at or above both channels. Thus, the intermediate energy range is not accessed, and the efficiency is reduced.

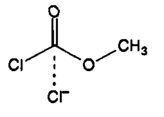
In summary, we have synthesized and isolated a putative intermediate in the reaction of $Cl^- + CH_3OCOCl$. Chemical-exchange experiments with labeled $CH_3OCOCl{\cdot}{}^{35}Cl^-$ and the binding energy of the complex indicate that the intermediate is best described as an unsymmetrical ion–dipole complex, where the chloride ion is electrostatically bound by the dipole of the neutral methyl chloroformate. Further, a covalent tetrahedral structure (7A) is ruled out by the observation that neither chemical-exchange nor photoactivation conditions can access a structure in which the two chlorines (in the $CH_3OCOCl_2^-$ intermediate) become equivalent. The exact structure of the ion–dipole complex, however, cannot be rigorously assigned. Both the bimolecular reaction and the energized decomposition of $CH_3OCOCl_2^-$ intermediates are observed to produce S_N2 products. This clearly indicates that a geometry (for the $CH_3OCOCl_2^-$ complex) amenable to S_N2 substitution (7B) must at least be accessible. A structure in which Cl^- is oriented toward the dipole of the carbonyl carbon (7C) is not ruled out by the inaccessibility of the covalent tetrahedral structure, although interconversion to a "substitution" geometry (7B) would have to be facile.



7A



7B



7C

Reactions of Cl^- + RCOCl (R = CF_3, CH_3, and *t*-Bu). The reaction of Cl^- with trifluoroacetyl chloride has only one available channel for reaction, the thermoneutral acyl-transfer reaction shown in eq 1. A rate of 1.77×10^{-10} cm^3 molecule^{-1} s^{-1}, corresponding to an efficiency of approximately 13%, was reported in a previous study from our lab.[10] The observation that the efficiency is significantly less than 50% indicates that some barrier to reaction is present, consistent with a double minimum potential energy surface.

Previous experiments by Han and Brauman have been reported[11] that probed the structure of the intermediate species in this reaction. These results indicated that the most likely structure for the intermediate in the reaction of Cl^- with CF_3COCl was an ion–dipole complex. Subsequent studies using new instrumentation, however, which sought to extend this work, found that the original results presented above were not reproducible.[12] Thus, other more extensive studies were performed and are described below.

Using the reaction sequence shown in eqs 5a–d, species corresponding to putative intermediates in the reaction of Cl^- with CF_3COCl were synthesized and isolated. In contrast to the results reported previously,[11] chloride-transfer experiments using $CH_3OH{\cdot}Cl^-$ indicate that the two chlorides in $CF_3COCl_2^-$ cannot be distinguished, that is, the two chlorines in isotopically labeled $CF_3COCl_2^-$ are observed to scramble. Further studies, which used $CF_3H{\cdot}Cl^-$, confirm that the chlorines cannot be distinguished. The observation that the isotope ratios in the $CF_3COCl_2^-$ reach 9:6:1 at long times provides further confirmation of complete scrambling.

IRMP activation experiments were conducted to obtain further information about the structure of the $CF_3COCl_2^-$ adduct. Energization and subsequent unimolecular decomposition of $CF_3COCl_2^-$, in which only $^{35}Cl^-$ was donated from $CF_3H{\cdot}H^{35}Cl^-$, produced both $^{35}Cl^-$ and $^{37}Cl^-$ in a ratio of 3:1. If the $^{35}Cl^-$ donated by $CF_3H{\cdot}{}^{35}Cl^-$ remained distinct from the chlorine originally present in the neutral CF_3COCl and isomerization did not occur following energization, then IRMP activation should produce only $^{35}Cl^-$. Thus, the 3:1 ratio of $^{35}Cl^-$ to $^{37}Cl^-$ indicates that the two chlorines in the $CF_3COCl_2^-$ adduct become equivalent under conditions of photoactivation.

Similar chloride-exchange studies were conducted with acetyl chloride and trimethyl acetyl chloride (eq 2) as substrates.[59] In both cases, complete scrambling of the two chlorines in the $RCOCl_2^-$ anion was observed. Replacing CF_3 with CH_3 or $(CH_3)_3C$, which are less electron-withdrawing, is expected to change the overall stability of the adduct. This is reflected in the

---

(56) Unimolecular decomposition occurs when the rate of dissociation competes with the rate of photon absorption. In general, for energies slightly above threshold, dissociation occurs before another photon can be absorbed. The energy of the infrared photon in these experiments is 3 kcal mol^{-1}. Thus, the maximum energy of activation is expected to be about 3–4 kcal mol^{-1} above a dissociation threshold.

(57) Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1991**, *113*, 9699.

(58) Both the efficiency of the bimolecular S_N2 reaction and the IRMP activation results indicate that the barrier lies approximately 3–4 kcal mol^{-1} below the entrance channel.

(59) The reaction of Cl^- with CH_3COCl proceeds with a rate of 1.19×10^{-10} cm^3 molecule^{-1} s^{-1} (efficiency = 5%), while the reaction of Cl^- with CH_3COCl proceeds with a rate of 0.68×10^{-10} cm^3 molecule^{-1} s^{-1} (efficiency = 2.8%).

decreased (~2–3 kcal/mol) Cl^- affinities of CH_3COCl and $(CH_3)_3CCOCl$ relative to CF_3COCl.

These observations do not provide sufficient evidence to identify conclusively the structures of the $RCOCl_2^-$ intermediates. The observation of scrambling indicates that a structure in which the two chloride ions become equivalent, possibly a covalent tetrahedral adduct, is accessible under the experimental conditions. This is, of course, consistent with the observation that the bimolecular addition–elimination reactions, which must pass through a tetrahedral structure, have a reasonable rate at room temperature.[10] It is possible, however, that the inability to isolate distinct intermediates for these systems is a consequence of the method of adduct formation. In thermoneutral reactions such as those studied here ($RCOCl + Cl^-$, R = CF_3, CH_3, and *t*-Bu), in which the reaction barrier lies below the entrance and exit channels, there is a region where partially stabilized adducts may be trapped between the entrance and exit channel but still have sufficient energy to interconvert across the reaction barrier. The detailed dynamics of the chloride-transfer reactions are not well known and may give rise to products with energies above the interconversion reaction barrier. Equilibration of the adducts across the barrier should be fast relative to thermalization by nonreactive collisions (at ICR pressures), leading to the observed scrambling. In support of this hypothesis, other, more recent experiments,[60] involving exothermic carbonyl displacement reactions in which the exit channel is lower in energy than the reaction barrier, show that equilibration (scrambling) in the isolated intermediates has not occurred.

Although the experiments reported here show that a tetrahedral species (intermediate or transition state) is energetically accessible under the experimental conditions, there is considerable indirect evidence which suggests the presence of an ion–dipole complex. First, the reactions are slower than encounter control,[10] suggesting a barrier. Second, the chloride binding energies in $CH_3COCl_2^-$, $(CH_3)_3CCOCl_2^-$, and $CF_3COCl_2^-$ are approximately 14.5, 15.5, and 18 kcal mol^{-1}, respectively, comparable to those of other known ion–dipole complexes[14] such as $t\text{-BuOH}\cdot Cl^-$ and $CF_3CF_2H\cdot Cl^-$. Third, facile Cl^- exchange (with CF_3H and MeOH) is unlikely for a covalently bound species. Fourth, the reaction of CH_3OCOCl, as well as reactions in exothermic systems,[60] shows unsymmetrical intermediates. Because a tetrahedral species is energetically accessible, it is possible that the ion–dipole complexes and a tetrahedral adduct are all present as intermediates and are capable of interconversion under the conditions of the experiment. Thus, while at least two minima are implicated for the bimolecular carbonyl displacement reactions shown in eqs 1 and 2 by earlier kinetic and theoretical studies, definitive experimental evidence regarding the entire potential energy surface remains to be provided.

V. Summary

The synthesis, isolation, and characterization by both chemicaland photochemical methods of species corresponding to intermediates in four thermoneutral displacement reactions at carbonyl centers have been accomplished. For the reaction of $Cl^- + CH_3OCOCl$, the intermediates are shown conclusively to be unsymmetrical ion–molecule complexes, and the possibility of a stable, covalent tetrahedral adduct is ruled out, consistent with a double minimum potential energy surface for the acyl-transfer reaction. Photoactivation of the intermediates results in unimolecular decomposition via an exothermic S_N2 substitution channel at the ester position.

For the reaction of Cl^- with acetyl chloride, trimethylacetyl chloride, and trifluoroacetyl chloride, a structure such as a covalent tetrahedral adduct in which the two chlorines become equivalent is energetically accessible. This observation, however, is not sufficient to identify unambiguously the intermediates as either covalent tetrahedral adducts or electrostatic complexes. Thus, while the binding energies of the complexes and the preexisting kinetic and theoretical data are consistent with a double minimum surface, further experiments which characterize directly the structure of the intermediate species are needed.

Acknowledgment. We are grateful to the National Science Foundation for support of this research. J.L.W. gratefully acknowledges the IBM graduate fellowship program for support.

Appendix

For the mechanism shown in Scheme 1, we can calculate the amount of Cl^- produced in each channel from the observed isotope ratios of the products.

$$\text{let } F_1 = \frac{\text{Cl}^- \text{ produced by channel 1}}{\text{total Cl}^- \text{ produced}}$$

$$\text{let } F_2 = \frac{\text{Cl}^- \text{ produced by channel 2}}{\text{total Cl}^- \text{ produced}}$$

The mechanism shown in Scheme 1 and the fact that the natural abundance of $^{35}Cl^-/^{37}Cl^-$ = $^3/_1$ allow us to define the fraction of $^{35}Cl^-$ produced in each channel:

$$\text{fraction } ^{35}\text{Cl}^- \text{ produced by channel 1} \equiv \frac{^{35}\text{Cl}(1)}{^{35}\text{Cl}(1) + {}^{37}\text{Cl}(1)} = 1$$

$$\text{fraction } ^{35}\text{Cl}^- \text{ produced by channel 2} \equiv \frac{^{35}\text{Cl}(2)}{^{35}\text{Cl}(2) + {}^{37}\text{Cl}(2)} = {}^3/_4$$

Experimentally, the ratio $^{35}Cl^-/^{37}Cl^-$ = $^6/_1$. Thus, the fraction of $^{35}Cl^-$ produced by channel 1 + channel 2 = $^6/_7$.

F_1 and F_2 are related as follows:

$$F_1 + F_2 = 1 \quad \text{and} \quad F_1 + {}^3/_4 F_2 = {}^6/_7$$

We now solve for the fraction of chloride produced by each channel:

$$F_1 = {}^3/_7 = 43\%, \quad F_2 = {}^4/_7 = 57\%$$

---

(60) Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.*, in press