J. Am. Chem. Soc. **1994,** *116,* 9216–9221

Direct Experimental Evidence for a Multiple Well Potential Energy Surface in a Gas-Phase Exothermic Carbonyl Addition–Elimination Reaction

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Received September 7, 1993. Revised Manuscript Received June 27, 1994[●]

Abstract: We define experimentally the potential energy surface for a gas-phase carbonyl addition–elimination reaction through the synthesis, isolation, and characterization of intermediates in an exothermic carbonyl displacement reaction. Chemical and photochemical experiments determine the structure and reactivity of these putative intermediates. For the reaction of CN^- with 3,5-difluorobenzoyl chloride, the intermediates are unsymmetrical ion–molecule complexes; we find no evidence for a stable, covalent, tetrahedral adduct. Photoactivation of the intermediates results in unimolecular decomposition across the reaction barrier producing the products of the bimolecular reaction. The observation of two distinct ion–dipole complexes as intermediates and the non-observation of a stable tetrahedral adduct provide direct evidence for a double minimum potential energy surface for the corresponding bimolecular reaction.

I. Introduction

Reactions at carbonyl centers are important in synthetic chemistry and in many biological systems. They also represent a fundamental class of chemical reactions. As such, they have been extensively studied, both in solution and in the gas phase.

Bender's classic experiments explored the mechanistic details of acyl transfer reactions in solution.[1] These experiments, which involved oxygen-18 labeling studies of the alkaline hydrolysis of esters, suggested that carbonyl addition–elimination reactions proceeded through a covalently bound, tetrahedral intermediate. Subsequent studies, which employed spectroscopic methods,[2] kinetic studies,[3,4] and breaks in pH rate profiles,[5-7] supported this hypothesis. Numerous reviews describe the rich history of these and other mechanistic studies of reactions at carbonyl centers.[8,9]

The mechanism of gas-phase carbonyl addition–elimination (AE) reactions is also interesting: in contrast to the solution phase, the role of tetrahedral adducts in AE reactions in the gas phase is not well-known. By analogy to solution-phase results, early models for gas-phase carbonyl AE reactions suggested a single-minimum potential energy (PE) surface (Figure 1), with a stable, covalent tetrahedral intermediate as the global minimum. Asubiojo and Brauman,[10] however, measured rates for a series of acyl transfer reactions and found rates significantly slower than the predicted collision rate, indicating bottlenecks to reaction. A single-minimum PE surface, which lacks an enthalpic barrier to product formation, could not accommodate this observation. Asubiojo and Brauman proposed a double minimum surface (Figure 2), with electrostatic complexes (the ion is bound by the dipole of the neutral molecule) as minima. The double-minimum surface also explained the properties of other classes of gas-phase ion–molecule reactions such as nucleophilic substitution and electron transfer.

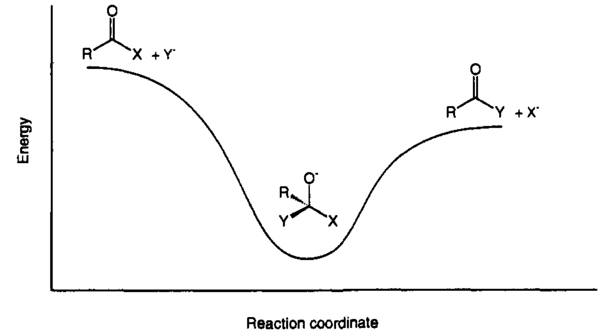

Figure 1. Schematic single-minimum potential energy surface for an exothermic gas-phase carbonyl addition–elimination reaction.

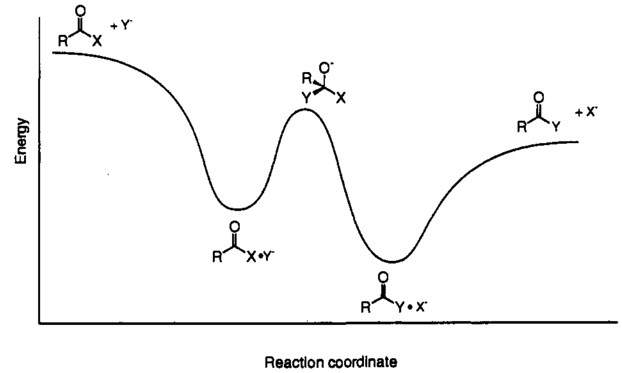

Figure 2. Schematic double-minimum potential energy surface for an exothermic gas-phase carbonyl addition–elimination reaction.

Although the double-minimum surface can successfully model gas-phase carbonyl reactions, verification of the model by an experiment that does not rely on inference is desirable. The synthesis and direct characterization of intermediates in a carbonyl AE reaction is one possible approach to verifying the model. A single-minimum surface predicts a stable tetrahedral intermediate; a double-minimum surface predicts unsymmetrical ion–dipole complexes. In a recent study from our laboratory,[11] we synthe-

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[●] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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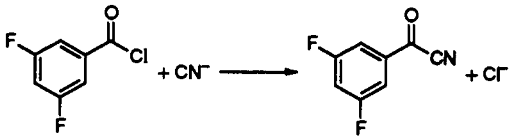
sized, isolated, and characterized, by both chemical and photochemical methods, reactive intermediates for the system shown in eq 1, which also had a competing and exothermic channel for S_N2 substitution at the ester position (eq 2). These experiments found intermediates that were unsymmetrical ion–molecule complexes and ruled out the possibility of a stable, covalent, tetrahedral adduct. The thermoneutral reactions shown in eq 3 were also studied. For the reaction of Cl^- with acetyl chloride, trimethylacetyl chloride, and trifluoroacetyl chloride, we found no conclusive evidence to distinguish between covalent, tetrahedral adduct, and electrostatic complexes. The binding energies of the complexes and the existing kinetic and theoretical data, however, suggested electrostatic complexes.

$$CH_3OCOCl + {}^*Cl^- \rightarrow CH_3OCO^*Cl + Cl^- \quad (AE) \quad (1)$$

$$CH_3OCOCl + {}^*Cl^- \rightarrow CH_3{}^*Cl + CO_2Cl^- \quad (S_N2 \text{ displacement}) \quad (2)$$

$$RCOCl + {}^*Cl^- \rightarrow RCO^*Cl + Cl^- \quad (R = CF_3, CH_3, t\text{-Bu}) \quad (3)$$

In this paper, we extend our studies of potential energy surfaces for gas-phase AE reactions at carbonyl centers. We report the synthesis, isolation, and characterization, both by chemical and photochemical methods, of intermediates in the exothermic displacement reaction shown in eq 4. The presence of a strong thermodynamic driving force alters the PE surface dramatically (compared to a thermoneutral reaction) and provides information concerning the generality of the experimental methodology. We find two distinct intermediates and demonstrate that they are unsymmetrical ion–molecule complexes. Further, we find no evidence for a stable, covalent, tetrahedral adduct. Photoactivation of the intermediates results in unimolecular decomposition across the reaction barrier and produces Cl^- (and by inference the corresponding acyl cyanide): this observation suggests that the isolated intermediates are relevant to the bimolecular reaction. The identification of two distinct ion–dipole complexes as intermediates and the non-observation of a stable tetrahedral adduct provide compelling evidence for a double-minimum PE surface for the carbonyl AE reaction in eq 4.



(4)

II. Experimental Section

Instrumentation. Our experiments used a Fourier transform IonSpec OMEGA ion cyclotron resonance (FT-ICR) spectrometer equipped with impulse excitation.[12] The ICR consisted of a 1 in. × 1 in. × 1.5 in. rectangular cell, constructed of polished 0.020 in. oxygen free hard copper (OFHC) plates, in which all ion generation, ion–molecule reactions, and ion detection takes place. These plates were mounted on Vespel rods that formed the structural frame for the cell. A stainless-steel high-vacuum can, placed between the poles of a Varian electromagnet operating between 0.8 and 1.2 T, enclosed the frame and cell. The high vacuum can had 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). A polished copper mirror in the rear of the cell reflected the incident light back through the cell, and out the KCl window. Varian leak valves controlled the entrance of neutral samples into the high vacuum can. An ion gauge (Varian 844) monitored pressures of the neutral species in the ICR cell. This ion gauge was calibrated against a capacitance manometer for accurate values of the pressure. The pressures in the high-vacuum can were between 10^{-8} and 10^{-6} Torr.

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

IRMP activation experiments used the multimode output of a tunable Lumonics TEA 103-2 CO_2 pulsed laser. A mirror focused the laser beam, an iris reduced the beam to the desired spot size, and the light entered the ICR cell through the KCl window. After the laser beam passed through the ion cloud, a mirror in the back of the ICR cell reflected the pulse back through this ion cloud. CaF_2 flats of varying thickness attenuated the intensity of the laser pulse. A Scientech 365 power and energy meter with a Scientech 38-0102 volume absorbing disk calorimeter measured the pulse energies. Dividing the energy by the measured area of the beam pulse provided the fluence of the incoming beam. This fluence was multiplied by two to determine the effective fluence. IRMP experiments used the 9.6 μm, P(18) branch, corresponding to a wavelength of 1048.66 cm^{-1} (3.0 kcal mol^{-1} $photon^{-1}$). The absorption rates for pulsed IRMP activation experiments are estimated[13] 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, with the laser blocked (light off), provided "light off" data: subtraction of the "light off" data from the "light on" data corrected for background peaks. For each data point, we averaged multiple scans (50–500) to obtain reproducible ion abundances; we averaged multiple data points (3–9) at each fluence.

Materials. Electron impact generated CN^- (m/z = 35, 37) from HCN (1–4 × 10^{-7} Torr) and Cl^- from $ClCO_2CH_3$ (5 × 10^{-7} to 8 × 10^{-7} Torr) and 3,5-difluorobenzoyl chloride (2 × 10^{-7} to 1 × 10^{-6} Torr). Methyl chloroformate, methyl cyanoformate, and 3,5-difluorobenzoyl chloride were obtained from Aldrich. HCN was obtained from Matheson. 3,5-Difluorobenzoyl cyanide was synthesized using a literature preparation.[14] Multiple freeze–pump–thaw cycles removed gaseous impurities from all samples.

Formation of Complex Ions. Under typical ICR operating conditions, intermediates in bimolecular reactions fragment to reactants or products before they can be detected. Excess energy is present in the reaction complex upon formation of the intermediate, but processes such as collisional cooling, which might remove this excess energy, do not normally occur in the low-pressure regime of an ICR (10^{-8} Torr) with sufficient frequency to be useful experimentally. We used the method developed by McMahon and co-workers[15–19] to synthesize species corresponding to intermediates in the gas-phase carbonyl AE reaction, eq 4. The sequence shown in eq 5 prepared the adducts $M{\cdot}CN^-$. Chloride ion (and cyanide ion), generated via electron impact (eq 5a and 5b), reacted with methyl cyanoformate, $NCCO_2CH_2$, to give the cyanocarbonate anion (eq 5c), which then donated cyanide ion to form the desired adduct (eq 5d). Adducts $M{\cdot}CN^-$

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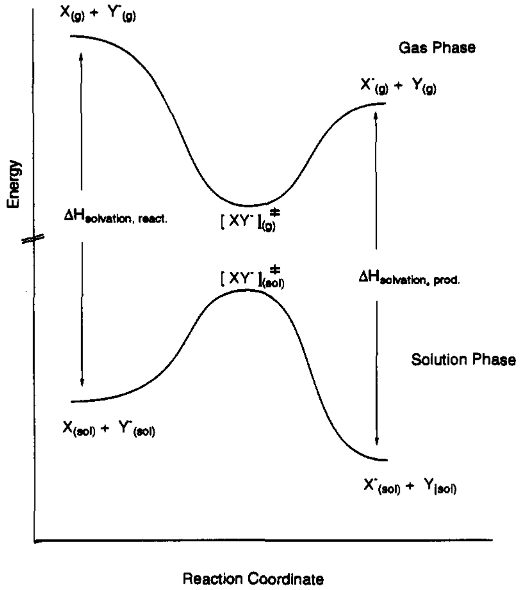


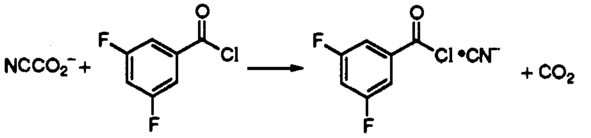
Figure 3. Solution-phase vs gas-phase potential energy surfaces. No mechanism for reaction is implied.

created in this fashion were trapped in the ICR cell for 1–2 s, typical for stable ions in our ICR spectrometer. Preparation of adducts M•Cl⁻ used a similar sequence (not shown) with methyl chloroformate instead of methyl cyanoformate. Chloride ion, generated via electron impact, reacted with methyl chloroformate, $ClCO_2CH_3$, to give the chlorocarbonate anion, which donated chloride ion to form the desired adduct. Adducts M•Cl⁻ created in this fashion were trapped in the ICR cell for 1–2 s.

$$NCCO_2CH_3 \xrightarrow{e^-} NC^- + CO_2CH_3 \quad (5a)$$

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

$$Cl^- + NCCO_2CH_3 \longrightarrow NCCO_2^- + CH_3Cl \quad (5c)$$

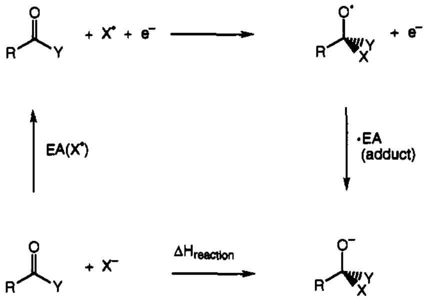


(5d)

III. Background

The mechanism of carbonyl AE reactions in the gas-phase differs significantly from the mechanism of these reactions in the solution phase. In solution, activation barriers that separate reactants and products arise from a combination of desolvation energies and intrinsic barriers to formation of transition states and/or intermediate species. In the gas phase, however, reactions can take place in the absence of solvent, which changes dramatically the interactions between reacting species.[20] Electrostatic attractions between an ion and the dipole of a neutral molecule favor association: reactants and products are thus often higher in energy than associated species. Consequently, gas-phase PE surfaces appear "inverted" relative to PE surfaces in solution (Figure 3).

Early models for gas-phase carbonyl AE reactions posited a single-minimum potential energy (PE) surface, with a covalent, tetrahedral intermediate as the global minimum (Figure 1). Asubiojo and Brauman,[10] however, observed that many displacement reactions at carbonyl centers proceeded with an efficiency[21] significantly less than unity, even for highly exothermic reactions, suggesting a bottleneck to products. They proposed a double-minimum PE surface to explain these observations (Figure 2).



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

Figure 4. Thermochemical cycle for predicting relative stabilities of tetrahedral adducts.

In the double-minimum PE surface, the tetrahedral adduct is a saddle point between two electrostatic (ion–dipole) complexes and a transition state for interconversion of these complexes. An ion–dipole complex formed from reactants can either cross this transition state barrier to products or revert to reactants. The transition state to reactants is favored entropically (higher *A* factor) compared to the transition state to products. The rates for dissociation (of the complex) to reactants thus compete with the rates for dissociation to products, even when the reaction barrier is below the entrance channel. This competition reduces the efficiency of product formation.

The topography of PE surfaces for gas-phase AE reactions depends critically on the relative stability of intermediates. The single-minimum and double-minimum PE surfaces, for example, can be interconverted by modulating the relative stability 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 AE reactions, the binding energy is between 12 and 20 kcal mol⁻¹. The stabilities of tetrahedral addition products, however, are more variable. A thermochemical cycle[22,23] shows that the difference in electron affinities between the attacking nucleophile and the tetrahedral adduct affects the overall enthalpy of adduct formation (Figure 4). If the difference between the reactants and products in the upper reaction (carbonyl + X• vs neutral adduct) is small relative to the difference between the corresponding ionic reactants and products (a rough approximation), the heat of reaction for the addition reaction that forms 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. Accordingly, tetrahedral adducts have been observed as stable species for alkyl anion and hydride nucleophiles.[24–26] For nucleophiles such as OH⁻ and RO⁻, which have intermediate electron affinities, the stability of the tetrahedral adduct (relative to an electrostatic complex) is more difficult to predict. In short, both tetrahedral adducts[23,27–30] and ion–dipole complexes[31–34] have been observed for the reaction of OH⁻ and alkoxides with carbonyl

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[21] The efficiency (Φ) ≡ (number of collision producing products)/(total number of collisions).

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compounds. Most relevant to the experiments presented here, experimental[15-19,35] and theoretical[34,36-38] studies found ion–dipole complexes for nucleophiles with very high electron affinities (e.g. Cl^-, CN^-).

Characterization of intermediate species in a carbonyl AE reaction probes the topography of the PE surface. If a reaction proceeds on a double-minimum surface, it should be possible to isolate two distinct intermediates, both having the structure of an unsymmetrical ion–dipole complex. Conversely, if a reaction proceeds on a single-minimum surface, only one covalently bound tetrahedral intermediate should be present. In a recent study from our laboratory,[11] we showed that reactive intermediates for the reaction of Cl^- with CH_3OCOCl were unsymmetrical ion–molecule complexes; we also ruled out the possibility of a stable, covalent, tetrahedral adduct. Note, however, that this system had a competing and exothermic channel for S_N2 substitution at the ester position (eq 2) that was the dominant pathway for both the bimolecular reaction and photochemical decomposition of the intermediates. Interpretation of the PE surface for reaction at the carbonyl center was thus difficult. For the reaction of Cl^- with acetyl chloride, trimethylacetyl chloride, and trifluoroacetyl chloride, which lack a competing channel, we found no conclusive evidence to distinguish between a covalent tetrahedral adduct and an electrostatic complex. While the binding energies of the complexes and the existing kinetic and theoretical data suggested that an electrostatic complex was most probable, no direct evidence indicated unequivocally that carbonyl addition–elimination reactions proceeded via a double-minimum surface.

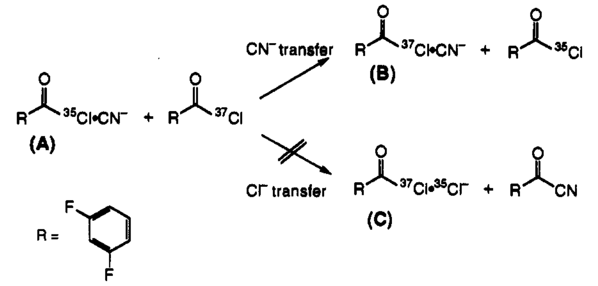
The exothermic gas-phase AE reaction of $CN^- +$ 3,5-difluorobenzoyl chloride (eq 4) was selected as a viable system to provide this evidence, based on the following criteria: (i) no competing reactions were present, that is, the only energetically available pathway for reaction was an addition–elimination reaction; (ii) the gas-phase bimolecular reaction proceeded with an observable rate, indicating that any barrier to product formation was accessible under ICR conditions; (iii) the intermediate species were sufficiently stable for isolation, but not so stable as to prevent photodecomposition; (iv) the system had a sufficient vapor pressure for gas-phase studies; and (v) the C–F bonds served as an infrared chromophore and thus facilitated IRMP activation.

IV. Results and Discussion

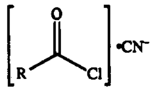
Kinetics. The bimolecular reaction of CN^- with 3,5-difluorobenzoyl chloride (eq 4) is estimated to be exothermic ($\Delta H^\circ = -33$ kcal mol^{-1}) based on the difference between the C–Cl and C–CN bond strengths and the electron affinities of Cl and CN. It proceeds at a rate of 1.5×10^{-9} cm^3 s^{-1}, corresponding to an efficiency[21] of approximately 50%. Only Cl^- and by inference 3,5-difluorobenzoyl cyanide were observed as products of the bimolecular reaction.

Structure of Intermediates. Using the reaction sequence shown in eq 5a–d, species corresponding to the adduct of 3,5-difluorobenzoyl chloride and CN^- ($m/z = 202, 204$) were synthesized. The reaction sequence shown in Scheme 1 characterized structurally the putative reaction intermediates. Double-resonance ejection of all ions with mass other than $m/z = 202$ isolated the adduct **A** (Scheme 1). The adduct **A** was allowed to react with neutral 3,5-difluorobenzoyl chloride, which had a natural chloride isotope abundance ($^{35}Cl^-$:$^{37}Cl^- = 3{:}1$). This reaction formed the adduct **B** (m/z 204), indicating transfer of CN^-. The rate observed for CN^- transfer was slow ($<10^{-10}$ cm^3 molecule^{-1} s^{-1}), consistent with the thermoneutrality of the transfer reaction and that only 3,5-difluorobenzoyl chloride neutrals that contain ^{37}Cl (1/4 of total neutrals) produce an observable product.[39] Formation of the adduct **C** ($m/z = 213$) was not observed, indicating that transfer of Cl^- did not occur for the adduct **A**, despite the significant exothermicity ($\Delta H^\circ = -33$ kcal mol^{-1}) associated with production of the RCOCN product. Further, it is a general observation that chloride and cyanide binding energies are similar for most neutrals that form electrostatic complexes.[16,18,35] Thus, formation of a Cl^- adduct is not forbidden thermodynamically. The complexation energy for formation of the adduct **A** (cyanide binding energy of 3,5-difluorobenzoyl chloride) was between[15,35] CF_3H and SO_2 and was assigned a value of 19 ± 2 kcal mol^{-1}.

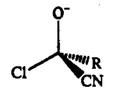
Scheme 1



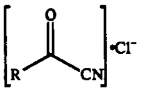
The observation that complex **A** transfers CN^- and did not transfer Cl^- suggested an unsymmetrical ion–dipole complex (structure **7a**, below) in which the CN^- was loosely bound to the neutral acyl chloride. This structure was also supported by the cyanide binding energy, which was comparable to that of other ion–dipole complexes. Furthermore, there was no evidence that suggested the intermediate we isolated was a covalent tetrahedral species (structure **7b**, below). Selective transfer of CN^- would be unlikely in a tetrahedral adduct where both ligands are bound covalently to the carbonyl center. In fact, a tetrahedral structure is likely to favor chloride transfer since the carbon–cyanide bond is significantly stronger (~15 kcal mol^{-1}) than the carbon–chlorine bond, and transfer of chloride would be accompanied by formation of RCOCN, which we estimate to be exothermic by 33 kcal mol^{-1}.



7a



7b



7c

To obtain information about the potential energy surface for the bimolecular reaction, it was necessary to verify that the putative intermediates we isolated were related chemically to the bimolecular reaction. IRMP activation[40,41] was used to energize the intermediates, and thus induce unimolecular dissociation. IRMP activation of the adduct **A** resulted in unimolecular decomposition to produce exclusively Cl^-, indicating that IRMP activation converted the intermediate **A** to the products of the bimolecular

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(39) The reaction of the adduct A with 3,5-difluorobenzoyl chloride containing $^{35}Cl^-$ is also likely to occur. However, it results in no change in mass change, and is thus invisible in the ICR.

(40) 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.

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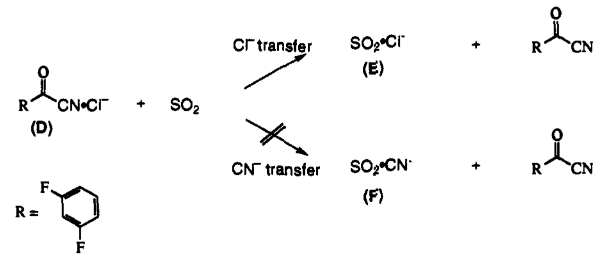
Scheme 2



reaction. The observation that IRMP activation did not produce CN^- indicated that the reaction barrier (to produce Cl^-) was at least[42] 3 kcal mol^{-1} lower in energy than the reactants (CN^-).

Species corresponding to the adduct of 3,5-difluorobenzoyl cyanide and Cl^- (m/z = 202, 204) were also synthesized using a similar sequence of reactions as in eq 5a–d, but substituting methyl chloroformate (for methyl cyanoformate) and 3,5-difluorobenzoyl cyanide (for 3,5-difluorobenzoyl chloride). We used the reaction sequence shown in Scheme 2 to probe the structure of the resulting complex. The adduct **D** (m/z = 202, 204) was isolated by double-resonance ejection of all other ions and allowed to react with neutral sulfur dioxide.[43] The adduct E (m/z = 99, 101) formed, indicating transfer of Cl^-. The adduct F (m/z = 88) was not observed, indicating that the adduct **D** did not transfer CN^-. The complexation energy for formation of **D** (chloride binding energy of 3,5-difluorobenzoyl cyanide) was between[18] SO_2 and CF_3H and was assigned a binding energy[44] of 18 ± 2 kcal mol^{-1}. IRMP activation of the adduct **D** also resulted in unimolecular decomposition to produce exclusively Cl^-.

The observation that complex **D** transferred Cl^- and not CN^- suggested an unsymmetrical ion–dipole complex (structure **7c**, above) with the Cl^- bound loosely to the neutral acyl cyanide. This structure was further supported by the chloride binding energy, which was comparable to other ion–dipole complexes. Complex **D** was also unambiguously different from complex **A**, which was observed only to transfer CN^-. Thus, the possibility of a single intermediate species was ruled out, and the presence of two distinct, stable intermediates was confirmed.

Conclusions. The results described above provide direct experimental evidence that the reaction shown in eq 4 proceeds on a multiple-well potential energy surface. Two distinct ion–molecule complexes, with either CN^- (the nucleophile) or Cl^- (the leaving group) bound electrostatically to the dipole of the neutral molecule, were identified as stable intermediates. Further, these intermediates were photoactivated and converted to the products of the bimolecular reaction. The observation that these intermediates were distinct and do not interconvert suggests that the two ion–dipole complexes are separated by a barrier that may be responsible for the non-unit efficiency. The non-observation of a stable tetrahedral intermediate is consistent with the proposal that a covalent tetravalent structure is at the top of this barrier, representing a transition state for interconversion of the two ion–dipole complexes.

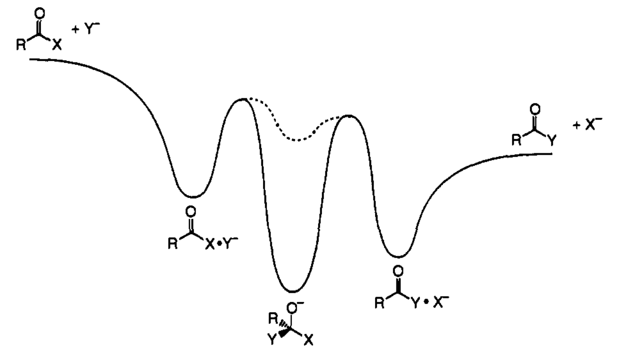


Figure 5. Schematic triple-minimum potential energy surfaces.

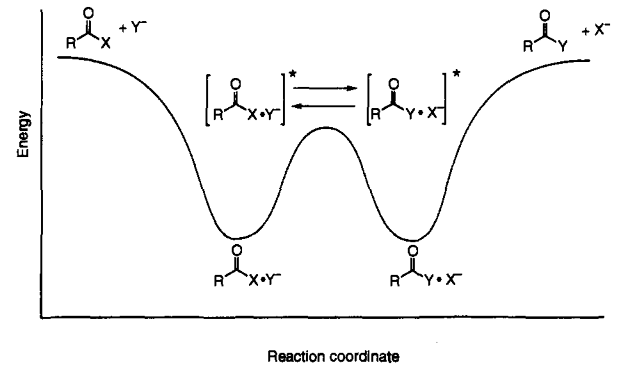


Figure 6. Potential energy surface for a thermoneutral gas-phase carbonyl addition–elimination reaction. Arrows represent interconversion of energized but trapped intermediates. See text for details.

While a double-minimum surface is the simplest multiple-well surface, the possibility of a more complicated potential surface, such as a triple-minimum surface, has been suggested.[20,45,46] For a triple-minimum surface, with a tetrahedral structure as a global minimum (Figure 5, solid curve), our data indicate that there must be a significant barrier between the ion–dipole complex and any tetrahedral adduct. We can approximate the minimum height of such a barrier as ~7–10 kcal mol^{-1}, the energy available from ambient collisions at 350 K. While this cannot be ruled out, it is not clear why such a barrier would exist. A triple-minimum surface, where the tetrahedral structure is a local minimum (Figure 5, dashed curve) at the top of a large barrier, is also possible and cannot be ruled out by our data.

As discussed in the background section, thermochemical arguments predict that nucleophiles with high electron affinities such as Cl^- and CN^- would form stable ion–dipole complexes, and not a tetravalent structure. The observation of a multiple-well system for the reaction in eq 4 confirms experimentally the predictions[22,23] of the thermochemical cycle shown in Figure 4. However, the generality of this result for other systems involving similar nucleophiles (e.g. Cl^-, CN^-, F^-) warrants discussion. In a previous experiment from our lab, we failed to obtain unequivocal evidence for stable ion–dipole complexes in the thermoneutral reactions of Cl^- with acyl chlorides (eq 3). It is possible, however, that the inability to isolate distinct intermediates for these systems is an artifact of the method of adduct formation. In a thermoneutral reaction, 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 (Figure 6). Adducts were made by transfer of Cl^- from CO_2 (binding energy ~8 kcal mol^{-1}) to the acyl chlorides (binding energies 14–18 kcal mol^{-1}). It is thus likely that a distribution of energies existed for the adducts, from the exothermicity of the Cl^- transfer reaction and more complicated dynamical effects.

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[42] Unimolecular decomposition occurs when the rate of dissociation competes with the rate of photon absorption. In general, for energies slightly above the 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.

[43] The neutral RCOCN does not have a convenient isotopic label (as did RCOCl). Thus, SO_2 was used in place of RCOCN, since the transfer of Cl^- from adduct **D** to RCOCN would not produce a change in mass, and hence would be invisible in the ICR. The Cl^- and CN^- affinity of SO_2 is slightly larger (~1.2 kcal/mol) than that of 3,5-difluorobenzoyl cyanide; however, this difference in binding energy is not expected to significantly affect the results.

[44] It is a general observation that CN^- and Cl^- binding energies are comparable for a given neutral. This, in combination with the similar polarizability and dipole moments of the two neutrals, accounts for the close agreement in complexation energies for adducts A and D.

[45] Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M. In *Ionic Processes In the Gas Phase*; Almoster Ferreira, M. A., Ed.; Kluwer Academic Publishers: Boston, 1984; NATO ASI Series Vol. 118.

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Unimolecular isomerization across the barrier could occur before collisional cooling is complete, resulting in scrambled adducts. In an exothermic reaction, however, where the exit channel (forming products) is at lower energies than the reaction barrier, no such region exists (Figure 2). Thus, any adducts not trapped in the potential well for the reactant complex simply dissociate to products. This explanation is supported by the observation that experiments with the thermoneutral S_N2 reaction of Cl^- + $NCCH_2Cl$ have also failed[47] to isolate distinct intermediates, although the double-minimum surface, and the existence of stable ion–dipole complexes which retain their identity, as indicated[48] by theory and experiment, has been unequivocally proven for other exothermic[49–51] systems. Thus, it is likely that the thermoneutral reactions in eq 3 were simply unsuitable systems for the experimental techniques we employed, and that the double-minimum surface, which is indicated by kinetic and computational results, is a correct model.

V. Summary

We report the synthesis, isolation, and characterization, both by chemical and photochemical methods, of species corresponding to intermediates in an exothermic carbonyl displacement reaction. The reaction of CN^- + 3,5-difluorobenzoyl chloride has two distinct intermediates that are unsymmetrical ion–molecule complexes. Further, we find no evidence for a stable, covalent, tetrahedral adduct. Photoactivation of the intermediates results in unimolecular decomposition across the reaction barrier to products. These studies provide direct experimental evidence for a multiple-well potential energy surface for a carbonyl AE reaction.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and to the IBM graduate fellowship program for support for J.L.W. We thank Dr. Mark J. Tebbe for assistance with the synthesis of 3,5-difluorobenzoyl cyanide.

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