metry. Most significant are the differences in the angles D–Cr–CO, where D is the center of the benzene ring (123.7 (1)°, 127.8 (1)°, and 127.8 (1)°). The benzene ring is thus bent toward one carbonyl group while the symmetry-imposed mirror plane of symmetry is maintained.

The reason for this is unclear. As an 18-electron complex, benzenetricarbonylchromium should not be subject to a second-order Jahn–Teller distortion.[13] There are no intermolecular distances between non-hydrogen atoms of less than 3.0 Å, so packing effects do not appear to be the cause, though this cannot be ruled out. In any case, it does seem that the bending of the benzene ring toward one carbonyl group has a noticeable effect on the deformation density around the chromium atom.[14]

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Supplementary Material Available: Table I, crystal data and details of data collection; Tables II and III, atomic coordinates and thermal parameters for full data and high-order refinements; Table IV, interatomic distances and angles; Figure 1, molecular structure, and Figures 2–9, selected sections through the electron deformation density (8 pages); Table V, observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(14) A referee has pointed out that such effects could be caused by anharmonic thermal motion of the chromium atom. The atom has, however, a small mean-square displacement (U_{eq} = 0.009 Å^2) and its thermal parameter is almost isotropic.

Intermediates and Transition States in Chloride Ion/Acyl Chloride Displacement Reactions

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In our previous gas-phase studies on reaction kinetics of nucleophilic substitution reactions at acyl halides, eq 1, we concluded

$$\mathrm{X^- + RCOY \rightarrow Y^- + RCOX} \qquad \mathrm{X = F, Cl, CH_3O, CN, HS;\ Y = Cl, Br} \quad (1)$$

that the loose ion-neutral cluster is the global minimum along the reaction coordinate and that there is a sizable barrier separating the reactant and product clusters.[1] We also suggested for the case of a degenerate chloride exchange reaction, that the tetravalent adduct is very likely a transition state rather than an intermediate in the corresponding displacement reaction.[1]

Since then, at least, two theoretical studies dealing with this problem have appeared.[2,3] We report here additional experimental evidence showing that the loose cluster ion does indeed exist in the gas phase as a stable species and that there is a sizable barrier to the exchange of the two chlorines in the ion-neutral cluster, $CF_3COCl{\cdot}Cl^-$.

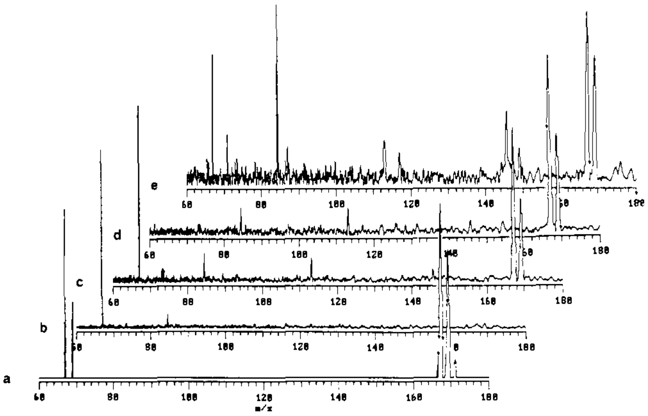

Figure 1. (a) 500 ms, 30 scans: $CH_3OH{\cdot}Cl^-$ (*m/z* 67, 69) and $CF_3COCl{\cdot}Cl^-$ (*m/z* 167, 169, 171). (b) 500 ms, preceded by an ion sweep out pulse (1-amu window centered at 67 amu), 50 scans. (c) 800 ms, 300 scans. (d) 800 ms, preceded by a second ion sweep out pulse (6-amu window centered at 169 amu), 300 scans. (e) 1100 ms, 1000 scans. In (b)–(e) the peak at *m/z* 84 is an artifact arising from 217.5-kHz noise. The signal-to-noise ratio becomes worse at longer delay times due to ion loss which reduces the ion abundance. The high-voltage ion ejection pulse also degrades the S/N ratio.

By analogy with solution-phase chemistry,[4,5] it is generally believed that a tetrahedral adduct is also a stable species in carbonyl addition reactions in the gas phase.[6] Some theoretical studies do show that such tetrahedral species are stable in the gas phase and are formed with small or no activation barriers from the separated anionic nucleophile and carbonyl compound.[7,8] Sheldon found three stable clusters/adducts formed from CH_3O^- and acetone at STO-3G level of calculation, with the tetrahedral adduct being the most stable.[9]

In most experimental gas-phase studies, initial nucleophilic attack at carbonyl carbon could only be inferred from the products generated; in the relatively few instances when the adducts were detected, no definite structure could be assigned for them from available experimental information.[10] In cluster ions formed by the addition of a solvated alkoxide anion to carbonyl compounds containing acidic α-hydrogens, a structure corresponding to an enolate anion solvated by an alcohol molecule is assigned.[2] Bartmess and co-workers put the adducts formed from addition of carbanions to carbonyl groups higher in energy than the corresponding ion-neutral loose complexes, leaving the question whether the tetrahedral adducts are transition state or stable

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intermediates unaddressed.[11] Few experimental examples for the existence of such tetrahedral intermediates have appeared.[12,13]

In a pulsed, Fourier transform, ion cyclotron resonance spectrometer,[14] methyl chloroformate gives CO_2Cl^- and $Cl_2CO_2CH_3^-$ which act as primary chloride ion donors through reactions[15] 2–6.

$$ClCO_2CH_3 + e^- \rightarrow Cl^- + CH_3CO_2^{\bullet} \tag{2}$$

$$Cl^- + ClCO_2CH_3 \rightarrow CO_2Cl^- + CH_3Cl \tag{3}$$

$$CO_2Cl^- + ClCO_2CH_3 \rightarrow Cl_2CO_2CH_3^- + CO_2 \tag{4}$$

$$CO_2Cl^- + M \rightarrow MCl^- + CO_2 \tag{5}$$

$$Cl_2CO_2CH_3^- + M \rightarrow MCl^- + ClCO_2CH_3 \qquad M = CH_3OH, CF_3COCl \tag{6}$$

$$CH_3OH{\cdot}Cl^- + CF_3COCl \rightleftharpoons CF_3COCl{\cdot}Cl^- + CH_3OH \tag{7}$$

Complex ions $CH_3OH{\cdot}Cl^-$ and $CF_3COCl{\cdot}Cl^-$ are thus formed as a result of (5) and (6) when M = CH_3OH and CF_3COCl (Figure 1a). At 500 ms after the electron beam pulse, double-resonance ejection of all ions but $CH_3OH{\cdot}{}^{35}Cl^-$ (*m/z* 67) leaves only this single complex ion (Figure 1b). $CH_3OH{\cdot}{}^{35}Cl^-$ then transfers its chloride ion to neutral molecules present in the gas mixture. After an additional time delay (300 ms) long enough for reaction 7 to reach equilibrium, a mass spectrum is recorded (Figure 1c), and the peaks correspond to $CH_3OH{\cdot}{}^{35}Cl^-$ (*m/z* 67), $CF_3CO^{35}Cl{\cdot}{}^{35}Cl^-$ (*m/z* 167), and $CF_3CO^{37}Cl{\cdot}{}^{35}Cl^-$ (*m/z* 169). Equilibrium 7 was inferred from the nearly time-invariant relative ion abundances at longer time delays and the observation of reaction in both directions.

The nonobservation of $CH_3OH{\cdot}{}^{37}Cl^-$ (*m/z* 69) and $CF_3CO^{37}Cl{\cdot}{}^{37}Cl^-$ (*m/z* 171) (Figure 1c) indicates that only chloride ion of the selected mass (35 in this study) can be transferred between the neutrals and that scrambling of isotopic chlorines in $CF_3COCl_2^-$ does not occur. The latter is further confirmed in the continued reaction sequence.

At the same time delay (800 ms) that the mass spectrum shown in Figure 1c is taken, a second double-resonance pulse ejects all ions but $CF_3COCl_2^-$ in which at least one of the two chlorines is ^{35}Cl (Figure 1d). Then, another time delay elapses and the mass spectrum (Figure 1e) is recorded. Here, only $CH_3OH{\cdot}{}^{35}Cl^-$ but not $CH_3OH{\cdot}{}^{37}Cl^-$ is observed. Similarly, only $CF_3COCl_2^-$ with at least one ^{35}Cl is present. This indicates that in $CF_3COCl_2^-$ the two chlorines are distinguishable—only the one which originally came from external source, $CH_3OH{\cdot}{}^{35}Cl^-$, can be passed on to another neutral acceptor. Thus the two chlorines in CF_3COCl_2 are not equivalent. The barrier must be significant considering that some 10 kcal/mol or more unfixed energy is available in the collision complex formed from the chloride donor and acceptor due to ion–dipole interactions.

A similar experimental sequence established that the two chlorine atoms in $Cl_2CO_2CH_3^-$ are also not exchangeable under our experimental conditions.

The results are consistent with our proposal that reaction 1 occurs on a double-well potential energy surface.[1] The two intermediates can best be described as ion–neutral complexes loosely bound by charge–dipole and charge-induced dipole forces, with one chlorine atom covalently bonded to carbon while the other is only attracted to the neutral molecule by electrostatic interactions. The two intermediates, each having one or the other chlorine atom covalently bonded to carbon, are separated by a barrier which is responsible for the observed reaction kinetics.[1] At the top of the barrier is the tetravalent transition state.[1a,c] Although this structure is less stable than the charge–dipole complex, it is clearly more stable than one would expect based on simple thermochemical considerations,[1a,c] suggesting an unusual structure.[1c]

A triple-minimum surface with the tetravalent structure as a global minimum is not precluded by our results, provided that there is a substantial barrier between it and the loose ion–molecule complex. It is not clear, however, why such a barrier should exist. The barrier in our suggested surface arises because the tetravalent structure which is a minimum along one coordinate of the potential energy surface has become a saddle point connecting the more stable, loose ion–molecule complexes.[1a]

In support of our belief that the tetravalent adduct, $RCOCl_2^-$, is not a stable intermediate, we note that Bohme et al. have observed that very stable nucleophiles, F^-, Cl^-, CN^-, and NO_2^-, all failed to produce (covalent) adducts with formaldehyde in a flowing afterglow instrument.[13] They proposed that the very high electron affinities of these nucleophiles may explain their unwillingness to from a tetravalent adduct with a lower electron affinity. More completely, however, it is the overall reaction thermodynamics, which also includes contributions from the newly formed carbon–nucleophile bond, the broken carbonyl π-bond, and rehybridization at the carbon center in addition to change in electron affinities, which determines the feasibility of formation of the adduct.[1a,c]

In summary, all of our experimental evidence suggests that the tetravalent adduct, $RCOCl_2^-$, must be either a transition state or, possibly, an unstable intermediate (in the case of a three-minima surface). While our model reaction potential energy surface consists of two minima, any more complicated surface, for example, one involving three minima,[16,17] cannot be precluded based on currently available experimental evidence. For reactions with other nucleophiles and leaving groups,[2,3,6,7,9,12,13] the surface may be quite different. Thus, in those cases, the tetravalent adduct may be a global minimum.

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Acylnitrilium Ion Cyclizations in Heterocycle Synthesis. A Convergent Method for the Preparation of 2-Acylpyrrolines via the Intramolecular Acylation of Silyloxyalkenes with α-Keto Imidoyl Chlorides

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The polycyclic ring system of the alkaloid dendroxine (**1**) has remained a formidable challenge for efficient chemical synthesis.[1] As part of a unified approach to this, and related *Orchidaceae* metabolites, we required a practical synthesis for the pyrroline **3** (Scheme I).[2] Recently we reported the use of silver ion pro-

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