

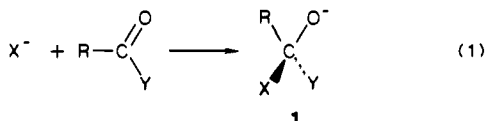
Ab Initio Study of the Displacement Reactions of Chloride Ion with Formyl and Acetyl Chloride

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Abstract: Ab initio molecular orbital calculations have been used to study the optimal reaction paths for the displacement reactions of chloride ion with formyl and acetyl chloride. Some comparative results for the reaction of fluoride ion and formyl fluoride are also reported. Geometry optimizations were carried out primarily with the 3-21+G basis set, while energies were computed at levels as high as MP3/MP2/6-31+G(d) for the reaction with formyl chloride. For formyl chloride, the tetrahedral adduct and a fully planar alternative with C_{2v} symmetry are both transition states at the 3-21+G level. Surprisingly, the latter is more stable according to the 3-21+G calculations. However, this preference is dramatically reversed by including the correlation energy at the MP3/MP2/6-31+G(d) level; the tetrahedral transition state is then favored by 11.5 kcal/mol. The preference for the C_{2v} -like form for the acetyl chloride adduct is greater than for formyl chloride with the 3-21+G basis set. In this case, the energies of the tetrahedral and C_{2v} -like forms are expected to be within 10 kcal/mol after electron correlation is considered. Computed charge distributions are also analyzed and suggest that the C_{2v} -type adducts may be better solvated than the tetrahedral ones. Overall, the traditional view of the central role of tetrahedral intermediates for addition reactions needs further examination.

In 1979, Asubiojo and Brauman reported ion cyclotron resonance findings for displacement reactions of nucleophiles including halide ions with acyl halides in the gas phase.¹ They were able to interpret their kinetic data in terms of double-well energy surfaces with ion-dipole complexes as the suggested intermediates. This proposal was provocative in view of the traditional view of the intermediacy of tetrahedral adducts **1** in addition reactions²



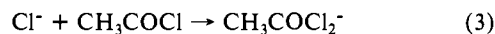
and since prior ab initio calculations for an albeit limited number of simple addition reactions found only the tetrahedral species as an energy minimum.^{3,4} As discussed elsewhere, the latter finding is biased by the use of small basis sets in the early work which leads to overly exothermic formation of the tetrahedral species. A recent investigation in our laboratory of $OH^- + H_2C=O$ using a large basis set with d-orbitals and diffuse functions did find a shallow ion-dipole minimum, though the tetrahedral adduct is still the global energy minimum.⁵

As described here, we have expanded our study of substitution reactions to the degenerate exchange reactions of Cl^- with $HCOC$ and CH_3COCl in order to address the proposal of Asubiojo and Brauman, particularly whether the reaction surfaces have one, two or three energy minima, and to obtain structural characterization of any intermediates and transition states. Simultaneously, Han and Brauman have extended the ICR work on Cl^- with CF_3COCl and CH_3OCOCl and have shown that the two chlorines in the adducts are nonequivalent.⁶ This supports the double-well surface and the existence of a tetrahedral species as a transition state.⁶ Recently, Howard and Kollman have also performed a related ab initio study on the reaction of HS^- and formamide.⁷ In contrast to the results for OH^- with formamide,⁴ an ion-dipole complex rather than a tetrahedral adduct was found as an energy minimum.⁷ A prior ab initio study of $Cl^- +$

CH_3COCl should also be noted, though the enforced geometrical restrictions make the results incomplete in the present context.⁸

Computational Methods

The ab initio molecular orbital calculations for reactions 2 and 3 were carried out by using the GAUSSIAN/82 program on a Gould 32/8750 computer.⁹ Geometries for all structures were fully



optimized by using analytical energy gradients and the 3-21+G basis set.¹⁰ The basis set is of the split-valence type with a set of diffuse s and p orbitals on all atoms except hydrogen. Diffuse functions are well-known to be important for describing the electronic structure of anions, particularly those containing first-row elements.^{5,10-12} The choice of the 3-21+G basis set for the present study was also based on previous calculations for many anions which have established that the basis set yields results in excellent accord with experimental structural and thermodynamic data including gas-phase acidities.¹¹ Nevertheless, the effect of basis set extension on the geometries for the stationary points in reaction 2 was shown to be slight though optimizations with the 6-31+G(d) basis set.¹⁰ Besides the diffuse functions, a set of d-orbitals is included on each non-hydrogen atom in this case.

Furthermore, since geometries distorted from equilibrium are considered along the reaction paths, the effects of electron correlation on the energetics for reaction 2 were also studied. Second- and third-order Møller-Plesset perturbation theory were used with the 6-31+G(d) basis set on the 3-21+G optimized geometries. Thus, the standard notation for these calculations is MP3/MP2/6-31+G(d)//3-21+G.¹¹ The MP3/MP2 calculations did not include the core orbitals and are generally comparable to configuration interaction with full double excitations. The larger system size for reaction 3 precluded calculations at this level, though extrapolations from the results for reaction 2 can be considered.

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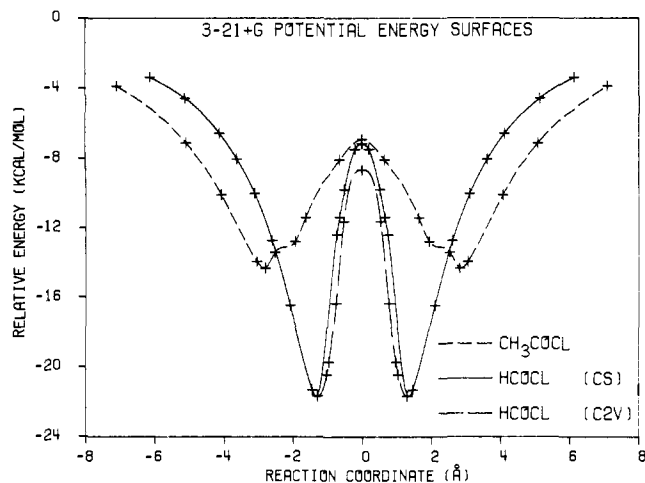


Figure 1. Calculated potential energy surfaces for the reactions of chloride ion with formyl and acetyl chloride. For HCOCl, two pathways are shown passing through transition states **2** (solid curve) and **4** (long dashes). The reaction coordinate is defined as the difference in the two C-Cl distances. Energies are in kcal/mol relative to the separated reactants, $\text{Cl}^- + \text{RCOCl}$. Results are from ab initio calculations with the 3-21+G basis set.

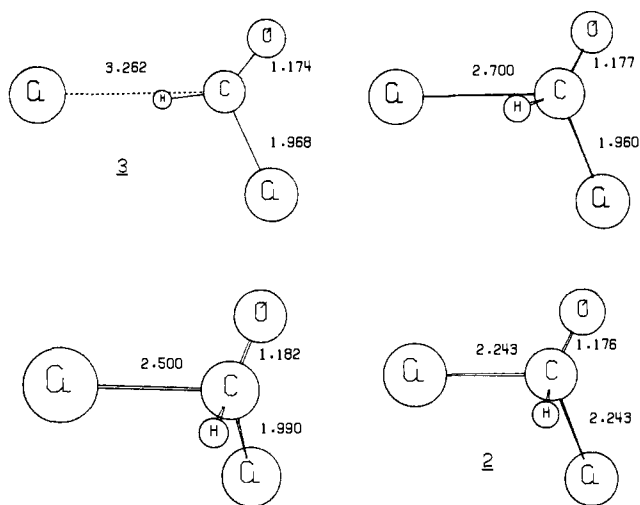
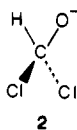


Figure 2. Structures computed with the 3-21+G basis set along the reaction path to transition-state **2** for the reaction of $\text{Cl}^- + \text{HCOCl}$. Structure **3** is the ion-dipole complex corresponding to the energy minimum in Figure 1. Bond lengths are in Å throughout. Full geometrical details for the stationary points are provided as Supplementary Material.

Zero-point vibrational energies were computed for the stationary points in reaction 2 by using the 3-21+G basis set and analytical second derivatives of the energy.⁹ Some comparative results for the reaction of fluoride ion with formyl fluoride are also reported and were obtained at the 3-21+G//3-21+G level.

Results and Discussion

$\text{Cl}^- + \text{HCOCl}$. The study began by trying to locate a tetrahedral adduct **2** with C_s symmetry. Relaxation of the symmetry constraint in the 3-21+G calculations caused the structure to distort. Subsequently, a calculation of the vibrational frequencies for **2**



found one imaginary frequency, so the C_s structure is a transition state at the 3-21+G level. A reaction path was then followed by performing full geometry optimizations at 14 points as the nucleophilic Cl was gradually backed off **2**. The 3-21+G results are illustrated by the potential energy curve in Figure 1 (solid line)

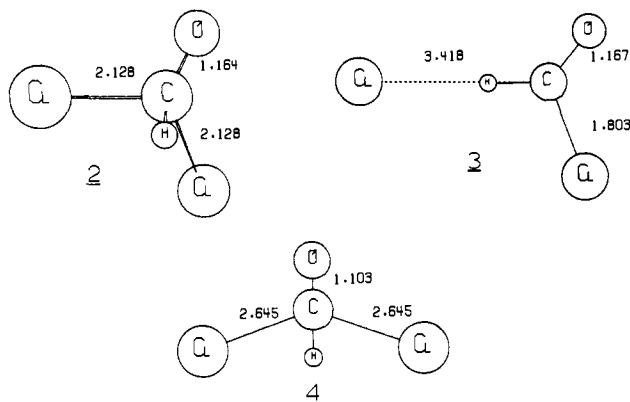


Figure 3. Structures computed with the 6-31+G(d) basis set for **2**, **3**, and **4**.

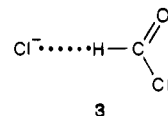
Table I. Energetic Results for the Reaction of $\text{Cl}^- + \text{HCOCl}^a$

$r(\text{C}\cdots\text{Cl})$	3-21+G	6-31+G(d)	MP2/ 6-31+G(d)	MP3/MP2/ 6-31+G(d)
C_s Path				
2.243 (2)	-7.1	4.8	-5.8	-1.4
2.300	-7.4	3.4	-7.6	-3.5
2.500	-9.8	-1.6	-9.0	-6.4
3.262 (3)	-21.7	-14.6	-17.5	-16.7
4.500	-12.7	-9.9	-9.9	-9.8
8.000	-3.4	-2.6	-2.4	
C_{2v} Path				
2.620 (4)	-8.7	3.3	8.6	10.2
2.700	-11.6	-1.0	-3.9	-2.0

^aEnergies are relative to the separated reactants in kcal/mol. All results using 3-21+G optimized geometries.

and the structures in Figure 2. Figure 1 is made symmetric by choosing the reaction coordinate to be the difference in the two C-Cl distances.

The energy profile has a double-well form. The only minima are for the planar ion-dipole complex **3** with $r(\text{C}\cdots\text{Cl}) = 3.26 \text{ \AA}$, as illustrated in Figure 2. Calculations of the vibrational fre-



quencies for **3** showed it to be a true energy minimum. The chloride ion is positioned roughly on the dipole axis, just slightly off the C-H bond vector. Searches for additional planar minima were unsuccessful. The structures for **2** and **3** were also optimized with the 6-31+G(d) basis set. As shown by comparing Figures 2 and 3, the additional atomic orbitals have little effect on the structures, particularly for the transition state **2**. The covalent and nonbonded C-Cl distances in **3** are lengthened and shortened, respectively, by ca. 0.16 Å in going to the 6-31+G(d) level. This probably results from some overestimation of charge transfer with the smaller basis set.

The well-depth for **3** relative to the separated reactants is 21.7 kcal/mol at the 3-21+G level, and the intrinsic barrier to **2** has a height of 14.6 kcal/mol. The basis set and correlation dependence of the energetic results is explored in Table I, while the total energies for the various separated species are recorded in Table II. For the reaction path to the C_s transition state, **2**, extending the basis set to 6-31+G(d) preferentially improves the description of chloride ion. This shifts the energy in the reactant region down; however, the effect is offset by the MP2 correlation correction which preferentially improves the more condensed structures farther along the reaction path toward **3** and **2**. Thus, the 3-21+G and MP2/6-31+G(d) results are similar, though the well-depth for **3** (17.5 kcal/mol) and intrinsic barrier (11.7 kcal/mol) are 3-4 kcal/mol less at the latter level. The well-depth only changes to 16.7 kcal/mol in advancing to the MP3 stage, while the

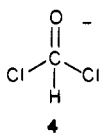
Table II. Calculated Total Energies for the Reactants^a

species	3-21+G	6-31+G(d)	MP2/	
			6-31+G(d)	MP3/MP2/ 6-31+G(d)
Cl ⁻	457.380 864	459.539 661	459.671 145	459.682 380
F ⁻	98.933 655	99.418 586	99.623 847	99.613 630
HCl	457.876 779	460.060 493	460.194 283	460.209 553
HF	99.506 083	100.013 982	100.202 922	100.201 854
CO	112.110 378	112.741 005	113.028 447	113.025 230
CHOC1	569.975 128	572.781 769	573.223 469	573.231 830
CHOC1 ^b		572.786 364	573.223 946	
CHOF	211.616 336	212.753 145	213.237 008	213.230 980
CH ₃ COCl ^c	608.814 218			
CH ₃ COCl ^d	608.812 074			

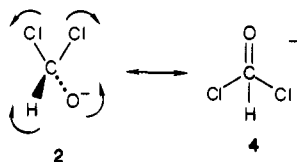
^aNegative of the total energy given in atomic units for geometries optimized at the 3-21+G level. ^bGeometry optimized at the 6-31+G(d) level. ^cMost stable conformer with H eclipsing C=O. ^dLess stable conformer with H eclipsing C—Cl.

transition state becomes more disfavored and the intrinsic barrier rises to 15.3 kcal/mol. It should be noted that the final predicted energy for **2** places the transition state 1.4 kcal/mol below the reactants or products. The zero-point energies were also computed and are 12.6, 12.7, and 12.7 kcal/mol for the reactants (HCOCl), **2**, and **3** with the 3-21+G basis set. Thus, changes in the vibrational energy have no significant influence on the energy surface. Another check on the energetics was made with the 6-31+G(d) optimized geometries for **2** and **3**. The energies for **2** and **3** relative to the reactants are altered by 1.2 kcal/mol or less at the 6-31+G(d) and MP2/6-31+G(d) levels by using the 6-31+G(d) geometries instead of the 3-21+G ones. This is consistent with the above statement that the difference in the 3-21+G and 6-31+G(d) results in Table I is largely due to the description of chloride ion. Overall, the MP3 results in Table I should have good quantitative accuracy based on previous findings.¹¹⁻¹³

Since the C₃ structure **2** turned out to be a transition state, we were interested to see if another tetravalent species might be a minimum. The most obvious alternative would be a planar structure of C_{2v} symmetry, **4**, although it violates usual valence



ideas. Accordingly, **4** was optimized in C_{2v} symmetry, and a subsequent vibrational frequency calculation showed that it too is a transition state at the 3-21+G level. Even more remarkably, **4** is 1.6 kcal/mol lower in energy than **2** with this basis set. This led us to calculate the inversion profile for the motion that interconverts **2** and **4**. The profile is shown in Figure 4 (solid curve)



as a function of the HCO angle. **2** and **4** are the only stationary points on this curve and are separated by a slight barrier of 0.7 kcal/mol. In fact, the curve corresponds to a ridge between the reactants and products. **2** and **4** are saddle points on the ridge and have separate valleys leading to the reactants/products.

The valley from **4** was then explored by gradually lengthening one C—Cl bond and optimizing all remaining variables. This pathway also leads to the ion-dipole complex **3** as illustrated by the structures in Figure 5 and the energy profile in Figure 1 (long dashes). The optimized structure for **4** in Figure 5 is unusual with long C—Cl bonds of 2.62 vs. 2.24 Å for **2**. The C—O bond length

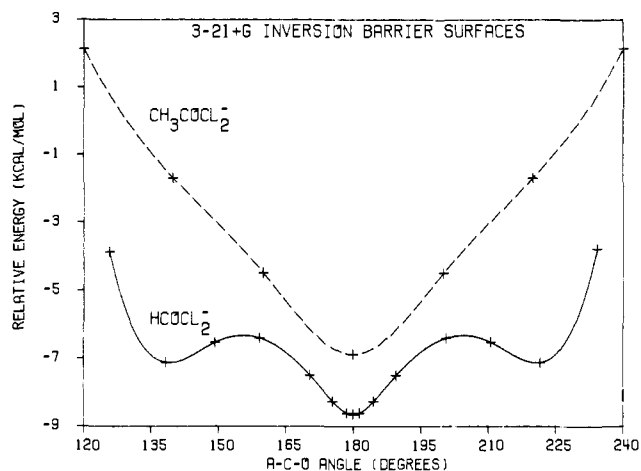


Figure 4. Computed energy profiles for the interconversion of **2** and **4** (solid curve) and **5** and **6** (dashed curve). Energies from 3-21+G calculations are relative to the separated reactants, Cl⁻ + RCOCl. The abscissa gives the HCO angle for HCOCl₂⁻ and the CCO angle for H₃CCOCl₂⁻.

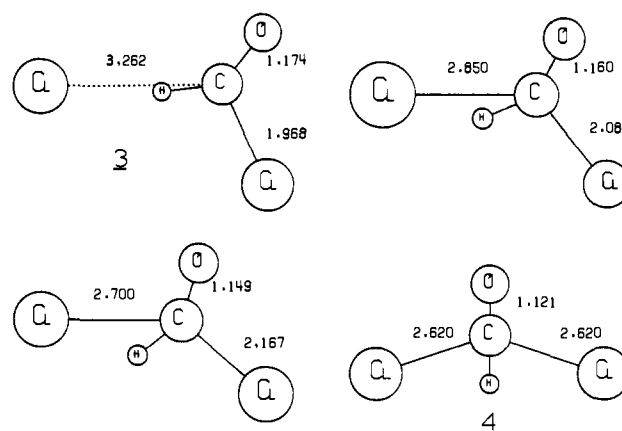


Figure 5. Structures computed with the 3-21+G basis set along the reaction path to transition state **4** for the reaction of Cl⁻ + HCOCl.

of 1.12 Å in **4** can be compared with the 3-21+G values for formyl chloride (1.18 Å) and carbon monoxide (1.13 Å; experimental,¹⁴ 1.13 Å). The obvious benefit of planarity for **4** is the extended π-system, especially retention of the C—O multiple bond. However, this comes at the expense of weakening the σ bonds, particularly to the chlorines.

In view of the long bonds in **4**, the zero-point energy could be expected to be lower than for **2**. This is the case; however, the difference is only 0.8 kcal/mol at the 3-21+G level. Thus, zero-point energy changes are not important for this and presumably other related, degenerate displacements such as reaction 3. Nondegenerate processes generally show larger zero-point effects, e.g., 3–4 kcal/mol for the S_N2 reaction of OH⁻ + CH₃Cl.¹³

The geometry of **4** was also optimized with the 6-31+G(d) basis set. Again, comparison of the structures in Figures 3 and 5 shows little difference between the 3-21+G and 6-31+G(d) predictions. The effect on the Hartree-Fock energies is also similar to the results for **2**. The reactants become stabilized by 11.9 and 12.0 kcal/mol relative to **2** and **4** in going from 3-21+G//3-21+G to 6-31+G(d)//3-21+G, as shown in Table I. Use of the 6-31+G(d) geometries does not change these results much; **2** and **4** are predicted to be 6.0 and 5.6 kcal/mol higher in energy than the reactants at the 6-31+G(d)//6-31+G(d) level vs. 4.8 and 3.3 kcal/mol at 6-31+G(d)//3-21+G(d). Thus, the Hartree-Fock calculations uniformly find **4** lower in energy than **2** by 0.4–1.6 kcal/mol plus 0.8 kcal/mol for the difference in zero-point energies.

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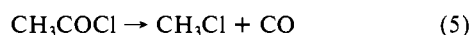
This preference for the planar transition state **4** is dramatically reversed by addition of the correlation energy. As revealed in Table I, while **2** is stabilized by 6.2 kcal/mol in going from the 6-31+G(d) to MP3 levels, **4** is destabilized by 6.9 kcal/mol. Apparently, the long bonds and the planar, less compact structure for **4** cause it to benefit less from the correlation correction than **2**. The net result is that the tetrahedral transition state **2** ends up 11.6 kcal/mol lower in energy than **4**. It is unlikely that **4** remains as a transition state, i.e., the solid curve in Figure 4 probably becomes a double well with the 180° structure **4** as a maximum. In view of the effect of the correlation energy on the relative energies of **2** and **4**, it would be desirable to use the Møller–Plesset calculations for the geometry optimizations. This is currently impractical since the single-point MP3/MP2 calculations reported here took about 2 days each on a Gould 32/8750 which is typically 3–5 times faster than a VAX 11/780. Nevertheless, the findings that **2** is a transition state and that **2** and **4** are at all close in energy are novel.

Cl⁻ + CH₃COCl. The corresponding reaction with acetyl chloride was also studied with 3-21+G calculations since this compound has been used in the gas-phase experiments.¹ It is a liquid at room temperature and boils at 51 °C, whereas formyl chloride is relatively unstable and decomposes to HCl and CO even at -60 °C in 1 h in chloroform.¹⁵ For reference, we did compute the energy changes for reactions 4 and 5, as summarized below. In view of the changes in bonding, electron correlation is important to obtain highly accurate results for such reactions.



$$\Delta E(3-21+G // 3-21+G) = -7.5 \text{ kcal/mol}$$

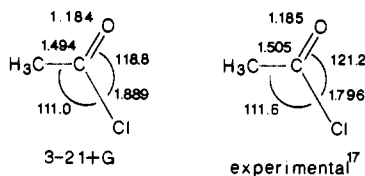
$$\Delta E(\text{MP3/MP2/6-31+G(d)} // 3-21+G) = -1.9 \text{ kcal/mol}$$



$$\Delta E(3-21+G // 3-21+G) = 2.3 \text{ kcal/mol}$$

$$\Delta H(\text{experimental},^{16} 25 \text{ °C}) = 12.5 \text{ kcal/mol}$$

Nevertheless, loss of CO is found to be less favorable for acetyl chloride by ca. 10 kcal/mol at the 3-21+G level. Comparisons can also be made with experiment for the geometry and rotational barrier of acetyl chloride. The geometrical results at the 3-21+G level are close to the combined electron diffraction/microwave data,¹⁷ though the computed C–Cl bond length is too long by 0.09 Å. Moreover, the calculations yield a preference of 1.35 kcal/mol for the methyl rotamer with a hydrogen-eclipsing oxygen rather than chlorine (Table II), which is in good accord with the experimental rotational barrier of 1.26 kcal/mol.¹⁷



Given the experience with formyl chloride, the study of the displacement reaction for acetyl chloride began with construction of the inversion profile for interconversion of the methyl analogues of **2** and **4**. The results are given by the dashed curve in Figure 4. Though it might have been expected that steric congestion for the methyl group would make **6** relatively less favorable, in fact,

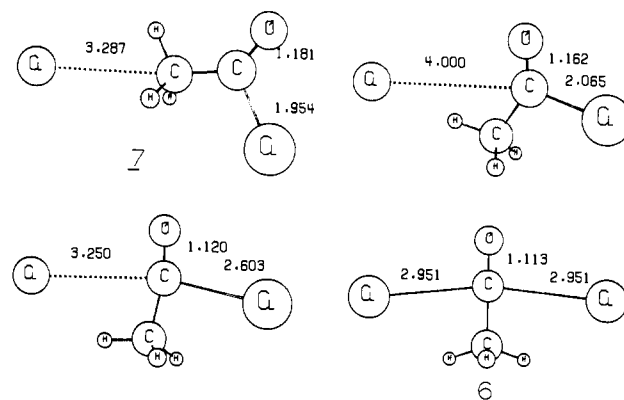
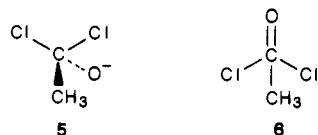
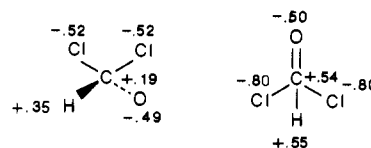


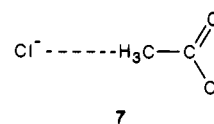
Figure 6. Structures computed with the 3-21+G basis set along the reaction path between the ion-dipole complex **7** and the transition state **6** for the reaction of $\text{Cl}^- + \text{H}_3\text{CCOCl}$.

the 3-21+G calculations no longer find the tetrahedral adduct as a stationary point on the ridge between reactants and products. Instead **6** is 5.2 kcal/mol lower in energy than a structure like **5** with a CCO angle of 140°. The reason for the increased preference for the C_{2v} -like structure **6** can be attributed to substantial positive charge on the carbonyl carbon which is stabilized by the methyl substituent. This is apparent in the 3-21+G charges obtained from Mulliken populations for **2** and **4** as shown below.



Thus, **4** has significant formyl cation character which certainly benefits from substitution by electron-donating groups. Of course, based on the results for formyl chloride, electron correlation is expected to strongly influence the relative energies of **5** and **6**. This point will be returned to farther below.

The reaction path to **6** was then explored as before by progressively lengthening a C–Cl bond and reoptimizing all remaining geometrical parameters with no constraints. The resultant energy profile is given by the curve with short dashes in Figure 1 and key structures between the ion-dipole complex **7** and **6** are il-



lustrated in Figure 6. The only minimum is for the ion-dipole complex which has the chloride ion again close to the dipole axis, now 3.29 Å from the backside of the methyl carbon. The chloride ion is about 1.5 Å farther from the carbonyl carbon in **7** than in **3**, so the interaction energy is only 14.3 kcal/mol vs. 21.7 for **3** at the 3-21+G level. Furthermore, in view of the basis set and correlation dependence of the results for formyl chloride in Table I, the 3-21+G interaction energy for **7** is expected to be 25% or 3–4 kcal/mol too favorable. This adjustment would bring the predicted value into excellent agreement with the estimate of ca. 11 kcal/mol made by Asubiojo and Brauman from their ICR experiments.¹

From the energy profiles in Figures 1 and 4 it is highly probably that **6** is a transition state at the 3-21+G level, though the requisite calculations of the vibrational frequencies were not executed for proof. The intrinsic barrier between **7** and **6** was found to be 7.5 kcal/mol with the 3-21+G basis set. It is also notable that the non-hydrogen atoms remain close to coplanar throughout the reaction path in Figure 6. They are coplanar in **7**, and the deviation is only a few degrees in **6**. The structure for **6** is again interesting with its long C–Cl bonds of 2.95 Å. The lengthening

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of the bonds as compared to **4** (2.65 Å) and the widening of the C-Cl angle to 166° from 143° both help accommodate the increased steric requirements of the methyl group.

The influence of electron correlation on the relative energies of **2** and **4** is remarkably profound (Table I). Assuming the effects are quantitatively similar for **5** and **6**, there would be a net ca. 13 kcal/mol relative gain for **5** that would place it about 5 kcal/mol lower in energy than **6**. Also, relative to the separated reactants, **5** may be raised in energy by ca. (7.1 - 1.4 =) 5.7 kcal/mol. This would place **5** roughly 4 kcal/mol above the energy of the reactants. The issue was also addressed by Asubiojo and Brauman.¹ They could explain the observed efficiency for reaction 3 through RRKM calculations in which the transition state is ca. 7 kcal/mol below the energy of the reactants.¹ However, a resultant dilemma was an unreasonably high electron affinity for CH₃CCl₂O radical, i.e., the tetrahedral anion is too low in energy.¹ The higher energy for the supposed transition state **5** suggested here would help alleviate the dilemma, though the kinetic analysis might then need further study. A starting point could be the use of vibrational frequencies from ab initio calculations for the transition states in the RRKM computations.

Mechanisms for Addition Reactions. Two conclusions of general importance can be safely drawn from the present results. (1) The gas-phase displacement reactions for chloride ion with the acyl chlorides feature double-well energy surfaces with coplanar ion-dipole complexes as minima and with the tetrahedral adduct as the transition state. (2) The barrier to inversion of the tetrahedral transition state through a planar structure is surprisingly low, ca. 10 kcal/mol. From a theoretical standpoint, another significant finding is the remarkable dependence of the energetics for the inversion on the correlation energy. Caution must clearly be exercised in comparing the energies of unusual transition structures at lower levels of theory.

The present findings are fully consistent with the experimental work of Brauman and co-workers who insightfully proposed and supported the double-well energy surfaces for these reactions.^{1,6} The present structural and energetic results for the ion-dipole complexes and transition states complement their efforts. The next question is how general is the occurrence of double-well energy surfaces for such displacement reactions? To begin, the double-well form should be favored by weak bases as the nucleophiles. The formation of the tetrahedral adduct is then less exothermic. From a slightly different perspective, it would be unfavorable to disrupt the C-O π-bond in the acyl electrophile to form a single bond with a weak nucleophile. Clearly, two key factors in the overall energetics for eq 1 are the difference in gas-phase acidities for the two anions and the difference in bond energies between a C-O π-bond and a C-X single bond. The former has a strength of ca. 90 kcal/mol, and some C-X single bond energies are for X = N (69-75), O (85-91), F (116), S (66), Cl (79), Br (66), and I (52).¹⁸ Also, since thiolate, chloride, bromide, and iodide ions are much weaker bases in the gas phase than alkoxides,¹⁹ these nucleophiles should all favor ion-dipole complexation over formation of tetrahedral adducts with most acyl electrophiles including acid halides, esters, and amides. This would, in turn, cause these systems to be biased toward the double-well surfaces. At the other extreme, C-F bonds are unusually strong, and fluoride ion is similar in gas-phase basicity to simple alkoxides.¹⁹ Consequently, formation of the tetrahedral adducts should be very favorable energetically with fluoride ion, which would lead to either single-well or triple-well energy surfaces with acyl electrophiles. The situation with alkoxides as nucleophiles is less clear and should be sensitive to substitution for both the nucleophile and electrophile. Hydroxide ion is representative of the highly basic extreme for such nucleophiles; it should provide significantly exothermic formation of the tetrahedral adducts and

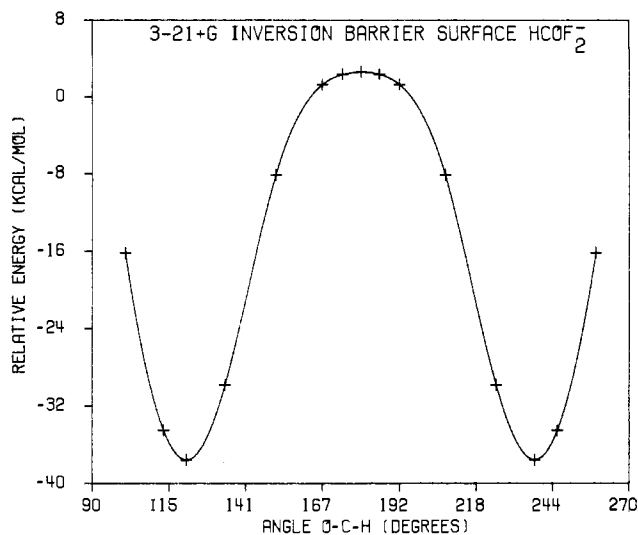


Figure 7. Computed energy profile for inversion of the tetrahedral intermediate, HCOF₂⁻, in the reaction of F⁻ + HCOF. Energies from 3-21+G calculations are relative to the separated reactants. The abscissa gives the HCO angle.

again single- or triple-well energy surfaces.

These notions are supported by the present findings for reactions 2 and 3 and the corresponding experimental data.^{1,6} The earlier ab initio study of reaction 3 also yielded a double-well energy profile; however, the geometrical variation was limited, and the minima were identified as π-complexes rather than the coplanar ion-dipole complexes.⁸ Furthermore, the ab initio results for OH⁻ + H₂C=O did show a triple-well surface with the tetrahedral adduct as a minimum, 35 kcal/mol lower in energy than the reactants.⁵ The recent ab initio findings of Howard and Kollman also fit the pattern with preference for ion-dipole complexation for HS⁻ with formamide and formaldehyde, though the lack of diffuse functions in their basis sets leaves some quantitative uncertainty. In addition, we have also studied the reaction of fluoride ion with formyl fluoride at the 3-21+G//3-21+G level. A triple-well energy surface is obtained, the ion-dipole complexes are 34.8 kcal/mol lower in energy than the reactants, the tetrahedral intermediate is an additional 2.8 kcal/mol more stable, and there are 10.5 kcal/mol activation barriers between the complexes and the tetrahedral species. On the basis of the experience with formyl chloride this qualitative result should not be affected by adding the correlation energy. Overall, it is apparent that there is a rich variety of energy surfaces for displacement reactions of anionic nucleophiles with acyl halides. In contrast, the possibilities for the corresponding S_N2 reactions with alkyl halides seem restricted to only the double-well form.¹³

One final topic worthy of general discussion is the likelihood of planar transition states such as **4** and **6**. We have also computed an inversion profile analogous to **2** ↔ **4** for HCF₂O⁻ with 3-21+G//3-21+G calculations, as shown in Figure 7. In this case, the inversion is highly unfavorable with the planar C_{2v} structure as a maximum, 40.2 kcal/mol above the tetrahedral intermediate. Addition of the correlation energy should accentuate the difference by analogy to HCCl₂O⁻. Since the inversion is accompanied by substantial elongation of the C-Cl bonds in **2** going to **4**, the process is facilitated by weak C-X bonds with low force constants for stretching in RCX₂O⁻. Referring back to the bond energies listed above or IR stretching frequencies, X = SR, Br, and I are the most likely candidates to favor the planar structure, while X = OR and F are the least likely. The suggestion by Dewar in 1949 that ester hydrolyses might proceed through such planar intermediates was imaginative but now clearly erroneous.²⁰

Of course, it would be nice to be able to accurately estimate the effects of solvation on the energy surfaces for the displacement

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reactions. This is difficult beyond the maxims that charge localization and separation of opposite charges make solvation more favorable. Consequently, the greater charge separation and increased concentration of charge on the chlorines for **4** as compared to **2** as indicated by the Mulliken populations shown above, suggest that **4** may be better solvated. It is probably best to consider this as a provocative notion since the Mulliken populations are open to criticism.¹¹ Nevertheless, it does stimulate one to consider what the true reaction pathway is for some common synthetic reactions such as thio ester formation from thiolates and acid halides in dipolar aprotic solvents. In any event, the present

results and the related experimental work^{1,6} demonstrate that the central role of tetrahedral intermediates in addition reactions is not as universal as commonly assumed.

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Supplementary Material Available: Full geometrical details for the acyl halides, ion-dipole complexes, and transition states for reactions 2 and 3 in Z-matrix format (7 pages). Ordering information is given on any current masthead page.

$^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ Electronic Transitions in Cobalt(II) Tetrachloride: An FT-IR and Inelastic Electron Tunneling Spectroscopy Study

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Abstract: The first two electronic transitions in tetraethylammonium cobalt(II) tetrachloride are observed by tunneling spectroscopy. The lowest energy transition [$^4A_2 \rightarrow ^4T_2$] is electric dipole forbidden, is the most intense transition observed in the tunneling spectrum, and extends from 2000 to 4100 cm^{-1} . The electric dipole allowed $^4A_2 \rightarrow ^4T_1$ transition is observed in both tunneling and FT-IR spectra and fills the region from 4450 to 7000 cm^{-1} . Significant structuring of this latter band is observed in both FT-IR and tunneling spectra. The inelastic electron tunneling spectroscopy (IETS) results reported are of special significance for several reasons: (a) the magnetic dipole transition is observed with large intensity, (b) significant structure is observed on an electronic transition, and (c) novel data acquisition and analysis techniques are used to extract high-quality electronic spectra from the overall tunneling spectra. We also show that the adsorption of cobalt(II) dichloride on alumina from solution yields (at least in part) surface-supported cobalt(II) tetrachloride ion.

Inelastic electron tunneling spectroscopy (IETS) has proven to be a very sensitive technique for the observation of vibrational spectra.¹⁻³ While most of the tunneling literature focuses on characterizing chemisorbed species on oxide surfaces, a small group of papers concerns the use of tunneling as a molecular spectroscopy.⁴⁻¹³ Because the selection rules for IETS are rather weak, vibrational modes which are silent in the IR or Raman, or both, may be directly observed in the tunneling spectrum.⁴⁻⁸ Thus, when used in concert with IR and Raman spectroscopy, tunneling spectroscopy extends the data base on which assignments may be made and often simplifies the assignment of normal mode frequencies.

Tunneling spectroscopy may also be used to study electronic transitions.⁹⁻¹³ Electronic transitions in rare-earth oxides,^{9,10} phthalocyanine dyes,^{9,11} large aromatic molecules,⁹ and transition metals^{12,13} have been observed by IETS. As a consequence of these studies, it is now known that spin-forbidden transitions ($\Delta S = \pm 1$) occur with intensities similar to spin-allowed transitions. Further, in a recent letter¹³ we suggested that magnetic dipole allowed

(electric dipole forbidden) transitions might also be observed with significant intensity. Given the richness of the data potentially available from IETS and the large classes of inorganic systems having low energy forbidden transitions,⁵ it is clear that tunneling studies can contribute significantly to our understanding of inorganic materials. One may ask, therefore, why little progress has been made in the analysis of electronic states by IETS. One major hindrance has been the need for better data acquisition and manipulation. Perusal of the IETS papers concerned with electronic transitions reveals that the data are acquired and displayed in d^2V/dI^2 format, they are often the result of a single scan or multiple scans of rather noisy data, and reference subtraction has not been employed. Thus, unless a large hump can be easily identified, no electronic transitions are reported.

Another problem is that much of the electronic state tunneling literature has been devoted to π to π^* transitions of large planar aromatic molecules which can significantly interact with the tunnel junction insulator or cover metal. Thus, it appeared that electronic transitions in IETS were always broad, unstructured, and often shifted in energy. Finally, because the molecule of interest may undergo chemical reaction with the oxide support used in IETS, the experimenter must be reasonably knowledgeable in his choice of support/adsorbate pair and adsorption conditions. All of these considerations relegated electronic state tunneling to an activity practiced by a few hardy souls.

We believe we have found a general solution to all (save the last) real and perceived difficulties. The present work has three objectives: first, to present new data on the electronic states of CoCl_4^{2-} ; second, to show that electronic transitions in IETS need not be broader than or shifted from electronic transitions observed optically; and finally, to describe the techniques used in obtaining high-quality electronic state spectra by IETS.

Experimental Section

Tunneling Instrumentation. The spectrometer used was recently described in the literature.¹⁴ The d^2V/dI^2 data presented were acquired

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