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Orientation Dependence of the Reaction of K + CH_3Cl

Robert G. A. R. Maclagan

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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Calculations are reported at the MP2/6-311++G(2df,2pd) level of theory on the reaction of K atoms with CH_3Cl, with different orientations of the CH_3Cl molecule with respect to the incoming K atom. As was found for the CH_3CN + K system, approach along a minimum energy pathway does not lead to electron transfer at the energies of the reported experiments. Stretching of the C−Cl bond of CH_3Cl facilitates electron transfer. The barrier to electron transfer is less for approach from the Cl end of CH_3Cl. Unlike the case for the CH_3CN + K system the barrier to formation of CH_2Cl^- + H is greater than that to form CH_3Cl^- or CH_3 + Cl^-.

I. Introduction

It is intuitively obvious that, with the exception of a totally symmetric molecule, the outcome of a collision of an atom with a molecule will depend on the orientation of a target molecule with the incoming collider. The collision of K atoms with oriented methyl halide molecules has been the subject of numerous experimental studies.[1] The effects of molecular orientation on the electron-transfer reaction have been reviewed by Brooks and Harland.[2] Results of oriented beam experiments on the CH_3Cl + K system have been reported by Harland et al.[3] The cross section for reaction from the Cl end was found to be greater than that for the CH_3 end.

Herschbach[5] makes the distinction between a "rebound" mechanism applicable to K + CH_3I and a "stripping" mechanism applicable to K + X_2 where the harpoon mechanism is applicable. For rebound mechanisms the cross section is expected to to be small, while the cross section is expected to be large where a stripping mechanism occurs. The reaction of K atoms with CH_3Cl was studied by Husain and Lee.[4] They obtained the following Arrhenius parameters for the reaction: $A = 3.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $E_a = 32$ kJ mol^{-1}. The reaction rate is 2 orders of magnitude smaller than that for reactions usually described by using an electron jump or harpoon mechanism.

However, Brooks and Harland[2] and Harland et al.[3] did use electron jump language to discuss this reaction. When this is done the reaction is assumed to be:

$$K + CH_3Cl \rightarrow K^+ + CH_3Cl^- \rightarrow \text{products}$$

The uncoupling of the charge transfer and any bond breaking allows one to focus on the anion species formed, with no further role being played by the electron donor, such as the K atom in this reaction. Under the conditions in which this reaction is studied experimentally, there is sufficient translational energy available to separate the charged species formed.

We have recently reported[6] calculations on the orientation dependence of the reaction K + CH_3CN studied experimentally by Harris et al.[7] It was found that approach along a minimum energy pathway does not involve a simple electron jump mechanism. Stretching of the C−C bond of CH_3CN facilitated electron transfer. For CN end approach electron transfer was found to occur on a repulsive surface while for methyl end approach it occurred on an attractive surface. For approach from the methyl end of the molecule, the barrier to the formation of CH_2CN^- was found to be lower than that for the formation of CH_3CN^- or CN^- as the K atom approaches closer to the CH_3CN molecule.

There have been some other suggestions that the stretching of a bond is important for ion-pair formation. Wiskerke et al.[8] have the following intriguing statement: "The quite strong dependence of the crossing radius on the stretching of CH_3I was pointed out long ago and has been periodically rediscovered." Aten and Los[9] have shown that in the K + X_2 systems, stretching of the X−X bond is necessary to explain the experimental results. This was also explored by Wu[10] and LaBudde et al.[11] using semiempirical potentials for M + CH_3X. In all these semiempirical studies the stretching of the C−X or X−Y bond tends to be discussed without reference to the position of the M atom. Our calculations would suggest that this is not correct.

In this paper we report calculations of the potential energy surface for the K + CH_3Cl reaction leading to electron transfer from the K atom forming CH_3 and Cl^- or KCl. Ab initio quantum mechanical calculations have not been reported on this system previously.

II. Computational Details

The calculations, performed with the GAUSSIAN 98[12] program, used the MP2/6-311++G(2df,2pd) level of theory. This was chosen because it gives very good values for the electron affinities for the halide atoms (F 3.435 eV (expt[13] 3.401 eV); Cl 3.506 eV (expt[14] 3.613 eV); Br 3.388 (expt[14] 3.364 eV)). This level of theory gives better agreement with experimental values for the halide electron affinities than results obtained with smaller basis sets and higher level theoretical methods such as QCISD(T) and CCSD(T). In addition this level of theory gave a very good description of the F^- + CH_3Cl potential energy surface.[15]

III. Results and Discussion

The optimized energies of all relevant species and the relative energies of various possible products relative to K + CH_3Cl

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TABLE 1: Total Energies of Stationary States

species	energy/hartree	relative energy/eV
CH_3Cl	−499.50770	
CH_3Cl^- [a]	−499.47705	
CH_3	−39.73512	
Cl^-	−459.75914	
CH_2Cl^-	−498.85922	
K	−599.36815	
K^+	−599.21172	
KCl	−1059.15559	
H	−0.49982	
$K + CH_3Cl$	−1098.87585	0.00
$K^+ + CH_3Cl^-$	−1098.68877	5.09
$KCl + CH_3$	−1098.89070	−0.40
$K^+ + Cl^- + CH_3$	−1098.70598	4.62
$K^+ + CH_2Cl^- + H$	−1098.57076	8.30

[a] CH_3Cl^- has a negative electron affinity. Calculations using bound state methods are strictly not valid.

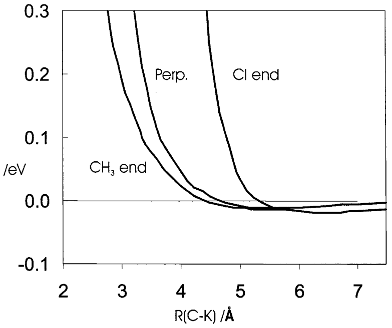

Figure 1. Optimized energies for the $CH_3Cl + K$ system as a function of $R(C-K)$, for minimum energy approaches from the Cl end, the CH_3 end, and perpendicular to the CCl direction in the $ClCH_1$ plane.

are given in Table 1. The reaction to form $CH_3 + KCl$ is exothermic with a calculated energy change of −0.40 eV. The calculated dissociation energy, D_e, of KCl is 5.03 eV. $R(K-Cl)$ was calculated to be 2.692 Å (expt 2.667 Å[16]). All other product channels are endothermic. The reaction to form $CH_2Cl^- + H + K^+$ is more endothermic than the corresponding reaction for CH_3CN,[6] where the calculated energy change was 7.20 eV.

The optimized structures were calculated for the $CH_3Cl + K$ system as a function of $R(C-K)$, for the K atom approaching from the Cl end, the methyl end, and perpendicular to the CCl bonds in a plane containing one methyl hydrogen atom (where the K−C−Cl angle is 90°and the K atom is in the H_1-C-Cl plane). The calculated structures are the minimum energy structures for a given $R(C-K)$.

The optimized energies for the $CH_3Cl + K$ system as a function of $R(C-K)$ are shown in Figure 1. In all cases there is only a shallow minimum. At short distances the energies are all steeply repulsive. The zero of energy is the calculated energy of $CH_3Cl + K$.

For Cl approach there is a minimum at $R(C-K) = 6.41$ Å with a well depth of 0.0184 eV. The potential becomes repulsive at $R(C-K) = 5.38$ Å. At this distance of approach the optimum value of $R(Cl-K)$ is 3.60 Å. Up to $R(C-K) = 4.50$ Å the ClCH angle remains constant at about 108.6°. With the bond length of KCl being calculated to be 2.69 Å and the C−Cl bond length in CH_3Cl being calculated to be 1.80 Å, the two colliding species are within van der Waals contact at a shorter distance of approach than $R(C-K) = 4.50$ Å. At closer approaches, the CH_3 approaches planarity. At $R(C-K) = 2.75$ Å, where the K−Cl bond is very compressed, the ClCH angle is 118.6°. The calculated interaction energy at $R(C-K) = 2.75$ Å is 26.25 eV.

Charge Transfer Along a Minimum Energy Pathway. The calculated Mulliken charge on the K atom, $Q(K)$, as a function of $R(C-K)$ is shown in Figure 2. At medium-large separation, the K atom is not positively charged, but negatively charged. The charge on the K atom reaches a minimum value of −0.243 at $R(C-K) = 3.63$ Å. The CH_3Cl molecule has a large spatial extent: $\langle R^2 \rangle = 36.6$ Å^2. Some of the more diffuse charge could be seen to belong more to the K atom than the CH_3Cl molecule, leading to the negative charge on the K atom. This could also be an artifact of the Mulliken partitioning of electronic charge. As the K atom approaches, $R(C-Cl)$ shortens significantly. At $R(C-K) = 3.63$ Å, $R(C-Cl) = 1.54$ Å. At $R(C-K) = 3.0$ Å, $R(C-Cl) = 1.32$ Å. The charge on the K atom does not become positive until about $R(C-K) = 2.6$ Å, when the interaction energy is ∼35 eV, much greater than the experimental energies of Harland et al.[3] For CH_3CN, the charge on the K atom did not become positive for approach from the CN end until the interaction energy was 16.7 eV.[6] Like the case for $CH_3CN + K$, the simple harpoon mechanism does not seem to apply for $CH_3Cl + K$.

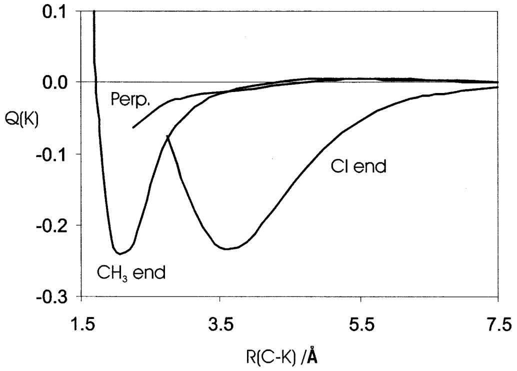

Figure 2. The charge on the K atom, $Q(K)$, as a function of $R(C-K)$, for minimum energy approaches from the Cl end, the CH_3 end, and perpendicular to the CCl direction in the $ClCH_1$ plane.

For approach from the CH_3 end the interaction is calculated to be initially attractive, reaching a minimum of −0.012 eV at 5.29 Å. This may be an artifact of the neglect of the basis set superposition energy. The interaction energy becomes repulsive at $R(C-K) = 4.45$ Å. The charge on the K atom also has a minimum value for CH_3 approach. The charge on the K atom is initially slightly positive before becoming negative. The minimum in charge of −0.251 occurs at $R(C-K) = 2.10$ Å. The charge on the K atom again becomes positive at $R(C-K) = 1.73$ Å. At this distance the C−H bond length is ∼2.05 Å and the interaction energy at this distance of approach is 5.8 eV. Full charge transfer has occurred when $R(C-K) = 1.5$ Å and the interaction energy is 9.2 eV. In contrast to the case with approach from the Cl end, $R(C-Cl)$ increases as $R(C-K)$ decreases. At $R(C-K) = 1.7$ Å, when the K atom is just positive, $R(C-Cl) = 1.971$ Å, only slightly longer than the calculated value for CH_3Cl of 1.799 Å, but at $R(C-K) = 1.5$ Å, when the electron transfer from the K atom is complete, $R(C-Cl)$ is stretched to 2.743 Å.

For approach perpendicular to the C−Cl bond, there is a shallow minimum at $R(C-K) = 5.502$ Å, with a well depth of −0.0116 eV. The K atom is still not positive at $R(C-K) = 2.25$ Å. As the K atom approaches, the $ClCH_1$ bond angle increases, being 144.1° at $R(C-K) = 2.25$ Å.

Calculations at other orientations at $R(C-K) = 2.50$ and 3.00 Å did not show significant difference from what would be expected from interpolating the results for $\angle ClCK = 0°, 90°$, and 180°.

Cl End Approach. For approach from the Cl end of CH_3Cl along a minimum energy path, electron transfer does not occur

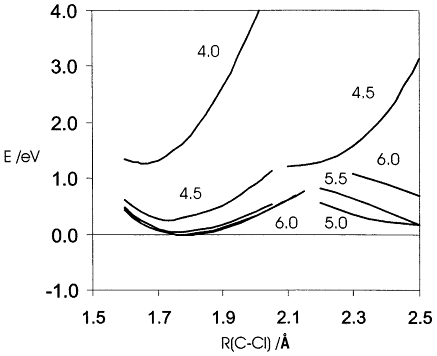

Figure 3. Optimized energies as a function of R(C−Cl) for R(C−K) = 4.00, 4.50, 5.00, 5.50, and 6.00 Å for approach of K from the Cl end of CH_3Cl. The zero of energy is the calculated energy of CH_3Cl + K.

by an electron jump mechanism. For CH_3CN[6] it was found that electron transfer could occur if the C−C_{CN} bond was stretched. In Figure 3 the optimized energies of the CH_3Cl + K system as a function of R(C−Cl), for R(C−K) = 4.0, 4.5, 5.0, 5.5, and 6.0 Å, are shown. The zero of energy is the energy of separated K + CH_3Cl. Gaps occur in the curves about the point of charge transfer/avoided crossing where the Hartree−Fock approximation is not valid. For the geometries shown in Figure 3 a single reference treatment is valid, as demonstrated by a coefficient for the Hartree−Fock term of 0.925 or greater in CISD calculations. There is negligible spin contamination with S2 being 0.780 or less. As R(C−Cl) increases for a given R(C−K), the charge on the K atom becomes more negative, until a curve crossing occurs at R(C−Cl) ≈ 2.1−2.3 Å, and the K atom becomes positive. The electron is transferred to the Cl atom with the CH_3 entity being only slightly negatively charged. For R(C−K) > 4.5 Å, dissociation occurs to $CH_3 + Cl^-$. The calculated energy for the reaction $K + CH_3Cl \rightarrow K^+ + CH_3 + Cl^-$ is 4.62 eV. For shorter distances of approach, R(K−Cl) is less than in KCl. Calculations at the same level of theory give R(K−Cl) = 2.692 Å and D_e = 4.28 eV for KCl. Dissociation into $K^+ + Cl^-$ requires 5.03 eV. As R(C−K) decreases, the barrier to charge transfer decreases from ~1.04 eV for R(C−K) = 6.0 Å to ~0.70 eV for R(C−K) = 5.0 Å before increasing to 3.00 eV for R(C−K) = 4.0 Å. R(C−Cl) is stretched 0.35−0.45 Å to allow charge transfer. This is less than the 0.55 Å $R(C_{Me}-C_{CN})$ needed to be stretched for K + CH_3CN. The harmonic vibrational frequency for the C−Cl stretching mode calculated at the MP2/6-311++G(2df,2pd) level of theory is 770.6 cm^{-1} (=0.096 eV). At the energies of the experiments of Harland et al.[3] the C−Cl vibration could easiy be excited to reach the avoided crossing. When the electron transfer occurs, the potential energy surfaces for R(C−K) = 5.0, 5.5, and 6.0 Å, which were very close before electron transfer, separate, with the surface for R(C−K) = 5.0 initially being the lowest in energy, whereas before electron transfer, it was slightly higher in energy. This contrasts with the corresponding surfaces for K + CH_3CN.[17]

CH_3 End Approach. The optimized energies as a function of R(C−Cl) for R(C−K) = 2.5, 3.0, 4.0, and 5.0 Å for approach from the methyl end are shown in Figure 4. The zero of energy is again the energy of separated K + CH_3Cl. The avoided crossing occurs with a higher barrier than that for approach from the Cl end. The barrier varies from 2.33 eV at R(C−Cl) = 2.62 Å for R(C−K) = 5.0 Å to 1.12 eV at R(C−Cl) = 2.22 Å for R(C−K) = 3.0 Å. The barrier to ionization appears to be higher for methyl end approach. For R(C−K) > 5.0 Å dissociation of CH_3Cl occurs on charge transfer to form $CH_3 + Cl^-$. If we wish to describe the collision in terms of the centers of mass of the two colliding species, using R(C−K) as a measure of distance of approach is strictly not correct, as the center of mass of the CH_3Cl changes as the K atom approaches. If we calculate the distance from the K atom to the center of mass of the CH_3Cl molecule, then charge transfer occurs at 2.6−4.4 Å for Cl end approach and 4.0−6.8 Å for methyl end approach.

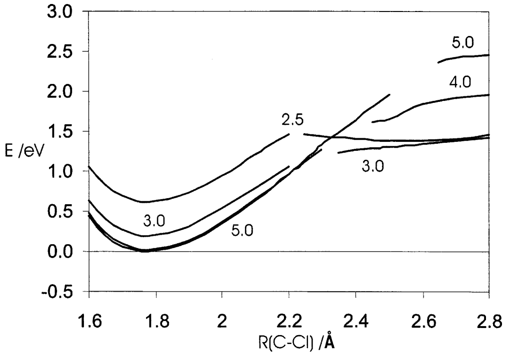

Figure 4. Optimized energies as a function of R(C−Cl) for R(C−K) = 2.50, 3.00, 4.00, and 5.00 Å for approach of K from the CH_3 end of CH_3Cl. The zero of energy is the calculated energy of CH_3Cl + K.

As was found for CH_3CN, the charge on the methyl group becomes more positive as the C−Cl bond is stretched. For R(C−K) = 5.0 Å, it reaches $Q(CH_3)$ = +0.37. For R(C−K) = 2.5 Å, it reaches a smaller value of +0.28. When the electron transfer occurs, the methyl group becomes negative. The charge on the methyl group becomes less negative as the C−Cl bond is further stretched.

CH_2Cl^- Formation. For the CH_3CN + K system, attack from the methyl end of CH_3CN leads to the preferential formation of CH_2CN^-. Calculations[6] revealed that the barrier to formation of CH_2CN^- was lower than that for the formation of $CH_3 + CN^-$. The formation of CH_2Cl^- was not reported by Harland et al.[3] Optimized energies as a function of $R(C-H_1)$, for R(C−K) = 2.5, 3.0, 4.0, and 5.0 Å, were calculated. The barrier to charge transfer, if it occurs, decreases as R(C−K) decreases. For R(C−K) = 2.5 Å it is 2.0 eV at $R(C-H_1)$ = 1.68 Å. At this R(C−K) distance, the barrier to charge transfer with the formation of $CH_3 + Cl^-$ is 1.5 eV at R(C−Cl) = 2.21 Å, which is significantly lower. For R(C−K) = 3.0 Å, it is 1.12 eV for $CH_3 + Cl^-$ formation and 2.60 eV for CH_2Cl^- + H formation. For R(C−K) = 4.0 and 5.0 Å charge transfer had not occurred when $R(C-H_1)$ = 2.0 Å.

IV. Conclusions

As was found for the CH_3CN + K system, a simple electron jump does not occur with the CH_3Cl + K system along a minimum energy pathway. For electron transfer to occur the C−Cl bond needs to be stretched 0.31−0.52 Å for approach from the Cl end and 0.43−0.84 Å for approach from the CH_3 end. The variation in R(C−Cl) for electron transfer with R(C−K) demonstrates that this reaction should not be discussed focusing solely on the CH_3Cl entity. The barrier to the formation of CH_2Cl^- + H is greater than that to form CH_3Cl^- or $CH_3 + Cl^-$ for approach from the methyl end, unlike the case for CH_3CN + K.

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References and Notes

(1) Wiskerke, A. E.; Stolte, S.; Loesch, H. J.; Levine, R. D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 757 and reference therein.

(2) Brooks, P. R.; Harland, P. W. *Adv. Gas-Phase Ion Chem.* **1996**, *2*, 1.

(3) Harland, P. W.; Carman, H. S.; Phillips L. F.; Brooks, P. R. *J. Phys. Chem.* **1991**, *95*, 8137.

(4) Husain, D.; Lee, Y. H. *J. Photochem. Photobiol. A* **1988**, *42*, 13.

(5) Herschbach, D. R. *Adv. Chem. Phys.* **1966**, *10*, 319.

(6) Maclagan, R. G. A. R. *Chem. Phys. Lett.* **2003**, *373*, 586.

(7) Harris, S. A.; Harland, P. W.; Brooks, P. R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 787.

(8) Wiskerke, A. E.; Stolte, S.; Loesch, H. J.; Levine, R. D. *Phys. Chem. Chem. Phys.* **2000**, *2*, 757.

(9) Aten, J. A.; Los, J. *Chem. Phys.* **1977**, *25*, 47.

(10) Wu, K. T. *J. Phys. Chem.* **1979**, *83*, 1043.

(11) LaBudde, R. A.; Kuntz, P. J.; Bernstein, R. B.; Levine, R. D. *J. Chem. Phys.* **1973**, *59*, 6286.

(12) Frisch M. J.; Trucks G. W.; Schlegel H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(13) Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys Rev. A* **1989**, *40*, 3698.

(14) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *99*, 3730.

(15) Wang, H.; Hase, W. L. J. *Am. Chem. Soc.* **1997**, *119*, 227.

(16) Rice, S. A.; Klemperer, W. *J. Chem. Phys.* **1953**, *27*, 573.

(17) See Figure 3 of ref 6.