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Coupled cluster calculations for the S_N2 reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$

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Abstract

Coupled cluster calculations including single and double excitation operators plus a perturbative treatment of connected triples have been carried out for five stationary points of the potential energy surface of the S_N2 reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$. The ion–dipole complexes have well depths of 11.2 kcal mol^{-1} in the reactant and 18.2 kcal mol^{-1} in the product channel, respectively, and are separated by a barrier which is lower than the asymptotic reactant energy by 2.2 kcal mol^{-1}. The enthalpy of reaction at 298 K is calculated to be -8.15 kcal mol^{-1}. (Int J Mass Spectrom 201 (2000) 277–282) © 2000 Elsevier Science B.V.

Keywords: Coupled cluster calculations, S_n2 reactions; Ion-dipole couplexes

1. Introduction

Gas-phase nucleophilic bimolecular substitution (S_N2) reactions have attracted considerable interest over the last decade [1,2]. In particular, reactions of the type

$$X^- + CH_3Y \rightarrow XCH_3 + Y^- \tag{1}$$

where X and Y are halogen atoms have been studied. Due to the strong attractive interaction between the ions and the dipolar molecules intermediate complexes are formed on the reactant as well as the product side. These complexes correspond to relatively deep wells with a barrier in between. This barrier may be regarded as a well-defined transition state if it is located energetically above the reactants as in the case of the $Cl^- + CH_3Cl$ reaction. In asymmetric reactions like

$$Cl^- + CH_3Br \rightarrow ClCH_3 + Br^- \tag{2}$$

however, a situation may occur where the barrier is below the asymptotic reactant energy. In the framework of Langevin's ion–molecule capture theory [3] such a barrier should not be relevant for the reaction probabilities, cross sections, and finally rate constants. However, capture theory tends to overestimate the rate constants of S_N2 reactions by about 2 orders of magnitude [4], which suggests that intrinsic features of the potential energy surface (PES) are responsible for this discrepancy. In quantum mechanics a well can cause reflection of an incoming wave packet. This effect should be the most important reason for the

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small experimental rate constant of 10^{-11} cm^3 s^{-1} molecule^{-1} at 300 K [4].

Hase and co-workers constructed a PES from Hartree–Fock calculations with a relatively small split valence contracted Gaussian basis set (SV4PP for Cl and Br and 6-31G* for CH_3) and some experimental data [5]. Making use of this PES and time-independent quantum scattering theory, Schmatz and Clary calculated cross sections that strongly depend on the degree of initial excitation in the C–Br stretching vibration [6]. Experiments by Viggiano and co-workers [7] revealed that the internal CH_3Br temperature does not influence the rate constants. After applying a scaling procedure to the geometrical parameters of the saddle point, which did not affect the energetics, the influence of C–Br vibrational excitation in CH_3Br strongly decreased in the calculations of [6]. Therefore, it seems to be important to employ high level ab initio data in the construction of a PES. A first step toward a new PES for the title reaction is presented in this work.

Although all the species that correspond to the stationary points of the PES of this reaction have closed electron shells and can be described well by single-reference based quantum chemical methods, the effort to reach “chemical accuracy” (1 kcal mol^{-1} or better) is considerable. In practice, coupled cluster calculations including single and double excitation operators plus a perturbative treatment of connected triples (CCSD(T)) [8] are suitable for this purpose. Benchmark calculations of this sort for the reactions $F^- + CH_3Cl$ [9] and $Cl^- + CH_3Cl$ [10] have been presented recently. The most sophisticated ab initio study for the $Cl^- + CH_3Br$ reaction published so far consists of MP2 calculations with a VTZ++ basis set by Wu and Truhlar [11] who investigated the reactants and products as well as the saddle point.

2. Computational details

The electronic structure calculations were carried out with the MOLPRO98 suite of programs [12,13]. For most calculations a basis set of 257 contracted Gaussian orbitals (cGTOs) was used. It is comprised of the (s, p, d, f) functions of the augmented correlation consistent valence quadruple-zeta (aug-cc-pVQZ or avqz) basis for carbon [14], chlorine [14], and bromine [15], while the hydrogen basis may be briefly described as sp (avtz) + d (vtz), where vtz is a shorthand notation of Dunning’s cc-pVTZ basis [16]. All valence electrons were correlated in the CCSD(T) calculations.

For comparison, we also performed calculations with the X^{7+} and Y^{7+} cores of the halogen atoms simulated by pseudopotentials (PPs). The scalar-relativistic energy-consistent PPs of [17] have been used, together with corresponding optimized $(6s6p)/[4s4p]$ valence basis sets [18], which were supplemented by diffuse $(1s1p)$ functions and $(4d3f)$ polarization sets taken from the aug-cc-pVQZ basis [14,15]. (In the case of Br, the aug-cc-pVQZ $(13d)/[5d]$ set was truncated to $4d$ by leaving out the functions with the nine largest exponents.)

At the stationary points of the PES for reaction (2), calculations with a large basis set of 431 cGTOs have been carried out. It consists of the aug-cc-pV5Z basis set for chlorine and bromine, which includes three full sets of g functions and two full sets of h functions. The carbon basis chosen is cc-pV5Z and the cc-pVQZ basis is employed for the hydrogen atoms. These calculations are expected to yield results rather close to the basis set limit.

3. Results and discussion

The reaction profile of reaction (2) (see, e.g., Fig. 1 in [6]) shows five stationary points: the reactants (I), the entrance channel complex (II), the first order saddle point (III), the exit channel complex (IV), and the products (V). Calculated geometries and relative energies for the stationary points are given in Table 1. The CCSD(T) equilibrium geometry of CH_3Br(I) is in good agreement with experiment [19]. The largest difference occurs for the C–Br equilibrium distance which is too long by 0.011 Å mainly due to the neglect of core–valence correlation effects, relativistic effects, and basis set deficiencies. While all-electron and pseudopotential calculations yield almost identi-

Table 1
Geometrical parameters and relative energy of stationary points for reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$

Ref.	Stationary Point	Method	Basis	r_{CH}(Å)	θ_{HCBr}(°)	R_{CCl}(Å)	R_{CBr}(Å)	E (kcal mol^{-1})
[5]	I	SCF		1.077	107.7	∞	1.944	0
[11]	I	MP2	205 cGTOs	1.084	108.04	∞	1.937	0
*	I	CCSD(T)/PP		1.0850	107.79	∞	1.9413	0
*	I	CCSD(T)	257 cGTOs	1.0851	107.83	∞	1.9452	0
[19]	I	exp.		1.082	107.7	∞	1.934	0
[5]	II	SCF		1.071	106.8	3.221	1.991	−10.74
*	II	CCSD(T)/PP		1.0814	107.43	3.076	1.9842	−11.44
*	II	CCSD(T)	257 cGTOs	1.0816	107.52	3.095	1.9863	−11.29
[5]	III	SCF		1.062	92.3	2.469	2.458	−2.91
[11]	III	MP2	205 cGTOs	1.070	90.9	2.310	2.397	−1.0
*	III	CCSD(T)/PP		1.0718	91.23	2.347	2.413	−2.64
*	III	CCSD(T)	257 cGTOs	1.0718	91.20	2.354	2.422	−2.13
[20]	III	exp.						−2.5
[1]	IV	SCF		1.073	72.2	1.825	3.517	−21.21
*	IV	CCSD(T)/PP		1.0827	72.22	1.8263	3.280	−17.82
*	IV	CCSD(T)	257 cGTOs	1.0829	71.77	1.8203	3.318	−17.46
[5]	V	SCF		1.076	71.9	1.789	∞	−12.63
[11]	V	MP2	205 cGTOs	1.084	71.64	1.780	∞	−8.6
*	V	CCSD(T)/PP		1.0860	71.63	1.7816	∞	−7.81
*	V	CCSD(T)	257 cGTOs	1.0860	71.64	1.7869	∞	−7.60
[22]	V	exp.		1.0872	71.42	1.7756	∞	
[23]	V	exp.		1.0854	71.42	1.7760	∞	

cal results for the geometrical parameters of the CH_3 group, the PP approach, which implicitly includes relativistic effects, performs slightly better for the C–Br equilibrium distance.

Upon formation of the complex in the entrance channel (II) the C–Br bond length is increased by 0.04 Å, whereas the changes of the umbrella bending angle and the C–H bond length are very minor. The C–Cl distance is calculated to be 3.10 Å which, mainly due to attractive dispersion interaction, is shorter than the corresponding self-consistent field (SCF) value by 0.13 Å. R_{CCl} seems to be a sensitive quantity as can be seen from the noticeable difference (0.02 Å) between the results of the all-electron and the PP calculations.

Compared to the free methyl halides, the C–Cl and C–Br distances at the saddle point (III) are longer by 0.52 Å and 0.48 Å, respectively. The C–Br distance is already somewhat longer than the C–Cl distance. The methyl group has an almost planar geometric structure. Compared to free CH_3Br, the C–H bond length at the saddle point is shortened by 0.013 Å. The SCF geometries and the corresponding CCSD(T) data show remarkable differences, in the case of R_{CCl} a contraction by 0.11 Å. In [6] it was shown that a modification of Hase's PES based on our preliminary CCSD(T) results for the geometrical parameters of the saddle point gave a better agreement with experimental findings. Only negligible changes in the cross sections are observed when the numerically exact CCSD(T) values of the geometrical parameters at the saddle point are employed. The height of the central barrier is a crucial quantity for the reaction dynamics. All-electron CCSD(T) calculations with the 257 cGTO basis set yield 9.16 kcal mol^{-1} with respect to the energy minimum in the entrance channel (II) or −2.13 kcal mol^{-1} with respect to the reactants. The present pseudopotential calculations yield 8.80 and −2.64 kcal mol^{-1}, respectively. The results of the single point calculations with the large basis set will be discussed below. With severe limitations the cal-

Table 2
Relative energies (in kcal mol^{-1}) from single-point calculations with a large basis set (431 cGTOs)[a]

Stationary Point	SCF	MP2	CCSD	CCSD(T)
I	0	0	0	0
II	−8.80	−11.21	−10.70	−11.31
	(−8.80)	(−11.09)	(−10.63)	(−11.23)
III	2.38	−0.69	−0.08	−2.33
	(2.37, 2.37)[b]	(−0.39, −0.38)[b]	(0.10, 0.10)[b]	(−2.13, −2.13)[b]
IV	−17.75	−17.94	−17.98	−18.24
	(−17.75)	(−17.84)	(−17.92)	(−18.18)
V	−10.63	−8.17	−8.79	−8.53

[a] Counterpoise corrected values are given in parentheses. All calculations were carried out at the CCSD(T) geometries of the stationary points from Table 1.

[b] First value refers to educts as reference system, second value to products.

culated energy of the barrier can be compared to the experimental result of −2.50 kcal mol^{-1}, which was obtained from an Arrhenius plot and corrected for the temperature dependence of the Arrhenius prefactor [20]. Using statistical rate theory models to fit the temperature-dependent rate constant, Wang and Hase [21] obtained values between −1.1 and −1.5 kcal mol^{-1}.

For the complex in the exit channel (IV), the difference between SCF and CCSD(T) C–H and C–Cl bond lengths is only minor, whereas R_{CBr} is contracted by as much as 0.2 Å. Referring to the product asymptotic energy the error of the SCF result is similar to the error of stationary point II with respect to the reactants. However, measured from the reactant asymptotic energy, the CCSD(T) energy of the exit channel complex is ~4 kcal mol^{-1} higher than the SCF result.

Results of the single-point calculations with the large basis set are given in Table 2. This table also considers the basis set superposition error, which was corrected for by the familiar counterpoise (CP) procedure of Boys and Bernardi [24]. Reference systems for the ion–dipole complexes (I) and (II) are the reactants and products, respectively. Both choices were made at the saddle point and almost identical results were obtained. As is obvious from Table 2, the CP corrections are only on the order of 0.1 kcal mol^{-1} for the ion–dipole complexes. At the saddle point, the CP correction for CCSD(T) is 0.20 kcal mol^{-1} so that a central barrier height of 9.10 kcal mol^{-1} and a relative energy of −2.13 kcal mol^{-1}, with respect to the reactants, results. In many cases, CP corrected and uncorrected energies converge to the same basis set limit from opposite sides. Our crude estimate of the CCSD(T) basis set limit is thus −2.2 ± 0.1 kcal mol^{-1}.

Calculated harmonic vibrational wavenumbers at the five stationary points of reaction (2) are listed in Table 3. The present CCSD(T) results should be accurate to ~10 cm^{-1}. The CCSD(T) values for the harmonic wavenumbers of the totally symmetric modes of the product CH_3Cl are taken from [9]. The harmonic vibrational wavenumbers for the methyl halides are in very good agreement with experimental data [25,26]. The curvature of the barrier, described by the force constant corresponding to the value of the imaginary frequency of the first order saddle point, is larger than the SCF result by 18%. The shape of the barrier is crucial for the dynamics of the reaction as it influences the onset of tunnelling and the shape of resonance states.

The harmonic vibrational wavenumbers from the PP calculations show only very small differences from our best values, the largest deviation being 14 cm^{-1} for the symmetric C–H stretching vibration at the saddle point.

A rather accurate value of the reaction enthalpy of reaction (2) may be obtained from the data of Tables 2 and 3 with a zero-point vibrational energy difference of 0.34 kcal mol^{-1}, as calculated within the

Table 3
Harmonic vibrational wavenumbers (in cm^{-1}) for stationary points of the reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$

Ref.	Stationary Point	Method	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8
[5]	I	SCF	3278	1484	642		3392	1620	1066	
[11]	I	MP2	3115	1356	650		3230	1502	981	
*	I	CCSD(T)/PP	3088	1339	621					
*	I	CCSD(T)	3087	1339	622		3197	1492	972	
[25]	I	exp.	3082	1333	617		3184	1472	974	
[5]	II	SCF	3334	1420	518	94	3471	1595	1032	71
*	II	CCSD(T)/PP	3128	1274	529	103				
*	II	CCSD(T)	3125	1276	531	102	3247	1476	932	76
[5]	III	SCF	3418	1203	172	380 i	3630	1549	974	183
[11]	III	MP2	3218	1033	197	493 i	3421	1418	971	200
*	III	CCSD(T)/PP	3192	1017	186	449 i				
*	III	CCSD(T)	3178	1020	186	450 i	3397	1420	972	185
[5]	IV	SCF	3314	1483	674	70	3438	1610	1099	65
*	IV	CCSD(T)/PP	3114	1346	659	84				
*	IV	CCSD(T)	3113	1338	659	84	3235	1498	1004	75
[5]	V	SCF	3268	1528	774		3374	1627	1130	
[11]	V	MP2	3111	1401	765		3222	1511	1052	
*	V	CCSD(T)/PP	3083	1390	746					
*	V	CCSD(T)	3080	1386	741		3184	1501	1034	
[26]	V	exp.	3088	1396	751		3183	1496	1037	

harmonic approximation, and the CCSD(T) energy difference of -8.53 kcal mol^{-1}. We obtain a reaction enthalpy at 0 K of -8.19 kcal mol^{-1}. Due to the similarity of the molecules CH_3Cl and CH_3Br the difference in mean vibrational energy at 298 K is very small and $\Delta_r H°(298\ K)$ is thus obtained to be -8.15 kcal mol^{-1}. This compares reasonably well with the recommended value of -7.10 kcal mol^{-1} [27].

4. Conclusions

The calculated quantities are sufficient for a statistical (e.g. Rice–Ramsperger–Kassel–Marcus [28] or statistical adiabatic channel model [29]) calculation of the reaction rates. However, in order to assess the reaction by classical or quantum dynamical methods PESs are needed because they provide a reliable description of the whole configuration space. Since the S_N2 system under investigation has 12 degrees of freedom, high level ab initio calculations become very time consuming. For that reason we have decided to restrict ourselves to a four-dimensional PES in the C_{3v} subspace which is currently under construction.

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