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Letter

The saddle point of the nucleophilic substitution reaction Cl^- + CH_3Cl: results of large-scale coupled cluster calculations

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Abstract. On the basis of large-scale coupled cluster calculations including connectedz triple substitutions in a perturbative way, the geometrical parameters of the D_{3h} saddle point of the Walden inversion reaction $Cl^- + CH_3Cl' \rightarrow ClCH_3 + Cl'^-$ are predicted to be R_s (C—Cl) = 2.301 Å and r_s (C—H) = 1.069 Å. The barrier height with respect to the reactants is recommended to be 11.5 ± 1.0 kJ mol^{-1}. Connected triple substitutions lower the barrier height by almost a factor of 2, but have very little influence on the geometric structure of the saddle point.

Key words: S_N2 nucleophilic substitution reactions – Coupled cluster calculations

The nucleophilic substitution (S_N2) reaction $Cl^- + CH_3Cl' \rightarrow ClCH_3 + Cl^{1-}$ is one of the fundamental reactions in physical organic chemistry and has been the subject of numerous experimental and theoretical studies (see Ref. [1] for a review). In a very recent paper by Clary and Palma [2] it has been shown, on the basis of three-dimensional quantum scattering calculations within the rotating bond approximation, that the length of the C—Cl bond R_s at the saddle point has a particularly pronounced effect on the reaction probabilities. It is obvious from Table 1 of Ref. [2] that this quantity is still not too well known from quantum chemistry calculations. Likewise, the height of the barrier with respect to the energy of the reactants has not yet been reliably established to an accuracy of better than 3 kJ mol^{-1}. It is the main purpose of this note to present accurate values for both R_s and the barrier height (BH).

We mainly make use of coupled cluster theory with single and double excitation operators plus a perturbative treatment of the effects of connected triple substitutions by means of the variants CCSD(T) [3] and CCSD-T [4]. All valence electrons are correlated in the calculations which were carried out with the MOLPRO suite of programs [5]. Two different basis sets were employed for the determination of the geometric structure of the saddle point. The first one (basis A) consists of 248 contracted Gaussian-type orbitals (cGTOs) and is the same as used in our previous investigation of the reaction $F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$ [6]. It is comprised of the (*s*, *p*, *d*, *f*) functions of the aug-cc-pVQZ basis of Dunning and coworkers [7–9] for carbon and chlorine. The hydrogen basis consists of the (*s*, *p*) part from the aug-cc-pVTZ basis augmented by the set of *d* functions from the cc-pVTZ basis. Since the hydrogen atoms act mainly as spectators in the reaction and have essentially no hydride character the use of a smaller basis set for them appears to be justified. The larger basis set (basis B) comprises 367 cGTOs and may be briefly described as *spdfg* (av5z) for chlorine, *spdfg* (v5z) for carbon and *spd* (vqz) for hydrogen, where obvious abbreviations are employed to designate the basis sets.

The saddle point of the S_N2 reaction studied has D_{3h} symmetry and is thus characterized by the C—Cl distance (R_s) and the C-H distance (r_s). Their calculated values are listed in Table 1, which also includes total energies, BHs with respect to the energy of the reactants and harmonic wavenumbers of the two totally symmetric vibrations.

As is usually observed, the results of the CCSD-T and CCSD(T) calculations are very similar. CCSD(T) calculations with the larger basis set yield R_s = 2.3071 Å. Owing mainly to the neglect of core-valence and core-core correlation effects, this value appears to be slightly too long. The same sort of calculations for CH_3Cl yields R_e (C—Cl) = 1.7821 Å, r_e (C—H) = 1.0853 Å, and β_e (H—C—Cl) = 108.43°, which can be compared with our recommended equilibrium geometry values [6] of 1.7762 Å, 1.0836 Å and 108.58°. Assuming the same error to hold for the CCSD(T) value of the C-Cl distance at the saddle point, we arrive at R_s = 2.301 Å. The same result is obtained when the data from the smaller basis set are employed. The present calculations thus give support to a modification of the potential energy surface of Vande Linde and Hase [10] as made by Clary and Palma [2] who obtained R_s = 2.30 Å. The CCSD(T) values for r_e of CH_3Cl are too long by 0.0024 Å (basis A [6]) and 0.0017 Å (basis B). We therefore recommend r_s = 1.069 Å. This value is shorter than the r_e value for CH_3Cl [6] by 0.015 Å. For comparison, the r_e values for CH_3, CH_4, and CH_3^+ are 1.076 Å [11], 1.086 Å [12] and 1.0876 Å [13], respectively.

According to the present calculations, connected triple substitutions have almost no influence on the geometrical parameters at the saddle point. Second-order Møller-Plesset perturbation theory (MP2) underestimates R_s by 0.020 Å (basis A) and 0.024 Å (basis B) and yields an excellent value for r_s. The self-consistent field (SCF) approach (basis B) overestimates R_s by 0.079 Å and underestimates r_s by 0.010 Å.

As is well known, BH with respect to the reactants is rather low [1, 10, 14–21]. CCSD(T) calculations with basis B yield 11.1 kJ mol^{-1} (see Table 1) and a slightly higher value of 11.6 kJ mol^{-1} is obtained by CCSD-T. Compared to CCSD-T or CCSD(T), the present SCF calculations overestimate BH by a factor of 3. Connected triple substitutions make a substantial contribution of −10 kJ mol^{-1}, i.e. they lower BH. MP2 performs remarkably well and overestimates BH by only 5–6 kJ mol^{-1}.

Harmonic vibrational wavenumbers for the totally symmetric vibrations ω_1 (symmetric C—H stretch) and ω_2 (symmetric C—Cl stretch) are listed in the last two columns of Table 1. Almost identical results are obtained with the two basis sets. According to the author's experience, the values calculated by CCSD(T)/basis B should be accurate to about 5 cm^{-1} for ω_1 and to about 2 cm^{-1} for ω_2. Compared to CH_3Cl [6], ω_1 is larger by as much as 288 cm^{-1}, or 9.4%. The large increase in the C—H stretching vibrational wavenumbers makes a substantial contribution to kinetic H/D isotope effects [17, 22].

Further basis set studies have been made in the form of single point calculations carried out with the recommended structures for the saddle point and CH_3Cl. The results are given in Table 2, which also includes values which were corrected for the basis set superposition error by means of the familiar counterpoise (CP) procedure of Boys and Bernardi [23]. This requires calculations for CH_3Cl and Cl^- with the full basis set of the complex and the geometrical parameters of the saddle point. In addition, CH_3Cl in its own basis has to be calculated with a distorted geometry corresponding to the saddle point. At the SCF level, the CP corrections are negligibly small for all basis sets employed. Beyond the Hartree-Fock approximation, the CP corrections are significantly larger for Cl^- compared to CH_3Cl. For example, at the CCSD(T) level the 377 cGTO basis yields a CP correction of 0.4 kJ mol^{-1} for CH_3Cl and a correction of 1.3 kJ mol^{-1} for Cl^-. This indicates that those basis set parts describing the CH_3 portion of the CH_3Cl molecule are not far from saturation. For the two largest basis sets employed (421 and 422 cGTOs) the CP corrections were not calculated but are estimated to be close to 1.0 kJ mol^{-1}. For sufficiently large basis sets, CP corrected and CP uncorrected values tend to converge to the same limit from above and below, respectively. We are thus tempted to recommend a BH of 11.5 ± 1.0 kJ mol^{-1}. Together with the accurate

Table 1. Saddle point properties

Method	Basis[a]	R_s (Å)	r_s (Å)	V_s (+959 E_h)	BH (kJ mol^{-1})	ω_1 (cm^{-1})	ω_2 (cm^{-1})
SCF	A	2.3811	1.0595	0.281125	30.4	3546.4	208.5
	B	2.3801	1.0590	0.279023	32.0	3545.9	208.5
MP2	A	2.2813	1.0690	−0.324988	15.7	3398.3	237.6
	B	2.2774	1.0680	−0.364923	16.8	3399.4	238.2
CCSD	A	2.3125	1.0690	−0.366496	19.9	3399.0	227.1
	B	2.3090	1.0680	−0.402706	21.2	3399.9	227.8
CCSD-T	A	2.3106	1.0713	−0.397130	10.4	3369.8	227.4
	B	2.3063	1.0702	−0.435863	11.6	3370.3	228.4
CCSD(T)	A	2.3116	1.0714	−0.397475	9.9	3368.3	226.7
	B	2.3071	1.0704	−0.436160	11.1	3368.9	227.8

[a] Basis A: 248 cGTOs; basis B: 367 cGTOs.

Table 2. Barrier heights (in kJ mol^{-1}) from single point calculations[a]

Method	302 CGTO[b]	367 CGTO[c]	377 CGTO[d]	421 CGTO[e]	422 CGTO[f]
SCF	34.9 (35.0)	36.2 (36.2)	36.2 (36.3)	36.2	36.2
MP2	14.9 (17.7)	16.8 (18.8)	16.2 (18.6)	15.4	16.2
CCSD	19.3 (21.2)	21.2 (22.4)	20.8 (22.4)	20.5	21.1
CCSD-T	9.7 (11.8)	11.6 (13.1)	11.1 (12.8)	10.7	11.2
CCSD(T)	9.2 (11.3)	11.1 (12.6)	10.6 (12.3)	10.2	10.7

[a] All calculations are carried out with the saddle point geometry recommended in this work (R_s = 2.301 Å and r_s = 1.069 Å) and the equilibrium geometry for CH_3Cl recommended in Ref. [6]. Counterpoise corrected values are given in parentheses

[b] *spdfg* (avqz) for chlorine and carbon and *sp* (avtz) plus *d* (vtz) for hydrogen

[c] *spdfg* (av5z) for chlorine, *spdfg* (v5z) for carbon and *spd* (vqz) for hydrogen

[d] *spdfg* (av5z) for carbon and chlorine, *sp* (avtz) plus *d* (vtz) for hydrogen

[e] *spdfgh* (av5z) for chlorine, *spdfg* (av5z) for carbon and *sp* (avtz) plus *d* (vtz) for hydrogen

[f] *spdfgh* (av5z) for chlorine, *spdfgh* (v5z) for carbon and *spd* (vqz) for hydrogen

geometrical parameters for the saddle point given earlier in this paper this value should form a reference value for the construction of accurate multidimensional potential energy surfaces for the title reaction. Work along these lines is in progress.

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