Origin of Anomalous Kinetic Parameters in Carbene 1,2-Shifts by Direct Dynamics

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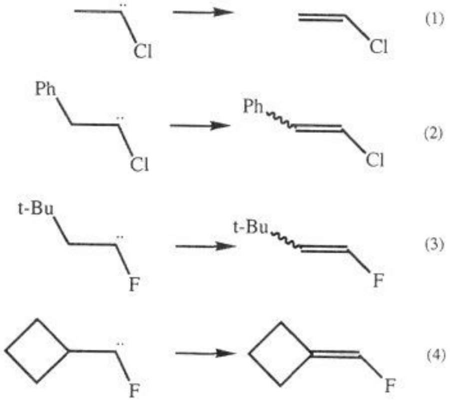
Systematic discrepancies have been found between experimental and calculated activation parameters for the hydrogen 1,2-shifts in singlet carbenes shown in eq 1–4. For the reaction



of methylchlorocarbene (1), experimental activation parameters $E_a = 4.9$ kcal/mol and $\Delta S^{\ddagger} = -16.7$ eu have been measured;[1] theoretical results at the MP4/6-311G**//MP2/6-31G* level are $\Delta E^{\ddagger} + \Delta ZPE = 11.5$ kcal/mol and $\Delta S^{\ddagger} = -3.1$ eu.[2] Experimental results for other carbenes are similar: benzylchlorocarbene (2) has $E_a = 4.9$ kcal/mol and $\Delta S^{\ddagger} = -10.6$ eu;[3] neopentylfluorocarbene (3) has $E_a = 3.3$ kcal/mol and $\Delta S^{\ddagger} = -19.8$ eu; and cyclobutylfluorocarbene (4) has $E_a = 3.8$ kcal/mol and $\Delta S^{\ddagger} = -21.6$ eu.[4] The experimental activation energies are very low, but the more surprising observation is the large negative entropy of activation. A single internal degree of rotational freedom is lost upon converting reactant to product, and a small negative activation entropy is expected. There have been several hypotheses offered to explain the source of the large negative entropy of activation. These include variational effects along the reaction path, hydrogen tunneling, and transition-state solvation effects.[1,5–7]

We have performed a dynamics calculation on the 1,2-shift of hydrogen in methylchlorocarbene. The direct dynamics procedure is that employed in the POLYRATE code of Truhlar *et al.*[8] A minimum energy reaction path in the region of the transition structure for the 1,2-shift was generated at the MP2/6-31G* level of theory.[9–12] The Page–McIver local quadratic approximation was employed to generate points along the intrinsic reaction path.[13] Energies, gradients, and second derivatives were evaluated at each point, and these were used with canonical variational transition-state theory (CVT) to calculate rate constants and isotope effects.

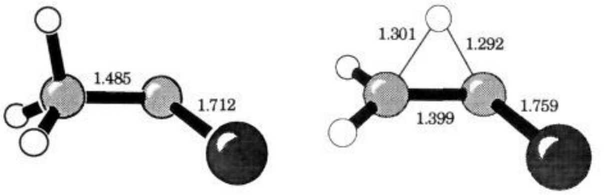


Figure 1. Methylchlorocarbene and transition structure for the 1,2-shift of hydrogen at the MP2/6-31G* level.[14]

The reactant and transition structure at the MP2/6-31G* level are shown with geometrical parameters in Figure 1.[14] The saddle point has the migrating hydrogen roughly symmetrically disposed between the carbons involved in the 1,2-shift. A similar transition structure has been reported for the vinylidene–ethylene rearrangement.[15,16]

Canonical variational transition-state theory[17,18] permits location of the point on the potential surface which corresponds to minimum reaction rate, which is the free energy maximum. For the 1,2-shift studied here, CVT predicts an insignificant shift of the saddle point from its position on the potential energy surface. That is, there is no significant variational effect on the location of the transition state in this 1,2-hydrogen shift. The effects of temperature and isotopic substitution were also investigated and were found to be insignificant. Therefore, canonical variational transition-state theory does not correct the discrepancies between calculated and experimental activation parameters.

Reaction rates with tunneling corrections were calculated with the centrifugal-dominant, small curvature, semiclassical, adiabatic, ground-state (CD-SCSAG) method.[19] The TST/CVT and CD-SCSCAG rate constants are compared with those from experiment in Table I. The tunneling correction increases the rate constant by 1 order of magnitude near room temperature. The rate enhancement due to tunneling reduces the effective activation energy and brings the calculated and experimental entropies of activation into much closer agreement. For the 1,2-hydrogen shift of methylchlorocarbene, the theoretical $\Delta S^{\ddagger}$ changes from −3.1 eu when calculated with use of TST/CVT to −14.9 eu with use of TST/CD-SCSAG (Table I). There is still a discrepancy between the experimental and calculated activation energies, but this may be due to remaining theoretical error as well as the solvation effects on experimental rates.

The experimental deuterium kinetic isotope effect at 294 K for the 1,2-hydrogen shift is small, $k_{H_3}/k_{D_3} = 1.4$,[5] especially for a reaction dominated by tunneling. The calculated primary isotope effect is about 3.0 from transition-state theory in the experimental temperature range. After the inclusion of the semiclassical, adiabatic, ground-state (MEPSAG)[20] tunneling correction, the primary kinetic isotope effect is reduced to $k_{H_3}/k_{D_3} = 2.6$.

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Table I. Experimental and Theoretical Reaction Rates and Activation Parameters for the 1,2-Shift of Hydrogen in Methylchlorocarbene (all results at $T = 298$ K)

	experiment[a]	CVT	CD-SCSAG[b]
k (s^{-1})	1.36×10^6	1.7×10^5	1.35×10^6
E_a (kcal/mol)	4.9 ± 0.5	10.9[c]	7.7
$\Delta S^\ddagger$ (eu)	−16.1	−3.2[d]	−14.9[e]
k_{H_3}/k_{D_3}	1.43[f]	2.9	2.6[g]

[a] Reference 1. [b] Transition-state theory rate constant with the centrifugal-dominant, small curvature, semiclassical, adiabatic, ground-state tunneling correction. [c] $\Delta E^\ddagger = 12.6$ kcal/mol + ΔZPE(MP2/6-31G*). [d] $\Delta S^\ddagger$ from partition functions for the reactant and the conventional transition state. [e] $\Delta S^\ddagger$ derived from the Arrhenius intercepts of CD-SCSAG rate constants at 300 and 302 K. [f] Reference 5. [g] MEPSAG isotope effect.

Remarkably, the isotope effect is smaller with inclusion of the tunnel correction, because the tunnel correction for deuterium is larger in this reaction than that for hydrogen. The tunneling corrections at 300 K for 1,2-shift are $k_H = 5.63$ and $k_D = 6.08$. This unusual effect was also noted in a theoretical study of the intramolecular proton transfer in the hydrogen oxalate anion.[21] The experimental value of k_{H_3}/k_{D_3} increases from 1.06 at 273 K to 1.84 at 343 K.[5] This unusual increase of the isotope effect with temperature is also found in theory: at the MEPSAG level, k_{H_3}/k_{D_3} increases from 2.91 to 3.06 from 100 to 200 K. Above 200 K, the classical rate exceeds that due to tunneling, and the isotope effect decreases with increasing temperature. This will be discussed in detail in a full paper.

Entropies of activation for several 1,2-shifts of carbon are in the range of $\Delta S^\ddagger = -20$ to -24 eu.[4,6,22] These entropies of activation are large and negative, like these for 1,2-shifts of hydrogen. Is heavy-atom tunneling involved? A preliminary investigation of this possibility was carried out by replacing the mass of hydrogen with that of CH_2 in the dynamics calculation. Comparison between TST and TST/MEPSAG rate constants indicated a rate enhancement of a factor of 8 at 300 K, suggesting that heavy atom tunneling may be important in 1,2-shifts involving heavy atoms as well.

The mechanism of the 1,2-shift of hydrogen in methylchlorocarbene is dominated by the tunnel effect. Experimental activation parameters, the small kinetic isotope effects, and trends in temperature dependence of the experimental kinetic isotope effects are reproduced satisfactorily by theory. Details of these comparisons and the potential energy surface will be presented in a full account of this work.

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