

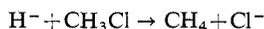
Theoretical Study of the $\text{H}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ Reaction

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Abstract

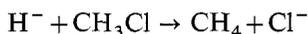
A theoretical study of the C_{3v} reaction path of the



$\text{S}_{\text{N}}2$ reaction with the use of the GAUSSIAN 70 program reveals an earlier departure of the leaving group than in other *ab initio* studies of similar reactions involving poorer leaving groups, and predicts an intermediate planar structure that is highly ionic and which should be represented as a tight ion triplet, $\text{H}^-[\text{CH}_3^+]\text{Cl}^-$.

Introduction

Recent *ab initio* theoretical investigations of $\text{S}_{\text{N}}2$ reactions have largely been restricted to anionic attack on singly substituted methanes, where the attacking and leaving groups have been H^- , F^- , or CN^- .¹⁻⁵ Among the common conclusions drawn from these studies are that the departure of the leaving group is delayed until the attacking group is nearly at its transition state position and that the transition state is highly ionic. We now present the results of LCAO-MO computations on the



$\text{S}_{\text{N}}2$ reaction, using the GAUSSIAN 70 program,⁶ which reveal for the first time interesting differences between this reaction and the corresponding reaction of methyl fluoride.²

Method

Optimized energies and geometries at several points along the C_{3v} reaction path, involving backside attack by the hydride ion, were calculated after allowing all parameters to be varied except the C-H bond length, which was held constant at 2.01 a.u.,

¹ Duke, A. J., and Bader, R. F. W., *Chem. Phys. Lett.*, 1971, **10**, 631.

² Dedieu, A., and Veillard, A., *J. Am. Chem. Soc.*, 1972, **94**, 6730.

³ Keil, F., and Ahlrichs, R., *J. Am. Chem. Soc.*, 1976, **98**, 4787.

⁴ Schlegel, H. B., Mislow, K., Bernardi, F., and Bottoni, A., *Theor. Chim. Acta*, 1977, **44**, 245.

⁵ Bader, R. F. W., and Gangi, R. A., 'Ab Initio Calculation of Potential Energy Surfaces' in 'Theoretical Chemistry' (Eds R. N. Dixon and C. Thomson) Vol. 2 (The Chemical Society: London 1975).

⁶ Hehre, W. J., Lathan, W. A., Ditchfield, R., Newton, M. D., and Pople, J. A., Gaussian 70 Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

a value found not to vary significantly in other *ab initio* calculations.^{2,3} The reaction path was initially investigated with the STO-3G basis set, and then at selected points with the 4-31G basis set using the STO-3G HCH angles.

Table 1. Features of the $\text{H}^- + \text{CH}_3\text{Cl} \rightarrow \text{CH}_4 + \text{Cl}^-$ S_N2 reaction

Energy in hartrees (1 hartree = 2625.5 kJ mol⁻¹), distances in Å, angles in degrees; values in parentheses obtained with 4-31G basis set, other values obtained with STO-3G basis set. $\angle\text{HCH}$ is of the methyl group; δ is for charges on the designated atoms

$R_{\text{C-H}}$	Energy	$R_{\text{C-Cl}}$	$\angle\text{HCH}$	δ_{H}	δ_{C}	δ_{Cl}
∞	-493.88050 (-498.96198)	1.809 (1.866)	109.83	-1 (-1)	-0.119 (-0.504)	-0.174 (-0.141)
4.2334	-493.89068	1.820	109.75	-0.999	-0.107	-0.222
2.646	-493.91378 (-498.99979)	1.927 (2.028)	110.60	-0.834 (-0.838)	-0.073 (-0.348)	-0.378 (-0.431)
2.300	-493.93090 (-499.00731)	2.073 (2.150)	114.31	-0.673 (-0.747)	-0.042 (-0.282)	-0.530 (-0.566)
2.220	-493.93831 (-499.01251)	2.140 (2.300)	117.70	-0.603 (-0.676)	-0.029 (-0.243)	-0.607 (-0.675)
2.100	-493.95524 (-499.02386)	2.330 (2.540)	119.96	-0.456 (-0.547)	-0.028 (-0.228)	-0.751 (-0.812)
1.958	-493.99203 (-499.04285)	2.907 (3.005)	114.62	-0.205 (-0.325)	-0.083 (-0.308)	-0.955 (-0.928)
1.852	-494.02022	3.094	113.31	-0.156	-0.102	-0.980

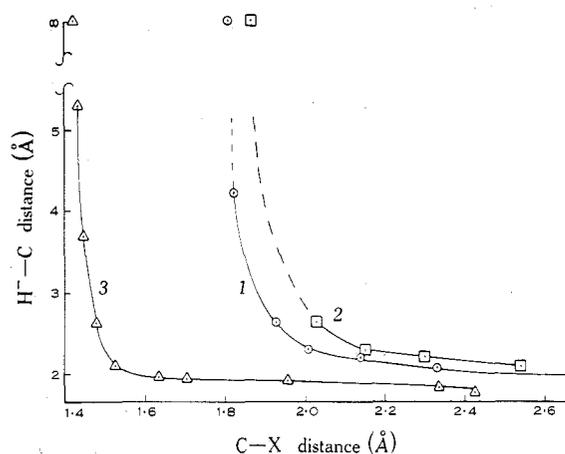


Fig. 1. Comparison of the effect of the leaving group (halide ion) on the stretching of the carbon-halogen (C-X) bond during the S_N2 reaction of H^- with CH_3Cl (curves 1 and 2) and CH_3F (curve 3). Curve 1 was computed with the STO-3G basis set, curve 2 with the 4-31G basis set, and curve 3 was drawn by using the results of ref. 2 obtained with a large spd basis set.

Results and Discussion

Our results (Table 1) reveal that the C-Cl bond begins to stretch well before the inversion of carbon occurs. The departure of the leaving group is earlier than that reported in the reaction of methyl fluoride with the same nucleophile² (Fig. 1). Thus, at a distance of 2.646 Å from the carbon atom, the approach of the hydride ion to methyl chloride leads to a stretching of the C-Cl bond by 0.12 Å with the STO-3G basis set, a stretch twice that encountered at the same distance for the C-F bond. The

4-31G basis set indicates an even greater degree of stretching of the C-Cl bond. In this reaction of methyl fluoride as well as the one involving attack by F^- , Dedieu and Veillard² emphasize the late departure of the leaving group as a salient conclusion of their studies. Our finding of an earlier departure of chlorine is very probably a consequence of the higher polarizability of the C-Cl bond and suggests that greater bond length distortions at larger incoming nucleophile-carbon distances might well be the rule for good leaving groups than poorer leaving groups. Keil and Ahlrichs³ have studied the energetics and transition state of the $H^- + CH_3Cl$ reaction, but they do not analyse the stretching of the C-Cl bond at various stages of the reaction. In their higher level study involving the coupled electron pair approximation, the total energy along the entire reaction path is always lower than that of the reactants, a feature also reproduced in our work; however, a local barrier at the transition state encountered by them is missing in our study, and is undoubtedly the result of differences in the basis sets employed.

The HCH bond angle (of the methyl group) does not increase steadily in the present investigation but rather decreases initially before it reaches a maximum value of about 120° , a phenomenon also noted and explained by Dedieu and Veillard² in the corresponding S_N2 reaction of methyl fluoride.

The charges on the atoms listed in Table 1 correlate well with the early departure of the leaving group, the negative charge on chlorine increasing steadily. However, when the incoming nucleophile is at a distance of 2.100 \AA , there is still a substantial negative charge on the nucleophile (about 0.5 unit), which indicates a high degree of ionic character of this intermediate state characterized by a planar methyl group. Because these charges are greater with the 4-31G basis set than with the STO-3G basis set, it appears that better basis sets are not likely to reduce the high degree of charge. While this intermediate may not be a true 'transition state', it might well be viewed as a tight 'ion triplet', $H^-[CH_3]^+Cl^-$. The fact that similar ionic transition states have been postulated in reactions of methyl fluoride² involving a more electronegative⁷ leaving group suggests that the ionicity is not solely dependent on electronegativity.

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⁷ Pauling, L., 'The Nature of the Chemical Bond' p. 90 (Cornell University Press: Ithaca, N.Y., 1960); Simons, G., Zandler, M. E., and Talaty, E. R., *J. Am. Chem. Soc.*, 1976, **98**, 7869.