MINDO Forces Study of the Uncatalysed and Acid-Catalysed Friedel-Crafts Reactions Between CH_3F and CH_4

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MINDO-forces calculations have been performed on the uncatalysed and acid-catalysed Friedel-Crafts reaction between CH_3F and CH_4. It has been found that the catalysed reaction is exothermic, spontaneous and has a smaller potential-energy barrier than the uncatalysed reaction. The mechanisms for uncatalysed and catalysed reactions are discussed.

Key words: Melting; Liquid Structure; Molecular Liquids

The Friedel-Crafts reaction is one of the most important catalytic processes in organic chemistry [1–3]. There has been considerable experimental [4–12] and theoretical [13–18] interest in this reaction. It has previously been shown that catalysts diminish the potential-energy barrier for the process between CH_3F and CH_4 [18]. The present paper aims at giving more theoretical insight in to this process.

This paper refers to the geometry, heat of formation, electron density, and entropy of uncatalysed and catalysed Friedel-Crafts reactions between CH_3F and CH_4 from calculations by the MINDO-Forces MO method [19], whereby the molecular energy of CH_3F and CH_4 obtained from the semiempirical MINDO/3 MO [20] was completely minimized according to the Murtagh-Sargent technique [21].

The derivative of the energy was calculated according to Pulay's method [22]. The program allows variation of the β parameter with geometrical change in a consistent way. A full description of the program and its application is given in [19a].

Results and Discussion

Uncatalysed Reaction

The methyl fluoride molecule approaches the methane molecule along the x-axis in the xy-plane (Figure 1).

For the calculation, the initial geometrical parameters are chosen for the point $R = 4$ Å on the reaction path. R is held constant during the minimization procedure, while the other geometrical parameters are completely optimized. The calculation for the other points along the reaction coordinate is initiated by a new choice of R. The results are tabulated in Table 1. The numbering of the atoms is shown in Figure 1.

The path for this reaction is obtained by plotting the values of the heat of formation against R, as shown in Figure 2. ΔH_f decreases to an intermediate at $R = 2.9$ Å, then passes a transition state at $R = 2.1$ Å and finally decreases towards the product at $R = 2.0$ Å.

Inspection of the geometrical parameters along the reaction path (Table 1) shows that the C2-F bond length increases up to 1.40 Å at $R = 2.9$ Å, then decreases to 1.346 Å at $R = 2.2$ Å, and finally increases to 1.420 Å.

Also the C1-H bond length increases along the reaction path, while the H-F bond length decreases and finally forms a bond distance 0.936 Å at $R = 2.0$ Å. Therefore the probability of formation of HF and C_6H_6 occurs at $R = 2.0$ Å.

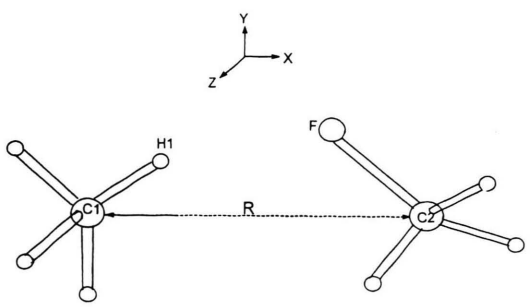

Fig. 1. Coordinates for uncatalysed reaction between CH_4 and CH_3F.

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Table 1. The heat of formation ΔH_f (in kcal/mole) and the distances (in Å) for the uncatalysed reaction.

C1-C2 = R	ΔH_f	C2-F	C1-H1	H1-F
4.0	–63.099	1.372	1.102	2.551
3.8	–63.047	1.373	1.103	2.342
3.6	–63.406	1.375	1.105	2.092
3.5	–88.406	1.423	1.138	1.132
3.4	–90.515	1.421	1.138	1.114
3.2	–94.267	1.420	1.144	1.097
3.1	–96.283	1.413	1.148	1.087
3.0	–96.533	1.407	1.154	1.082
2.9	–96.584	1.409	1.161	1.073
2.8	–96.383	1.382	1.170	1.061
2.7	–94.436	1.373	1.181	1.051
2.6	–91.214	1.365	1.192	1.041
2.4	–83.791	1.350	1.229	1.016
2.3	–78.922	1.347	1.255	1.003
2.25	–75.392	1.347	1.265	0.998
2.2	–72.764	1.346	1.290	0.988
2.15	–70.707	1.349	1.326	0.977
2.1	–67.970	1.354	1.363	0.968
2.05	–79.278	1.412	2.095	0.937
2.0	–80.216	1.420	2.138	0.936

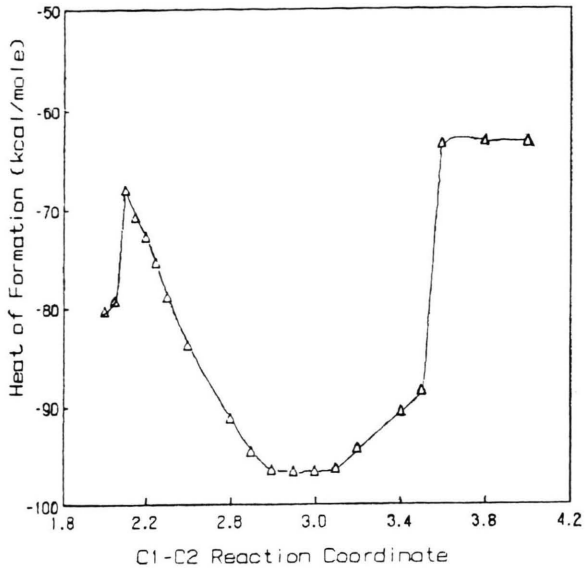


Fig. 2. Reaction path between CH_3F and CH_4.

The alkylation reaction involves formation of C1-C2 and H-F bonds, while the bonds C1-H and C2-F are broken. At the transition state, the interatomic distance between C1 and C2 (2.1 Å) is still greater than that corresponding to ethane (1.540 Å), but it is smaller than that obtained by Branchadell et al. [18] (C1-C2 = 2.283 Å). The present calculation also shows that the HF bond length at the transition state (R = 2.1 Å) has reached 0.968 Å, in better agreement than previous results [18] (1.496 Å).

Figure 3 is a contour map of the heat of formation, illustrating that the reaction is endothermic, in agreement with Branchadell et al. [18]. The calculated activation energy for this reaction is 28.618 kcal/mole, while the reaction enthalpy is 16.370 kcal/mole. The change in entropy is 0.479 cal/deg · mole. From the calculated enthalpy and entropy changes, the Gibbs free energy change is calculated to be 16.227 kcal/mole, i.e. the reaction is non-spontaneous.

Also the electron density along the reaction path was calculated (Table 2) showing that the electron density on C2 increases as it approaches C1, and at the same time the fluorine atom density decreases along the reaction path. The electron densities on C1 and C2 are almost equal at R = 2.0 Å, which indicates the formation of C_6H_6.

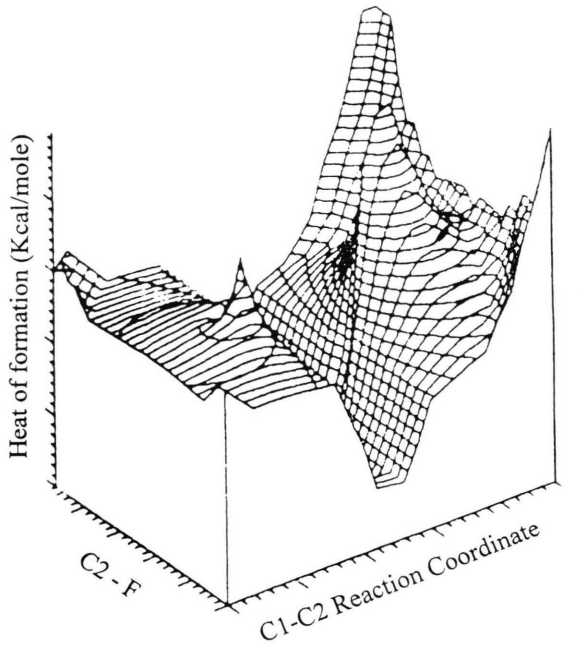


Fig. 3. A contour map of the uncatalysed reaction.

Catalysed Reaction

The CH_3FH^+ approaches CH_4 along the X-axis in the XY-plane, as in case of the uncatalysed reaction (Figure 4). The initial geometrical parameters are chosen for R = 4.0 Å on the reaction path. R is held constant during the minimization procedure, while the other geometrical parameters are completely optimized. The calculation for other points along the reaction coordinate is initiated by a new choice of R. The results are listed in

Table 2. Variation of the electron densities along the uncatalysed reaction path.

C1-C2 = *R*	C1	C2	F
4.0	3.965	3.482	7.326
3.8	3.967	3.483	7.325
3.6	3.970	3.489	7.327
3.5	3.968	3.678	7.262
3.4	3.960	3.696	7.251
3.2	3.937	3.730	7.229
3.1	3.923	3.746	7.215
3.0	3.908	3.756	7.206
2.9	3.892	3.764	7.196
2.8	3.872	3.773	7.184
2.7	3.856	3.777	7.176
2.6	3.841	3.779	7.171
2.4	3.805	3.787	7.158
2.3	3.787	3.791	7.154
2.25	3.781	3.790	7.156
2.2	3.770	3.796	7.150
2.15	3.759	3.805	7.143
2.1	3.749	3.812	7.138
2.05	3.835	3.872	7.009
2.0	3.828	3.857	7.029

Table 3. The heat of formation ΔH_f (in kcal/mole) and the distances (in Å) for the acid-catalysed reaction.

C1-C2 = *R*	ΔH_f	C2-F	C1-H1	H-F
4.0	114.044	1.439	1.135	2.203
3.8	114.774	1.435	1.140	2.088
3.6	116.152	1.425	1.140	2.030
3.4	118.151	1.418	1.141	2.004
3.2	120.179	1.428	1.130	1.996
3.0	123.168	1.427	1.122	2.035
2.95	71.137	1.608	1.223	1.007
2.9	71.169	1.591	1.224	1.007
2.85	71.452	1.575	1.225	1.007

Table 3. The numbering of the atoms is shown in Figure 4.

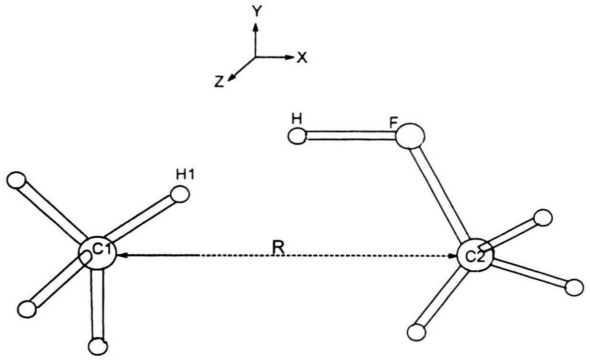


Fig. 4. Coordinates for acid catalysed reaction between CH_4 and CH_3FH^+.

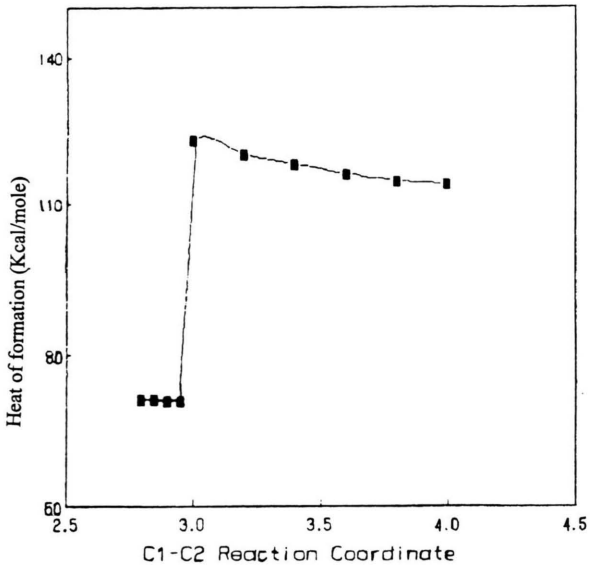


Fig. 5. Reaction path between CH_3FH^+ and CH_4.

The path for this reaction is obtained by plotting the heat of formation against *R*, as shown in Figure 5. It goes through a transition state at $R = 3.0$ Å and proceeds towards the product at $R = 2.95$ Å, i.e. it represents the probability of formation of C_2H_6 and H_2F^+.

Inspection of the geometrical parameters along the reaction path (Table 3) shows that the C2-F bond length decreases slightly till $R = 3.0$ Å (transition state), and then increases at $R = 2.9$ Å, the C1-H1 bond length increases along the reaction path, while the H-F distance decreases along the reaction path, which may represents the probability of H_2F^+ formation. It can be seen from Table 3, that the geometry of the transition state is closer to the reactants than the products, i.e. the reaction is exothermic. This result is in agreement with Hammond's suggestion [23, 24] that, in a highly exothermic reaction, the transition state should resemble the reactants.

The calculated activation energy for this reaction is 9.121 kcal/mole, which indicates that the catalyst diminishes the potential energy barrier of the process as compared to the uncatalysed one (28.618 kcal/mole). The reaction enthalpy for this reaction is –42.909 kcal/mole, i.e. the reaction is exothermic. The change in entropy is –6.356 cal/mole · deg. From the calculated enthalpy and entropy change, the Gibbs free energy change is calculated to be –41.012 kcal/mole, i.e. the reaction is spontaneous.

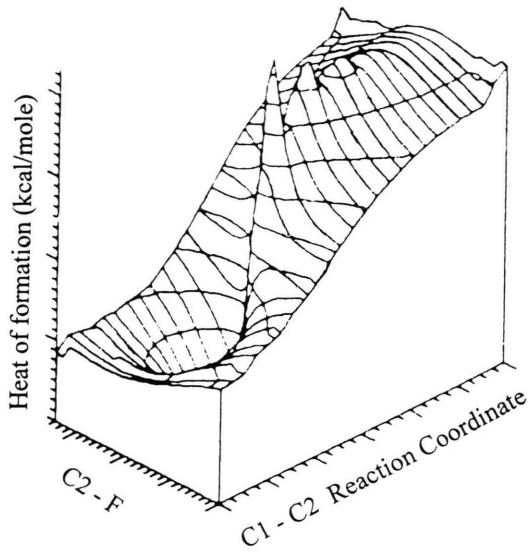


Fig. 6. A contour map for the catalysed reaction.

Table 4. Variation of the electron densities along the acid-catalysed reaction path.

C1-C2 = *R*	C1	C2	F	H1	H
4.0	3.907	3.449	7.300	1.104	0.518
3.8	3.896	3.445	7.318	1.092	0.512
3.6	3.901	3.461	7.324	1.074	0.514
3.4	3.918	3.467	7.332	1.046	0.517
3.2	3.917	3.461	7.284	1.104	0.513
3.0	3.917	3.461	7.256	1.103	0.526
2.95	3.888	3.878	7.024	0.802	0.789
2.9	3.889	3.878	7.023	0.802	0.786
2.85	3.891	3.875	7.022	0.802	0.782
2.8	2.888	3.878	7.020	0.798	0.784

In Fig. 6 a contour map is shown between the heats of formation (in the Z-plane), the formation of the C1-C2 bond (in the *X*-plane), and the break of the C2-F bond (in the Y-plane). Figure 6 illustrates that the reaction is exothermic.

Also the electron density along the reaction path was calculated (Table 4). It can be seen that the electron density on C2 increases along the reaction coordinate while that on C1 decreases slightly; and that at the transition state (R = 2.95 Å) these electron densities are almost equal. The electron densities on F and H1 decrease along the reaction coordinate, while that on H increases. At R = 2.95 Å the electron densities on H1 and H are almost equal, which may indicate the formation of H_2F^+.

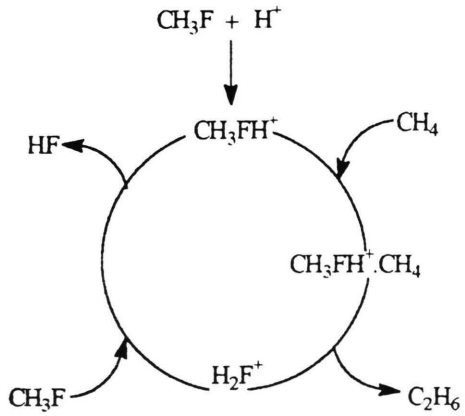
The suggested mechanism is represented in Scheme 1, which involves the formation of the complex $CH_3FH^+ \cdot CH_4$ and dissociation into ethane and protonated hydrogen fluoride.

$$CH_3FH^+ + CH_4 \rightarrow CH_3FH^+ \cdot CH_4 \downarrow C_2H_6 + H_2F^+ \downarrow HF + H^+$$

Scheme 1

This mechanism is different from that suggested in [18] because we have chosen the same model for both reactions, i.e. the reactions proceed in the *XY*-plane, while two different models were considered in [18].

The mechanism for the whole process is given in Scheme 2, in wich protonated methyl fluoride attacks methane to yield $CH_3FH^+ \cdot CH_4$. This complex dissociates into C_2H_6 and H_2F^+. Finally this H_2F^+ transfers its proton to a new methyl fluoride molecule to give HF and CH_3FH^+.



Scheme 2

Conclusion

It is found that the catalysed reaction has a smaller energy barrier than the uncatalysed one. Also, the entropy at the transition state for the catalysed reaction (45.1 cal/deg · mole) is greater then that for uncatalysed reaction (42.2 cal/deg · mole), which indicates that the complex at the transition state for the catalysed reaction is more free to move or more loose to proceed faster to the product as compared to the uncatalysed reaction. Also, it is found that the catalysed reaction is exothermic, spontaneous and takes place through a multistep mechanism.

These calculations were performed for the gas phase and differ for solutions due to presence of charged structures. But our calculations may be helpful for the understanding of the general trends of acid catalysis in Friedel-Crafts reactions.

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