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MINDO/2 Calculations on the Reaction of Methyl Radicals with Ethylene and Butadiene

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Semiempirical calculations using the MINDO/2 procedure have been carried out on the potential surface for the reaction of a methyl radical with ethylene and *trans*-butadiene. The transition state is predicted to be reactant-like in character and no evidence of resonance stabilization of the activated complex is found for butadiene. It is conjectured that the experimentally observed lowering of the activation energy for butadiene relative to ethylene may be attributed to differential correlation effects.

Introduction

The addition of methyl radicals to unsaturated substrates has been experitally studied both in the gas phase [1–5] and in solution [6]. Little theoretical work has been carried out on such reactions, outside of relating observed reaction rates to empirical reactivity indices [7] and a semiempirical calculation by Basilevsky and Chlenov [8], using π-electron theory with corrections for changes in hybridization. It is interesting that, in spite of severe approximations, the latter study predicts an excellent value for the activation energy for the addition of a methyl radical to ethylene.

The theoretical approaches taken to date yield little reliable information concerning the details of the potential surface, the geometry and electron distribution of the transition state, and the effects of substituents on these quantities. We have, therefore, undertaken initial studies on the reaction of methyl radicals with ethylene and *trans*-butadiene using an all-valence electron semiempirical method in order to begin to develop an understanding of the factors which appear important in determining the potential surface and activation energy for radical-molecule addition reactions.

Calculations

All calculations were carried out using Dewar's MINDO/2 method [9, 10] with the parameterization given in the second paper [10]. This formulation was chosen since it appears to be the best technique available at the present time for calculations of this kind. It has been parameterized to directly yield good values for heats of formation, geometric variables, and force constants for bond stretches. The method consistently predicts C–H equilibrium distances which are about

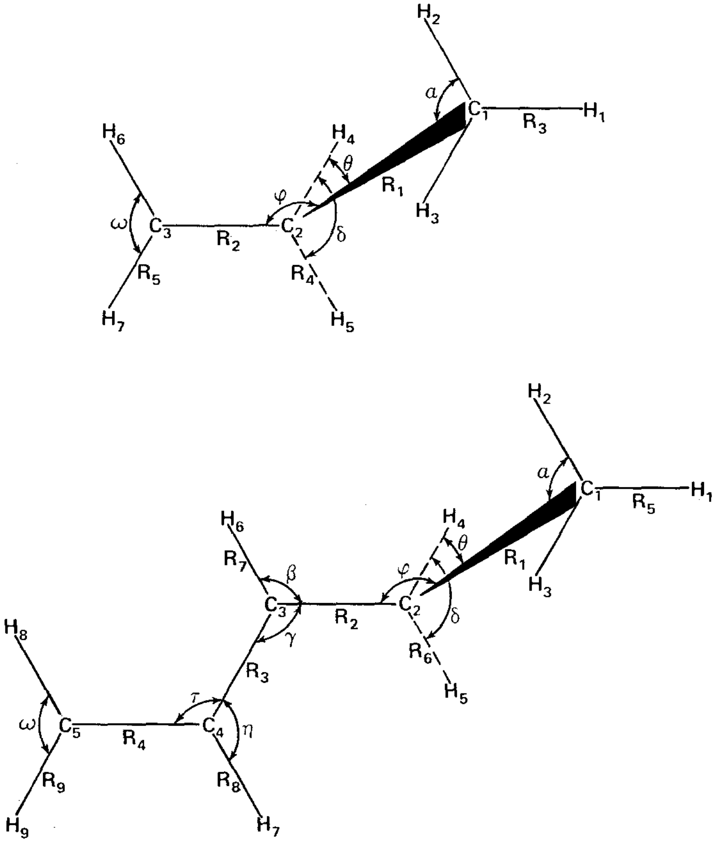

Fig. 1. Geometrical variables

0.1 Å too large, but this presents no serious problems and corrections are easily made. The open-shell calculations were carried out using Roothaan's method [11] rather than the "half-electron" approach of Dewar [12].

Fig. 1 shows the geometrical parameters which are varied during the course of the two addition reactions under consideration. Several assumptions have been made in order to keep the number of variables to a minimum. The substrate is constrained to be planar except for the hydrogen atoms bonded to the nucleus under attack. The methyl group is taken to have a symmetric-top configuration about the C–C axis, and in butadiene the hydrogen nuclei on the terminal carbons are taken to be symmetrically placed relative to the axes labeled as distances R_2 and R_4 in Fig. 1. These approximations are not unreasonable and since they are made consistently, it is expected that their effect will be small.

The calculations were carried out by choosing values of R_1 and exhaustively minimizing the energy with respect to all of the other variables. It is expected that a true minimum has been found in all cases except, perhaps, those for which R_1 is greater than 3 Å where the energy is very insensitive to small changes in the angle φ.

Table 1. *Computed results for* $CH_3\cdot + C_2H_4$[a]

$R_1 =$	∞	4.0	3.2	2.8	2.6	2.4	2.3	2.2	2.1	1.9	1.7	1.496[b]
R_2	1.309	1.309	1.310	1.311	1.312	1.314	1.316	1.319	1.323	1.427	1.442	1.456
R_3[c]	1.078	1.081	1.082	1.084	1.086	1.088	1.089	1.091	1.094	1.097	1.111	1.110
R_4[c]	1.095	1.095	1.095	1.096	1.096	1.097	1.098	1.099	1.100	1.105	1.111	1.119
R_5[c]	1.095	1.095	1.095	1.095	1.095	1.095	1.095	1.095	1.095	1.091	1.091	1.091
α	—	97.0	98.5	100.2	101.4	103.0	104.0	105.0	106.2	108.6	111.1	114.0
Θ	—	82.7	82.5	83.4	84.7	87.1	88.8	90.8	93.1	104.6	107.7	110.9
δ	111.4	111.5	111.7	111.9	112.1	112.0	111.9	111.8	111.4	107.6	105.0	102.2
φ	—	104.0	106.1	106.6	106.0	104.6	103.6	102.5	101.5	107.3	110.3	112.9
ω	111.4	111.4	111.3	111.3	111.3	111.3	111.3	111.2	111.2	113.7	113.6	113.5
E[d]	0.0	1.12	3.69	6.15	7.55	8.73	9.06	9.06	8.56	−3.13	−25.8	−37.6

[a] All distances in Angströms, all angles in degrees.
[b] Predicted equilibrium configuration of product.
[c] C–H distances corrected for 0.1 Å excess computed by MINDO/2.
[d] Energy in kcal/mole relative to isolated reactants.

Table 2. *Computed results for* $CH_3\cdot + C_4H_6$[a]

$R_1 =$	∞	2.8	2.6	2.4	2.3	2.2	2.1	1.9	1.7	1.497[b]
R_2	1.320	1.322	1.323	1.326	1.328	1.331	1.336	1.440	1.456	1.470
R_3	1.451	1.451	1.451	1.450	1.449	1.449	1.448	1.430	1.430	1.431
R_4	1.320	1.320	1.320	1.320	1.320	1.321	1.321	1.324	1.324	1.324
R_5[c]	1.078	1.084	1.086	1.088	1.089	1.091	1.094	1.097	1.102	1.111
R_6[c]	1.096	1.097	1.097	1.098	1.099	1.100	1.101	1.106	1.112	1.120
R_7[c]	1.105	1.106	1.106	1.106	1.106	1.107	1.107	1.103	1.103	1.103
R_8[c]	1.105	1.105	1.105	1.105	1.105	1.105	1.105	1.105	1.105	1.105
R_9[c]	1.096	1.096	1.096	1.096	1.096	1.096	1.096	1.096	1.096	1.096
α	—	100.3	101.5	103.1	104.0	105.1	106.3	108.7	111.3	114.2
Θ	—	81.8	83.2	85.7	87.4	89.7	92.0	104.3	107.2	110.4
δ	111.0	111.6	111.8	111.8	111.7	111.6	111.1	107.0	104.4	101.7
φ	—	109.6	109.0	107.5	106.6	105.4	104.6	108.7	111.3	113.8
β	119.2	119.2	119.2	119.1	119.1	119.0	118.9	117.2	117.2	117.2
γ	125.3	125.6	125.7	125.9	125.9	126.0	126.2	125.8	126.0	126.2
τ	125.3	125.2	125.2	125.0	125.0	125.0	125.0	124.2	124.1	124.0
η	115.5	115.7	115.7	115.9	116.0	116.1	116.1	116.8	117.0	117.0
ω	111.0	111.0	111.0	111.0	111.0	111.0	111.0	111.0	111.0	111.0
E[d]	0.0	6.32	7.74	8.90	9.18	9.11	8.46	−5.75	−28.4	−39.9

[a] All distances in Angströms, all angles in degrees.
[b] Predicted equilibrium configuration of product.
[c] C–H distances corrected for 0.1 Å excess computed by MINDO/2.
[d] Energy in kcal/mole relative to isolated reactants.

Results and Discussion

The results of the calculations are given in Tables 1 and 2. The activation energy is predicted to be 9.1 kcal/mole for the reaction of a methyl radical with ethylene and 9.2 kcal/mole for the reaction with butadiene. This assumes that zero-point effects are properly absorbed in the MINDO parameterization and that other factors are not important. The predicted values of R_1 for the activated complex are 2.25 Å and 2.27 Å for ethylene and butadiene, respectively. The observed activation energy for the ethylene reaction is 7.8–8.9 kcal/mole [1–4] in the gas phase, so that the computed result is in good agreement with experiment. There does not appear to be a similar gas-phase result for butadiene, but experimental data in hydrocarbon solution [6] indicates that the activation energy for the reaction of this molecule with a methyl radical should be at least 2 kcal/mole less than the ethylene value. Our computed results for this system do not reflect this observed change. We will return to this point later.

It is seen from inspection of Tables 1 and 2 that the geometry of the substrate is only slightly perturbed as the transition state is approached, the major effect being the out-of-plane bending of the hydrogens bonded to the carbon atom under attack. These hydrogens are bent out of the plane defined by the remainder of the olefin by about 7° in the activated complex. There is only a slight stretching of these same C–H bonds, and a slightly larger expansion of the C–C bonds labeled R_2 in Fig. 1. The methyl radical is somewhat more distorted as the substrate is approached. The C–H bonds become a little longer and the angle between the C–H bonds and the 3-fold methyl top axis increases from 90° at infinite separation to about 104.5° in the transition state.

In keeping with the small geometric changes noted in the approach to the activated complex, there is only a slight electronic rearrangement. It is found in both reactions that the main effect on the electron distribution is a lisght build-up of charge density on the methyl hydrogens so that the methyl group as a whole tends to become slightly negative as the transition state is approached. This effect is small, leading to a predicted total negative charge on the methyl group of about 0.04 electrons in the transition state. This charge is mostly transferred from the CH_2 group under attack, leading to a decreased charge density at the carbon and hydrogen nuclei.

The form of the open-shell molecular orbital is also of interest. The calculations indicate that this MO remains highly localized on the methyl carbon for R_1 values greater than 2.1 Å although delocalization increases as the distance R_1 approaches the transition state value. Thus at infinite separation the open-shell MO is a $2p$ orbital centered on the methyl carbon, so that the open-shell charge density at this center is 1.0. In the activated complex the open-shell charge density at this carbon is about 0.86 in both cases studied. The $2s$ orbital of the methyl carbon becomes increasingly important in the open-shell MO near the transition state, reflecting the change in hybridization as the methyl group is deformed. The charge density in this $2s$ orbital is about 0.14 in the activated complex.

Although it is often dangerous to try to draw too many conclusions from semiempirical calculations, it is felt that there is sufficient evidence to question the role of resonance stabilization of the transition state as the cause for the experimentally observed difference between the activation energies for the reaction of a methyl radical with ethylene and butadiene. The basis of this assertion lies in the fact that the predicted transition states are essentially product-like insofar as the substrate is concerned, with no tendency in butadiene to become allylic-like in the activated complex. Resonance stabilization is only observed much later in the course of the reaction as the transition state is passed and the product is formed. The completely parallel path of the reaction in both case up to and past the activated complex further weighs against the resonance stabilization theory.

The results computed by Basilevsky and Chlenov [8] using a much cruder approach are in remarkable agreement with the present study for the addition of a methyl radical to ethylene. The Basilevsky-Chlenov calculation predicts a transition state with $R_1 = 2.3$ Å and an activation energy of 7–9.7 kcal/mole, depending on the type of approximation used. Their approach seems to have much merit, especially for more complex reactions such as occur in free-radical polymerization, and it should be investigated further to ascertain whether it is capable of predicting basic trends in radical-molecule addition reactions.

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