

THE RELIABILITY OF MINDO METHOD FOR CHARACTERIZING THE TRANSITION STATE STRUCTURES IN RADICAL ADDITION REACTIONS

Robert PONEC and Jaroslav MÁLEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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The additions of the methyl radical and hydrogen atom to ethylene were chosen to test the reliability of MINDO method for predicting the transition state structures. It has been shown that the structures obtained at the level of the MINDO method differ markedly from the *ab initio* calculated structures.

The synthetic utility of the knowledge of free-radical reactivities is now well recognized^{1,2}. A great number of studies have been devoted to the qualitative description of the effect of structure upon reactivity and selectivity in radical reactions³. The first attempts to interpret quantitatively the radical reactivity were based on correlations with various quantum chemical indices of reactivity such as free valence, localization energy *etc.*⁴⁻⁷. As all these correlations are restricted only to interpretations of the relative reactivity within a class of structurally similar compounds, it is clear that such an approach does not represent any really fundamental solution of the problem of reactivity of radicals. In this area, there still remains the problem of establishing the structure of transition states and the magnitude of the corresponding activation barriers as well as the unanswered question of the electrophilic or nucleophilic nature of radicals. A reliable characterization of the transition state structures, which is of prime importance for the theory of chemical reactivity in general, comes forward particularly in the studies of radical reactivity. Since the transition states cannot be determined experimentally, their structures can only be inferred from indirect experimental data; in the radical reactions, however, just these data may sometimes lead to controversial conclusions. For instance, the low activation energies and high reaction enthalpies characterizing often the radical reactions may suggest that, on the basis of the Hammond postulate⁸, the structure of transition states in such reactions will resemble that of the starting molecules. On the other hand, some kinetic data^{9,10} lead to the conclusion that the structure of the transition state is fairly close to that of products. Therefore, the best possible solution is the direct calculation of the transition state structures with the aid of quantum chemical methods. In this respect, the addition of the methyl radical to ethylene was investigated most thoroughly⁹⁻¹⁴. In the studies concerning this reaction, various quantum chemical methods ranging from the π approximation to *ab initio* procedures and various methods of characterization of the reaction coordinate were used to calculate the structures of transition states.

Since the choice of the quantum chemical method as well as the method adopted for characterizing the reaction coordinate may influence significantly the resulting structures, the main goal of this study is therefore to examine from both these aspects

the reliability of results obtained in the additions of the methyl radical and hydrogen atom to ethylene chosen as examples.

RESULTS AND DISCUSSION

Consider first the characterization of the reaction coordinate. In a series of studies investigating the addition of the methyl radical to ethylene at the level of the *ab initio* method, the use of conventional methods for the geometry optimization was hindered by a great number of degrees of freedom; the reaction coordinate was therefore constructed by means of a linear variation of geometrical parameters transforming the geometry of reactants into that of products^{9,13}. Such a procedure was utilized for interpreting the intramolecular selectivity in free radical additions to unsymmetrical alkenes¹³. As reported by Salem and coworkers¹³, this procedure led to unexpectedly large values of activation barriers which were attributed to insufficient flexibility of the minimal basis set. In the present study we can demonstrate that the resulting high activation barriers are not presumably due to the insufficient flexibility of the minimal basis set, but that they are likely a result of an improper choice of the method used for constructing the reaction coordinate. To substantiate our conclusion, we have carried out several model INDO calculations on the radical additions to ethylene following various ways of characterization of the reaction coordinate. In the crudest approach the reaction coordinate was modelled only by the distance of the C...X bond where X was the radical approaching perpendicularly to one of the ethylene carbon atoms, with all other degrees of freedom being fixed. As demonstrated in Fig. 1 (curve 1), even such an unreasonable reaction coordinate does not lead to occurrence of an activation barrier on the corresponding curve of potential energy. This failure of the CNDO and INDO methods to reproduce the activation barrier in radical reactions has already been described in the literature¹⁴. However, when the INDO method was used for calculating the potential energy along the reaction coordinate constructed by means of the method of linear increments, the activation barrier became clearly evident; for the addition of the fluorine atom to ethylene this barrier amounted to 126 kJ/mol (Fig. 1, curve 2). Essentially the same conclusion holds also for the addition of hydrogen or chlorine atoms and of the trifluoromethyl radical to ethylene¹⁵. These results clearly document that the occurrence of an activation barrier in the above cases is due only to the forced deformation of ethylene resulting from the use of the method of linear increments. This example also shows that a discussion of intramolecular selectivity in radical addition reactions which is based on such a method of construction of the reaction coordinate is almost certainly incorrect. At the same time, it is evident that a reliable characterization of the reaction coordinate requires extensive optimization of the molecular geometry. At the level of the *ab initio* method only the addition of the hydrogen atom to ethylene was investigated in detail¹⁶⁻¹⁸. Larger systems including the above addition of the

methyl radical required a limitation to semiempirical MO methods; however, only EHT and MINDO methods do reproduce the activation barriers in radical addition reactions¹⁴. The incapability of the EHT method to reproduce satisfactorily the bond lengths is generally known. For this reason, the only method characterizing reliably the transition state structure has been considered to be the MINDO method^{10,12}. However, during the last few years examples continue to appear indicating that even this method is most probably not reliable enough for predicting the molecular structures. The MINDO method overestimates systematically the C—H, O—H and N—H bond lengths by about 0.01–0.02 nm and, moreover, it leads to considerable errors in predicting the molecular geometry of simple molecules (water is assumed to have a linear structure¹⁹) as well as clusters with intermolecular hydrogen bonding²⁰. These failures require a more profound analysis of reliability of the MINDO method also for radical addition reactions.

In our case, we have focused our attention on the calculation of the transition state structures and of the whole potential energy curves along the reaction coordinates for reactions of the methyl radical and hydrogen atom with ethylene. The addition of the hydrogen atom appears to represent an ideal system for such a study as in this case the MINDO structures can be compared with the results of recent *ab initio* calculations. As the reaction coordinate we have chosen the distance C...X between the attacking radical and one of the ethylene carbon atoms. For several fixed values of this distance the geometry was optimized with respect to all remaining degrees of freedom. The optimization was carried out by using the gradient technique²¹ within the framework of the Longuet-Higgins-Pople RHF method for the description of open-shell molecules²². The calculated profiles of the potential-

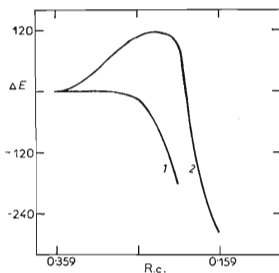
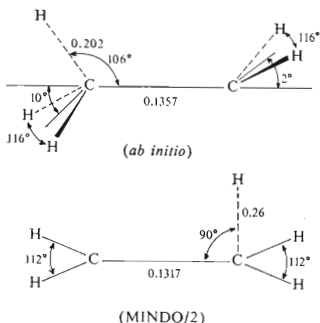


FIG. 1
Dependence of the potential energy ΔE , kJ/mol upon the reaction coordinate (C...F) (in nm) for the addition of the fluorine atom to ethylene. 1 Perpendicular approach of the fluorine atom and fixed geometry of ethylene; 2 reaction coordinate constructed by means of the method of linear increments

energy hypersurfaces along the reaction coordinate are given in Figs 2 and 3. The corresponding structures of the transition states are illustrated in Schemes 1 and 2.



SCHEME 1

Another problem of the quantitative characterization of radical reactivity concerns the prediction (reproduction) of activation barriers for the free-radical addition reactions. The available experimental and theoretically calculated data of activation bar-

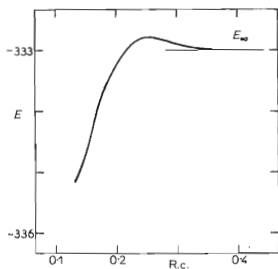


FIG. 2

Dependence of the potential energy E , eV upon the reaction coordinate (C...H) (in nm) for the addition of the hydrogen atom to ethylene

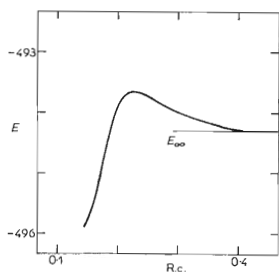
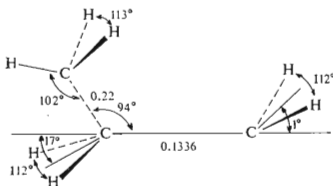


FIG. 3

Dependence of the potential energy E , eV upon the reaction coordinate (C...CH₃) (in nm) for the addition of the methyl radical to ethylene

riers for the additions of the methyl radical and hydrogen atom to ethylene are compared in Table I. Our MINDO/2 calculations give an activation barrier equal to about 17 kJ/mol for the addition of the hydrogen atom and to about 63 kJ/mol for the addition of the methyl radical. The value calculated for the latter reaction is higher than that resulting from the experimental data²³ and the earlier MINDO calculations^{10,12}. Our markedly larger value of the activation barrier is deemed to be a result of the open-shell treatment. A similar overestimation of activation barriers obtained by calculations based on the half-electron method has already been described by Dewar¹⁰. For this reason, also the barrier calculated by us for the addition of the hydrogen atom to ethylene may be somewhat overestimated; unfortunately, a considerable scattering of the experimental as well as *ab initio* calculated data (Table I) does not allow to evaluate unambiguously the reliability of values determined theoretically by means of the MINDO method.



SCHEME 2

TABLE I

Comparison of experimental and theoretically calculated values of activation barriers (kJ/mol) for additions of the methyl radical and hydrogen atom to ethylene

CH ₃ [•]		H [•]	
Experiment	Theory	Experiment	Theory
28.5–37.3 ^a	33.1 ^b	2.1–30.1 ^f	0 ^g
	36.0 ^c		9.2 ^h
	38.1 ^d		53.6 ⁱ
	56.1 ^e		69.1 ^j
			21.4 ^k

^a Ref.²³; ^b UHF method; ^c Roothan RHF method¹⁰; ^d Roothan RHF method¹²; ^e half-electron method¹⁰; ^f ref.²⁴; ^g ref.¹⁶; ^h UHF method – 4–31G basis set¹⁷; ⁱ RHF method – STO-6G basis set²⁵; ^j RHF method – “double zeta” basis set²⁵; ^k RHF+CI method²⁵.

The activation barriers for the addition of the hydrogen atom to ethylene calculated by Nomura and Iwata²⁵ appear to attain somewhat unusually high values. This result again is presumably due to the use of the RHF method known to describe improperly the wave function in the region of the transition state. By including the configuration interaction, which compensates the insufficiencies of the single-determinant wave function, the magnitude of the activation barrier declines to a more realistic value²⁵, *i.e.* 21.4 kJ/mol (Table I). Of the results available to date, presumably the most reliable data are those given by Nagase and Kern¹⁷; by using these data the absolute rate constants and the magnitude of the kinetic isotope effect were reproduced with a remarkable accuracy²⁶.

Let us now discuss the reliability of the transition state structures calculated first for the addition of hydrogen atom to ethylene. For the reasons mentioned above, the *ab initio* structure reported by Nagase and Kern¹⁷ was taken as a standard. A comparison of results obtained with both methods reveals that the MINDO calculated structure differs markedly from the *ab initio* structure. The most significant difference concerns the newly formed C—H bond, where the distance calculated by us (about 0.26 nm) is too long when compared to the standard value of 0.20 nm. Furthermore, according to the MINDO structure the CCH angle between the C—C bond and the approaching hydrogen atom is equal to about 90° contrasting markedly with the value of 106° given by Nagase and Kern¹⁷. Similarly, a great difference exists between the lengths of the C—C bonds for which the MINDO method affords a value of 0.1317 nm and the *ab initio* procedure that of 0.1357 nm. Scheme 1 shows that the MINDO structure is fairly close to that of isolated ethylene, with the hydrogen atom approaching from a distance of 0.26 nm to one of the carbon atoms; on the other hand, a clean pyramidalization on the attacked carbon atom is encountered in the structure proposed by Nagase and Kern¹⁷. Similar, though not so dramatic differences occur also in the addition of the methyl radical to ethylene. Unfortunately, in this case no *ab initio* data are available, but a comparison with the MINDO results reported by Dewar and Olivella¹⁰ and Hoyland¹² allows to test the effect of parametrization (MINDO/2 vs MINDO/3) and various versions of the open-shell treatment. It has already been shown that the half-electron method used by us overestimates, when compared with the Roothan RHF method or UHF method, the magnitude of the activation barrier. As to the reproducibility of the geometrical parameters of transition states, the differences between the methods compared here are smaller than for the addition of the hydrogen atom to ethylene; nevertheless, significant deviations are inherent also in addition of the methyl radical to ethylene. The most important discrepancy concerns the CCC angle between the C—C bond of ethylene and the approaching methyl radical. Hoyland¹² as well as Dewar and Olivella¹⁰ have reported a value of about 108° corresponding essentially to a tetrahedral arrangement on the attacked carbon atom. In the present study we have found a value of about 94°. The same value was calculated independently by Gey²⁷.

All the differences given above suggest that even for a relatively well investigated reaction such as the addition of the methyl radical to ethylene the structure of the transition state is not known with acceptable reliability; various versions and parametrizations of the MINDO method lead to quite different results. Furthermore, significant differences between the MINDO calculated and the relatively well established *ab initio* structures for the addition of the hydrogen atom to ethylene cast only more doubt on the general reliability of the MINDO method for characterizing the structures of the transition states in radical addition reactions.

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