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Theoretical Study of the Addition of Vinyl and Cyclopropyl Radicals to Ethylene

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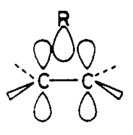
The addition of vinyl and cyclopropyl radicals to ethylene has been examined by the UMINDO/3 method. Both reactions have been shown to involve a reactant-like transition state with a σ-configuration geometry that clearly rules out the formation of a π-complex structure. In the case of cyclopropyl addition, the structure found for the transition state is further supported by the calculated weak kinetic deuterium isotope effect, in agreement with experiment. The importance of the contribution to the kinetic deuterium isotope effect of the new vibrational modes created at the transition state is discussed.

Introduction

A great deal of work in the investigation of the mechanistic aspects of the addition of free radicals to unsaturated compounds has been concerned with the structure of the transition state involved in these reactions.[1] There are two limiting structures which one may assume for the transition state, a π complex and a σ complex. In a π-complex transition state (1), there is a symmetric overlap between the singly occupied oribtal of the radical (R) with both 2p AO's forming the multiple bond producing a structure close to that of the original reactants; i.e., little or no rehybridization of the substrate or radical is involved in the formation of this transition state. In contrast, the formation of a σ transition state (2) involves an efficient overlap between the singly-occupied orbital of the radical with one of the terminal 2p AO's contributing to the multiple bond of the unsaturated substrate and in this case it might be assumed that the two reactants undergo a certain degree of rehybridization, so that the transition state resembles more the product radical than the reactants.



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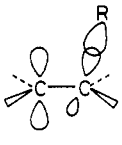

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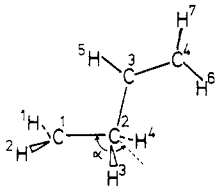

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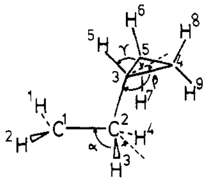

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In the case of the addition of alkyl π-radicals such as methyl, it was formerly thought that the reaction takes place via a π-complex transition state, but arguments based on simple LCAO–MO theory[2] make this unlikely. Later MO calculations[3] on the potential surface for the addition of methyl radical to olefins have shown that the transition state has a σ-complex configuration with a structure which is an interesting combination of reactant-like and product-like features; i.e., the methyl group adopts a product-like configuration while the olefinic moiety remains essentially reactant-like; the forming CC bond being very long ($\sim$2.3 Å). On the other hand, it has been suggested[4-6] that the addition of hydrocarbon σ-radicals such as vinyl, cyclopropyl, phenyl, etc., takes place via a π-complex transition state. The different nature of the transition states involved in the additions of π- and σ-radicals to unsaturated substrates has been explained by arguing that in π-radicals the density of the unpaired electron is equally spread out over the two lobes of the 2p AO, whereas for σ-radicals the unpaired electron is located in a highly directional hybrid AO which projects away from the neighbouring atoms, so that the repulsive interactions between the σ-radical and an unsaturated molecule are small in the transition state with the result that a π-complex structure is preferred over its σ-complex counterpart. A similar π-complex transition state in the case of a π-radical would produce considerable steric interactions.

The addition of vinyl radical to ethylene has been recently studied theoretically by Arnaud et al.[7] by using MNDO semiempirical SCF-MO method.[8] This calculation led to a reactant-like transition state with a σ-complex structure and an energy barrier height of 18.2 kcal/mol. While no experimental value seems to be available for this reaction, the activation energies for addition reactions of alkyl radicals to ethylene are in the range 3–10 kcal/mol,[9] implying that the calculated MNDO value is undoubtedly much too large. Furthermore, use of MNDO suffers from the theoretical objection that its present parametrization underestimates the strength of three-center bonds.[10] One might therefore expect an overdestabilization of the hypothetical π-complex transition state with respect to its alternative σ-complex structure.

Some insight into the structural details of the transition state involved in the radical addition reactions may be

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(1) Review: Tedder, J. M.; Walton, J. C. *Adv. Phys. Org. Chem.* **1978**, *16*, 51.

(2) See: Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(3) See: Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978**, *100*, 5290 and references therein.

(4) Mile, B. *Angew. Chem.* **1968**, *7*, 507. Bennet, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1.

(5) Stefani, A. P.; Chuang, L. Y.; Todd, H. E. *J. Am. Chem. Soc.* **1970**, *92*, 4168.

(6) Hay, J. M. "Reactive Free Radicals"; Academic Press: New York, 1974; p 112.

(7) Arnaud, R.; Duady, J.; Subra P. *Nouv. J. Chim.* **1981**, *5*, 181.

(8) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(9) Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds"; Butterworths: London, 1972.

(10) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

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provided by the measurement of the secondary kinetic isotope effects (KIE's). In particular, the experimental values of the rate constant ratios (k_D/k_H) for the addition of cyclopropyl radicals to ethylene and propylene and their deuterated analogues are about 1.1.[5] Following an early suggestion by Streitwieser,[11] this small inverse KIE has been interpreted as an indication of the π-complex nature of the corresponding transition state.[5] KIE's result from changes in the force constant of vibrations which accompany the change from reactants to the transition state and the inverse secondary deuterium effect must result from an overall increase in the sum of the force constants in the transition state.[12] It was pointed out by Streitwieser that this change is probably due to the transformation of a soft out-of-plane CH bending vibration of the trigonal olefinic group to a stiffer bending vibration of the tetrahedral group in the product radical. Assuming that this theoretical prediction is valid, the calculated value of k_D/k_H for a radical addition proceeding through a σ transition state is about 1.82.[11]

We recently reported a theoretical (MINDO/3[13]) analysis of the secondary kinetic deuterium effect in the addition of methyl radical to ethylene.[14] The results showed that the main contribution to the KIE comes from new isotope sensitive vibrations created on passing from the reactants to the transition state. The changes in the force constants of ethylene due to the rehybridization of the trigonal olefinic carbon make a minor contribution. Consequently, it can be thought that the above mentioned KIE evidence concerning the π-complex nature of the transition state for the addition of cyclopropyl radical to olefinis is inconclusive.

In summary, it is felt that there is insufficient evidence to establish whether or not a π-complex transition state is involved in the addition of hydrocarbon σ-radicals to olefins. In view of this uncertainty, we though it would be of interest to reinvestigate the addition of vinyl and cyclopropyl radicals to ethylene by using the MINDO/3 method, which has been found to give excellent results for either the intermolecular or intramolecular addition of radicals to CC multiple bonds.[3,15]

Procedure

The calculations were carried out by the MINDO/3 method with the standard parameters.[13] Open-shell species were calculated by using a spin-unrestricted version (UMINDO/3[16]) of MINDO/3. Although use of an unrestricted wave function suffers from the formal theoretical objection that it is not an eigenfunction of the total spin angular momentum operator $\mathbf{S}^2$, this problem did not raise any difficulties in the present calculations because the calculated expectation values of $\mathbf{S}^2$ indicated that the contamination by higher spin states was unimportant.

All equilibrium geometries were determined by minimizing the total energy with respect to all geometrical parameters, using the standard DFP (Davidon–Fletcher–Powell[17]) procedure. The transition states were found by the usual reaction coordinate method and refined by minimizing the scalar gradient of the energy.[18] All stationary points were checked[18] by calculating and diagonalizing the Hessian (force constant) matrix by using Cartesian coordinates. Convergence was confirmed by the presence of six near-zero eigenvalues, all the other eigenvalues being positive for minima while a transition state has one negative eigenvalue.[18]

Table I. UMINDO/3 Calculated Geometries and Heats of Formation (ΔH_f) for the Addition of Vinyl Radical to Ethylene[a]

parameters[b]	reactants	transition state	product
C_1C_2	1.314	1.327	1.454
C_2C_3		2.325	1.489
C_3C_4	1.291	1.300	1.327
C_3H_5	1.083	1.090	1.113
$C_1C_2C_3$		109.5	120.6
$C_2C_3C_4$		124.3	132.0
$H_3C_2H_4$	110.8	111.2	101.3
$H_5C_3C_4$	146.0	136.2	116.0
α	180.0	167.5	118.5
$C_1C_2C_3C_4$		112.9	120.0
$H_1C_1C_2C_3$		89.0	1.5
ΔH_f[c]	81.7	91.0	37.4

[a] Bond lengths in Å; bond angles and dihedral angles in degrees. [b] Atom numbering refers to 3. [c] Values are given in kcal/mol at 25 °C.

Molecular entropies were obtained from the calculated geometries and vibrational frequencies in the usual manner.[19]

The isotopic rate ratios k_H/k_D were calculated within the framework of the transition state theory in the rigid-rotor-harmonic-oscilator (RRHO) approximation and by neglecting tunnelling effects with the use of the equation[20]

$$\frac{k_H}{k_D}\frac{s_2{}^A s_2{}^B s_1{}^C}{s_1{}^A s_1{}^B s_2{}^C} = (\mathrm{MMI})(\mathrm{EXC})(\mathrm{ZPE}) \qquad (1)$$

where superscripts A, B and C refer to reactants A and B and the transition state C, subscripts 1 and 2 refer to light and heavy isotopes, respectively, and s's are symmetry numbers. The terms MMI, EXC, and ZPE represent the contributions from the translational and rotational energies, vibrational energies, and the zero point energies, respectively. In order to carry out an analysis of the KIE's enterely in terms of the normal vibrational modes it is most convenient to express the isotopic rate ratio by using the standard form of the Bigeleisen equation[20]

$$\frac{k_H}{k_D}\frac{s_2{}^A s_2{}^B s_1{}^C}{s_1{}^A s_1{}^B s_2{}^C} = \frac{\nu_1{}^\ddagger}{\nu_2{}^\ddagger}(\mathrm{VP})(\mathrm{EXC})(\mathrm{ZPE}) \qquad (2)$$

where $\nu^\ddagger$ refers to the vibrational frequency of the imaginary mode (the reaction coordinate) of the transition state, the term VP represents the vibrational product, and the term EXC and ZPE have the same meaning as before. The detailed expressions of these terms and the MMI term have been previously reported[14] and will not be repeated here.

Results and Discussion

Addition of Vinyl to Ethylene. The calculated UMINDO/3 geometries and heats of formation of vinyl[21] and homoallyl[15] radicals and ethylene[22] have been reported previously. The optimized geometrical parameters and heat of formation of the calculated transition state are given in Table I together with those of the reactants and product. The calculated force constant matrix for this transition state had just one negative eigenvalue and an associated eigenvector which corresponded to the correct reaction coordinate (or transition vector[18]).

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(11) Streitwieser, A.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

(12) See: Van Hook, W. A. In "Isotope Effects in Chemical Reactions"; Collins, C. J.; Bowman, N. S., Eds.; Van Nostrand: New York, 1970.

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(21) Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

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It can be seen from Table I that the approach of the vinyl radical to the ethylene molecule is very unsymmetrical, the $C_1C_2C_3$ bond angle in the transition state (109.5°) being much closer to the value in the product (120.6°) than in a hypothetical π complex (~70°). In addition, the carbon skeleton has a gauche conformation with a dihedral angle $C_1C_2C_3C_4$ (112.9°) close to the value found for the most stable conformation of the product, i.e., the homoallyl radical.[15] There is, therefore, no question of a π-complex transition state being formed. Nevertheless, the calculated transition state has a reactant-like structure. Thus the nascent C_2C_3 bond is very long (2.325 Å), the ethylenic C_1C_2 bond is only 0.013 Å greater than the value calculated for ethylene, and while the methylene group $H_3C_2H_4$ is tilted out of the plane defined by the rest of the ethylene moiety, the angle of tilt (12.5°) is much less than it is in the product (61.5°). As regards the vinyl group, the major effect in passing from the reactants to the transition state is an appreciable closure of the angle $H_5C_3C_4$ and a slight stretching of bonds C_3C_4 and C_3H_5, reflecting only a small change in hybridization of atom C_3. These features suggest that the geometry of the vinyl moiety is only slightly perturbed in the transition state.

The calculated heat of reaction (−44.3 kcal/mol) is in reasonable agreement with that (ca. −38 kcal/mol) estimated from thermochemical data[23] and is entirely consistent with the reactant-like structure found for the transition state.

It is worth noting that the calculated structure of the transition state is very similar to that found by Arnaud et al.[7] by using the MNDO method. On the other hand, the structure of the ethylenic moiety in the transition state is almost identical to that calculated for the transition state of the addition reaction of methyl radical to ethylene.[3]

In keeping with the small geometrical changes noted in passing from the reactants to the transition state, there is only a slight electronic rearrangement. It is found that the main effect on the electron distribution is a slight buildup of electron density in the vinyl fragment, so that the total charge of the ethylene fragment is +0.025 in the transition state, suggesting a weak electrophilic behavior of vinyl radical towards ethylene. In the case of the addition of methyl radical to ethylene, the calculated total charge of the ethylene moiety was +0.020 e.[3] Consequently, one can conclude that both radicals exhibit the same electrophilic behavior toward ethylene.

Regarding the single occupied molecular orbital (SOMO), the calculations indicate that it is mainly localized on the C_3 (49%) and C_1 (24%) atoms in the transition state, while that in the reactants is highly localized (67%) on the vinyl radical center C_3.

The energy of the calculated transition state lies 9.3 kcal/mol above that of the reactants and the calculated activation entropy at 25 °C is −28.1 cal/(K mol). As indicated earlier, there is no experimental value for the activation parameters of this reaction but for the addition of alkyl radicals to ethylene the activation energies and entropies lie in the range 6 ± 3 kcal/mol and −26 ± 3 cal/(K mol), respectively.[9] It should be remarked that for the addition of methyl radical the calculated UMINDO/3 values for these parameters are 7.9 kcal/mol[3] and −26.8 cal/(K mol),[14] respectively, indicating once again the great similarity between both radical addition reactions. At this point one should mention that the present results suggest, not unexpectedly, that the activation barrier calculated by Arnaud at al.[7] is much too large, due probably to the tendency of the MNDO parametrization to overestimate the repulsion energies at large interatomic distances.[24]

Table II. UMINDO/3 Calculated Geometries and Heats of Formation (ΔH_f) for the Addition of Cyclopropyl Radical to Ethylene[a]

parameters[b]	reactants	transition state	product
C_1C_2	1.314	1.332	1.456
C_2C_3		2.276	1.509
C_3C_4	1.462	1.475	1.514
C_4C_5	1.507	1.504	1.486
C_3H_5	1.089	1.098	1.118
$C_1C_2C_3$		110.7	120.9
$C_3C_4C_5$	59.0	59.3	60.6
$C_5C_3C_4$	62.1	61.3	58.8
α	180.0	164.3	117.8
β		129.9	134.8
γ	148.2	134.1	116.4
$C_1C_2C_3H_5$		58.3	55.7
$H_1C_1C_2C_3$		88.3	10.2
ΔH_f[c]	68.5	80.2	32.9

[a] Bond lengths in Å; bond angles and dihedral angles in degrees. [b] Atom numbering refers to 4. [c] Values are given in kcal/mol at 25 °C.

Finally, some insight into the origin of the calculated activation barrier may be obtained by breaking down the total energy into one-center and two-center terms[25] and regrouping those terms associated with the ethylenic fragment into a single term $E(C_2H_4)$, those associated with the vinylic fragment into another single term $E(C_2H_3)$, and the bicentric terms between pairs of atoms belonging to different fragments into an intermolecular term E(inter). By difference between the values of these terms for the transition state and reactants, the activation barrier can be dissected into three local contributions, namely: $\Delta E(C_2H_4) = 16.4$, $\Delta E(C_2H_3) = 8.2$, and $\Delta E(\text{inter}) = -15.4$ kcal/mol. Since the intermolecular contribution is stabilizing, it becomes clear that the activation barrier is due to the intramolecular destabilization of the two fragments.

Addition of Cyclopropyl to Ethylene. The UMINDO/3 geometry and heat of formation of cyclopropyl radical has been reported previously.[22] With regard to the product, i.e., the 2-cyclopropylethyl radical (4), a complete geometry optimization was carried out. Two stable minima, corresponding to the antiperiplanar and synclinal conformations with respect to the C_2C_3 bond (see 4), were found in the UMINDO/3 potential surface; that for the former conformer was the lower in energy by 1.0 kcal/mol. Since the geometrical parameters of both conformers are very similar, only the geometry and heat of formation calculated for antiperiplanar 4 are shown in Table II together with those of the reactants. Note that the hydrogen atom H_1 prefers to eclipse the C_2C_3 bond, as found in previous UMINDO/3[3,15] and MNDO[7,26] calculations on the most stable conformation of β-substituted alkyl radicals.

The reaction paths for the conversion of the reactants into the above conformations of 4 were investigated in each case by using the C_2C_3 distance as the reaction coordinate. The two transition states located in this way were refined by minimizing the norm of the gradient of the energy and

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(23) Calculated from the the heats of formation of homoallyl free radical ($\Delta H_f°$ (298°) = 46.0 kcal/mol: Gordon, A. S.; Smith, S. R.; Drew, C. M. *J. Chem. Phys.* **1962**, *36*, 824), ethylene ($\Delta H_f°$ (298°) = 12.5 kcal/mol: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970), and vinyl radical ($\Delta H_f°$ (298°) = 71.5 kcal/mol: Defrees, D. J.; Mc Iver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334).

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it was verified that both structures were true saddle points on the potential surface. The geometries of these transition states are nearly identical, differing only in the orientation that the cyclopropyl group adopts around the forming C_2C_3 bond, which in turn correspond to those of the antiperiplanar and synclinal conformations of the product (**4**). The calculated activation enthalpies at 25 °C are 11.7 and 12.0 kcal/mol, respectively, and the corresponding activation entropies at the same temperature are −32.6 and −31.0 cal/K mol. No experimental data seems to be available for this reaction. From the calculated activation parameters the predicted rate ratio for the formation of the antiperiplanar and synclinal conformations of **4** is 1.403. Taking into account the great simmilarity between the calculated structures of both transition states, the remainder of the present discussion will refer to the lowest energy one. The optimized geometrical parameters and heat of formation for this transition state are given in Table II. As in the case of the addition reaction of vinyl to ethylene, the transition state has a structure that rules out the suggestion[5] of a π transition state. Thus the value (110.7°) of the $C_1C_2C_3$ bond angle is close to that in the product (120.1°). On the other hand the forming bond is again very long (2.268 Å), although somewhat shorter than in the vinyl–ethylene transition state (2.325 Å); the ethylenic CC bond (1.332 Å) remains almost at its value in ethylene (1.314 Å) and the tilting angle of the attacked methylene group (16.1°) is nearer to the value in ethylene (0°) than in the product (61.1°). Nevertheless, by comparing the geometrical parameters C_1C_2, α, and C_2C_3 of the transition states shown in Tables I and II it must be noted that for the addition of cyclopropyl radical to ethylene the transition state is somewhat more advanced torward the product than in the case of the addition of vinyl. As regards the cyclopropyl moiety, all the CC bond lengths almost remain at their values in the cyclopropyl radical. The only noticeable geometrical changes is in the γ angle (see **4**), which value in the transition state (134.1°) is midway between the values in the reactant (148.2°) and product (116.4°).

Judging by the above results, we conclude that the transition state for the cyclopropyl radical addition to ethylene is of the σ-complex type and very early along the reaction pathway. These conclusions are identical with those reached for other radical addition reactions studied up to data using UMINDO/3.[3,15]

As regards the electron distribution at the transition state, it is found that the total charge of the ethylene fragment is +0.108 e, indicating again an electrophilic behavior of cyclopropyl radical towards ethylene. This result is consistent with previous theoretical studies on different radical addition reactions to multiple bonds[26,27] but at variance with the above mentioned suggestion of Stefani et al.[5]

When the calculated activation barrier is considered, its value is about 3 kcal/mol higher than that calculated for the addition of vinyl radical. This result can be qualitatively understood recalling that the geometry of the transition state is slightly more advanced along the reaction path in the addition of cyclopropyl than in the addition of vinyl, so the destabilization energy due to the geometrical distorsion of the reactants is somewhat larger in the transition state of the former reaction. The breakdown of the calculated activation barrier in three local contributions, namely $\Delta E(C_2H_4) = 20.1$, $\Delta E(c\text{-}C_3H_5) = 14.3$, and $\Delta E(\text{inter}) = -22.8$ kcal/mol, obtained by the use of the energy partitioning procedure described for the vinyl–ethylene reaction, do indeed follow this pattern. Thus, the destabilization undergone by the ethylene fragment in passing from the reactants to the transition state is 3.8 kcal/mol larger for the addition of cyclopropyl than that calculated for the vinyl–ethylene reaction. The contribution $\Delta E(C_2H_4)$ is mainly the result of a substantial destabization (31.3 kcal/mol) of the bicentric term of the C_1C_2 bond and a small stabilization (−10.8 kcal/mol) of the monocentric term of atom C_1, reflecting the distorsion undergone by the CC double bond.

Table III. Calculated Secondary Kinetic Deuterium Effects for the Addition of Cyclopropyl and Methyl Radicals to Ethylene

	k_D/k_H		
reaction	25 °C	65 °C	100 °C
$c\text{-}\dot{C}_3H_5 + CD_2{=}CD_2/CH_2{=}CH_2$	0.990	0.986	0.983
$\dot{C}H_3 + CD_2{=}CD_2/CH_2{=}CH_2$	0.975	0.970	0.968

As noted above, Stefani et al.[5] have suggested the π-complex nature of the transition state in the addition of cyclopropyl on the basis of the weak kinetic deuterium effect ($k_D/k_H = 1.11$, at 65 °C) observed when the four ethylene hydrogens were substituted by deuterium atoms. Since the present results clearly rule out the π-complex nature of this transition state, we have calculated the KIE for this addition reaction as a check of our prediction. Table III shows the rate ratio k_D/k_H values calculated at different temperatures by the use of 1. Although these values are too low, as compared with the observed value at 65 °C, the present results agree fairly well with experiment in predicting a very small KIE and clearly weaken the arguments supporting the π-complex nature of the transition state on the basis of the observed low value of the secondary deuterium effect.[5] For the sake of comparison, the rate ratios k_D/k_H calculated[14] at the same temperature for the addition of methyl radical to ethylene are given in Table III. It is worth noting that both series of values are quite similar and that the slightly larger KIE observed for the cyclopropyl addition is well accounted for by the present calculations.

The analysis of the calculated KIE can be carried out following the same procedure described previously.[14] As shown there, one can break down the total KIE into the rotational–translational (MMI) and vibrational (EXC·ZPE) contributions. These contributions are given in Table IV for both radical addition reactions. It is seen that in both reactions the product of the EXC and ZPE terms contributes toward an inverse KIE ($k_D > k_H$) while the MMI terms contribute toward a normal KIE ($k_D < k_H$). The two contributions nearly cancel out and a very weak KIE results.

It is worthwhile to look more carefully at the vibrational contribution. Usually, the KIE in addition reactions involving olefins has been attributed to changes in vibrational frequencies accompanying the partial rehybridization of the reactant carbon atom during passage from the reactant to the transition state. However, as has been pointed out by Strausz et al.,[28] there are six new vibrational modes created at the transition state, one of which corresponds to the reaction coordinate, that can show a very important contribution to the KIE. From the detailed expressions of the EXC and ZPE terms[14] it is possible to calculate the contribution of each normal mode to the KIE

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(27) Ponec, R.; Málek, J. *J. Mol. Struct.* **1982**, *88*, 295.

(28) Safarik, I; Strausz, O. P. *J. Phys. Chem.* **1972**, *76*, 3613. Strausz, O. P.; Safarik, I.; O'Callaghan, W. B.; Gunning, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 1828.

Table IV. Decomposition of the Kinetic Deuterium Effects at 25 °C into Its Differents Components

reaction	EXC	ZPE	EXC·ZPE	MMI	k_D/k_H
$c\text{-}\dot{C}_3H_5 + CD_2{=}CD_2/CH_2{=}CH_2$	1.485	1.281	1.906	0.521	0.990
$\dot{C}H_3 + CD_2{=}CD_2/CH_2{=}CH_2$	1.314	1.220	1.602	0.608	0.975

Table V. Decomposition of the Vibrational Part of the Kinetic Deuterium Effect and Its Components into Contributions Associated with Vibrational Modes of the Reactants and the New Modes of the Transition State

vibrational modes	EXC·ZPE	EXC	ZPE
$c\text{-}\dot{C}_3H_5 + CD_2{=}CD_2/CH_2{=}CH_2$			
normal modes of the reactants	1.008	1.016	0.992
new normal modes of the TS	1.887	1.461	1.291
$\dot{C}H_3 + CD_2{=}CD_2/CH_2{=}CH_2$			
normal modes of the reactants	1.009	1.011	0.999
new normal modes of the TS	1.587	1.300	0.221

and, therefore, to determine the contributions of the new modes. We have performed such a decomposition of the vibrational terms EXC and ZPE. The contributions calculated for the vibrational modes of the reactants and for the new modes are given in Table V. It is seen that the whole vibrational contribution to the KIE is due to the new modes, since their contribution to the EXC term is larger than that to the ZPE term. Again the results for the addition of cyclopropyl and methyl radicals are completely equivalent. The analysis of the individual contributions of the new modes shows that the main contribution (1.389) to the total vibrational term (EXC·ZPE) comes from a normal mode fully localized on the ethylenic fragment. This normal mode is exactly the same as we have discussed in our previous theoretical analysis of the KIE in the addition of methyl radical to ethylene.[14] The other four real new modes are delocalized over the two fragments of the transition state and their contributions to the KIE are appreciably smaller (in the range 1.053–1.127) than that of the above indicated one.

Finally, it should be noted that the contributions of the new vibrational modes to the KIE should not be overestimated[28] because these modes are created at the expense of rotational and translational degrees of freedom lost by the reactants and, consequently, their contributions to the vibrational term (EXC·ZPE) will in part be cancelled out by the opposite contribution of the rotational–translational term (MMI). Thus, the real importance of the new vibrational modes can only by considered after taking into account the effect on the MMI term due to the decrease in the number of rotational and translational degrees of freedom. It becomes therefore necessary to discuss the calculated KIE entirely in terms of the vibrational frequencies of the reactants and the transition state by using eq 2. Again, the term VP can be analyzed in contributions of each normal mode as it has already been done with the EXC and ZPE terms. The total contribution of the new modes to the VP term was calculated to be 0.554. When the contribution of each new normal mode to the VP term is multiplied by the corresponding contributions to the EXC and ZPE terms, in order to calculate the total contribution of each new mode to the KIE, values less than 1.010 are obtained for the four delocalized modes, and the value 1.036 is obtained for the mode localized on the ethylenic fragment.

The results of the above analysis of the calculated secondary kinetic deuterium effect for the addition of cyclopropyl radical to ethylene, apart from some minor differences, are completely coincident with those obtained in our previous investigation on the methyl radical addition reaction. Consequently, a very weak KIE is perfectly consistent with a σ-complex structure of the transition state in both reactions.

Summary and Conclusions

The addition of hydrocarbon σ-radicals such as vinyl and cyclopropyl to ethylene takes place via a transition state that has a σ-complex configuration rather than the formerly suggested π-complex structure. This transition state possesses a reactant-like geometry; the forming CC bond is very long and the methylene group undergoes attack and is only slightly tilted out of the plane defined by the rest of the ethylenic moiety. The latter involves only a small change in hybridization of the attacked carbon atom during passage from the reactant to the transition state. The calculated electron distribution at the transition state indicates a weak electrophilic behavior of these σ-radicals towards ethylene. The above conclusions are identical to those attained in previous theoretical studies on the addition of methyl radical to olefins. The relatively low activation energy found for the above σ-radical addition reactions is mainly due to the intramolecular destabilization of the ethylene and radical fragments, reflecting the weak geometrical distorsion undergone by both reactants. On the other hand, the intermolecular interaction between these fragments leads to a considerable stabilization of the transition state.

In the case of the cyclopropyl addition reaction, the structure found for the transition state is further supported by the calculated low value of the secondary kinetic deuterium effect, that agrees fairly well with experiment. Hence, the hypothesis of a π-complex transition state is not only ruled out by the present UMINDO/3 calculations but ruled unnecessary to explain the observed KIE. As in the case of the addition of methyl to ethylene, the whole vibrational contribution to the KIE calculated for the addition of cyclopropyl is due to new normal modes created at the transition state rather than to a differential change in some vibrational frequencies of the reactants. Judging by these results, we suggest that the last is a common characteristic of all intermolecular radical addition reactions to unsaturated hydrocarbons.

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Registry No. Vinyl, 2669-89-8; cyclopropyl, 2417-82-5; ethylene, 74-85-1; deuterium, 7782-39-0.