

# Theoretical Study of Regioselectivity in Radical Additions to Substituted Alkenes. 1. Hydrogen Addition to Ethylene, Vinylamine, and Vinylborane

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**Abstract:** Hydrogen atom addition to ethylene, vinylamine, and vinylborane has been studied by UHF 3-21G + CIPSI calculations, with all important structures fully optimized by a gradient procedure. A net improvement is observed when polarization functions are introduced for the attacking radical. Entropies, Arrhenius parameters  $A$  and  $E_a$ , as well as absolute rate constants are calculated for the five reactions. The main results are the following: (1) Steric effects, as measured by the EX term of the Kitaura-Morokuma analysis, amount to 3-6 times the calculated barrier height, even for highly exothermic reactions. Despite the importance of steric effects, the preferential site of attack is not necessarily the site with the smaller steric repulsion. (2) The sum ES + CT + PL, corresponding to polar effects, equals roughly two-thirds of the EX term. However, a nucleophilic (electrophilic) radical will not prefer necessarily an attack on the site with the lower (higher) electronic density. (3) The molecular deformation DEF term, which correlates with the early character of the transition state, appears to be a good regioselectivity predictor. The scope and limitations of Canadell's rule are also discussed.

## I. Introduction

In sharp contrast with ionic additions to alkenes, whose regioselectivity is easily predicted by a single rule (the electrophilic reagent adds preferentially to the center having the higher electron density), radical additions give rise to a highly complex pattern of orientation. In review articles summarizing some 15 years of research work,<sup>2a,b</sup> Tedder and Walton emphasized that "no simple property could be used to determine the orientation of free radical additions" which depends on "the complex interplay of polar, steric and bond strength terms". In 1982, Tedder has proposed no less than five rules for the factors governing radical additions.<sup>3</sup> These rules are the following:

- (1) For steric reasons, a free radical will invariably prefer to add to the unsubstituted end of a monosubstituted olefin.
- (2) Conjugating substituents tend to enhance the rate of addition at the remote end of the double bond. Lone pairs, however, have only a small effect.
- (3) Polarity can have a major effect on the overall rate of addition.
- (4) For polysubstituted olefins, the regioselectivity is controlled principally by the degree of steric compression associated with forming the new bond.
- (5) Even when the regioselectivity is essentially controlled by steric compression, its magnitude can be influenced by polarity.

Recently, Giese<sup>4</sup> has formulated several rules, fundamentally similar to Tedder's, in which the important difference between  $\alpha$  and  $\beta$  substituent effects is stressed.

- (1) The regioselectivity is mainly determined by steric effects.
- (2) Substituents at the carbon of the alkene that is not attacked ( $\beta$  substituents) exert, on the whole, only polar effects on the rate of addition of free radicals.
- (3) Substituents at that carbon atom of the alkene which is attacked ( $\alpha$  substituents) exert both polar and steric effects on the rate of addition of free radicals.
- (4) Substituents at the radical center exert polar and steric effects on the rate of addition of alkenes.
- (5) The transition states for addition of alkyl radicals to alkenes lie so early on the reaction coordinate that the polar substituent effects can be described in terms of the frontier orbital theory.

Although many theoretical studies of radical additions have been published,<sup>5-8</sup> to the best of our knowledge, only in the paper of Koutecky, Koutecky, and Salem<sup>8a</sup> and in that of Poblet, Canadell, and Sordo<sup>6b</sup> has the general problem of regioselectivity been explicitly dealt with. Canadell and his co-workers suggested that the orientation is controlled by the SOMO-HOMO interaction. Koutecky, Koutecky, and Salem used a simple VB treatment with a three-center three-electron model and found that (1) if the attacking radical has approximately the same electronegativity as the carbon termini of the double bond, the reaction will most likely be under thermodynamic control and (2) if the electronegativity of the attacking radical is substantially different from that of the double bond termini, ionic factors will favor attack of an electronegative reagent at the unsubstituted end of electron-rich olefins and attack at the substituted end of electron-poor olefins. For an electropositive reagent, the predictions should be reversed.

Tedder's, Giese's, Canadell's, and KKS's rules thus provide some essential answers to the problem of orientation in radical additions. A better understanding of the scope and limitations of these rules requires, however, more precise information on several points.

In particular, although, according to Tedder and Giese, steric factors will normally prevail, Beckwith<sup>2d</sup> has remarked that "the

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(6) Addition of methyl radical: (a) Basilevsky, M. V.; Chlenov, I. E. *Theoret. Chim. Acta* 1969, 15, 174. (b) Hoyland, J. R. *Ibid.* 1971, 22, 229. (c) Fujimoto, H.; Yamabe, S.; Minato, T.; Fukui, K. *J. Am. Chem. Soc.* 1972, 94, 9205. (d) Nagase, S.; Takatsuka, K.; Fueno, T. *Ibid.* 1976, 98, 3838. (e) Clark, D. T.; Scanlan, I. W.; Walton, J. C. *Chem. Phys. Lett.* 1978, 55, 102. (f) Dewar, M. J. S.; and Olivella, S. *J. Am. Chem. Soc.* 1978, 100, 5290. (g) Canadell, E.; Poblet, J. M.; Olivella, S. *J. Phys. Chem.* 1983, 87, 424. (h) Poblet, J. M.; Canadell, E.; Sordo, T. *Can. J. Chem.* 1983, 61, 2068.

(7) Addition of fluorine atom: (a) Worry, G.; Marcus, R. A. *J. Chem. Phys.* 1977, 67, 1636. (b) Zvijac, D. J.; Mukamel, S.; Ross, J. *Ibid.* 1977, 67, 2007. (c) Hase, W. L.; Bhalla, K. C. *Ibid.* 1981, 75, 2807. (d) Schlegel, H. B. *J. Phys. Chem.* 1982, 86, 4878. (e) Schlegel, H. B.; Bhalla, K. C.; Hase, W. L. *Ibid.* 1982, 86, 4883. See also ref 6e.

(8) Addition of chlorine atom: (a) Koutecky, V. B.; Koutecky, J.; Salem, L. *J. Am. Chem. Soc.* 1977, 99, 842. (b) Quack, M. *Chem. Phys.* 1980, 51, 353. See also ref 5k.

(1) Associated with the CNRS (UA 506).

(2) (a) Tedder, J. M.; Walton, J. C. *Acc. Chem. Res.* 1976, 9, 183. (b) Tedder, J. M.; Walton, J. C. *Tetrahedron* 1980, 36, 701. See also: (c) Rüchardt, C. *Top. Curr. Chem.* 1980, 88, 1. (d) Beckwith, A. L. *J. Tetrahedron* 1981, 37, 3073.

(3) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 401.

(4) Giese, B. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 753.

outcome of homolytic additions to rigid or conformationally biased cyclic olefins is often consistent with the concept of stereoelectronic control". Moreover, Boldt and his co-workers<sup>9</sup> found a quite good correlation between superdelocalizability indexes, calculated by MINDO-3, and experimental kinetic data (relative rates or activation energies) for the additions of dicyanomethyl and trifluoromethyl radicals. These authors stated that, at least for *n*-alkyl and vinyl substituents, "the influence of steric effects can be neglected". A quantitative comparison of the respective influences of steric, polar, and stereoelectronic factors is therefore deemed necessary, especially in view of the more complicated case of polysubstituted olefins, where the difference of steric compression on competitive sites cannot always be easily appreciated. In any case, a good estimate of the order of magnitude of each intervening factor is a prerequisite for accurate predictions of the orientation which, as mentioned earlier, is the result of a delicate balance between several conflicting influences.

The major difficulty which then arises is due to the fact that, although steric and polar effects are widely used in a qualitative manner, their precise definitions vary with the authors. For example, Tedder and Walton<sup>2a</sup> suggested that polar influences can be expressed in terms of the electronegativity difference between the radical and the attacked site of the alkene. This has been taken as a fundamental assumption in the work of Koutecky, Koutecky, and Salem.<sup>8a</sup> Giese<sup>4</sup> considered that, at least for early transition states, polar effects can be described by the frontier orbital theory.

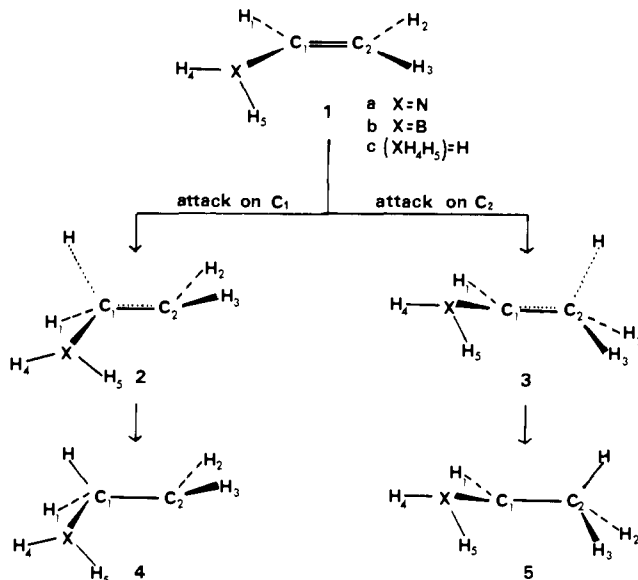
These two points of view are clearly related but not identical. Since stereoelectronic control can also be described in terms of the frontier orbital theory, can we consider that polar and stereoelectronic effects are but two aspects of the same orbital interactions, the difference being that, for polar effects, the accent is put on energy levels and electronic cloud distortion, while for stereoelectronic effects, the emphasis is on the change of overlap with the reagent's direction of approach? Last, but not least, what are exactly steric effects for two compounds interacting at large distances? Does this term mean essentially Coulombic repulsion, exchange repulsion, or structural deformation?<sup>2b,10</sup>

Another problem concerns the localization of the transition state on the reaction path. In his fifth rule (*vide supra*), Giese was careful to specify that the transition state is early for *alkyl radical* additions and gave no indication for other radicals. Clark, Scanlan, and Walton<sup>6c</sup> reviewed evidences for early as well as for late transition states and concluded from their calculations that in the reaction of F· with ethylene, "whilst geometry and total spin density indicate an early transition state, the considerable degree of charge separation of the  $\alpha$  and  $\beta$  electrons together with the partial transfer of a  $\beta$  electron to form the C-F bond (and consequent weakening of the double bond) correlate with a late transition state". This subtle distinction raises several related questions. Does an "early" transition state necessarily imply a "loose" structure with little bond formation and little change in the alkene and radical geometries? If this is the case, is it still possible to consider that steric effects remain predominant even when the distance between the reactants is large? Tedder and Walton<sup>2b</sup> gave an affirmative answer, observing that the "the experimental evidence is that appreciable bond deformation occurs very early in the addition process". On the other hand, Rüdhardt<sup>2c,10</sup> stressed the importance of polar effects in this type of reactions, cited several examples where steric effects introduced relatively small rate retardations or selectivity increases, and pointed out that, in the extreme case of Kornblum  $S_{RN}1$ -substitution reaction, bonds between two quaternary carbons can be formed with great ease and in good yields.

In this paper, we report an *ab initio* MO study of hydrogen atom addition to ethylene, vinylamine, and vinylborane, with the hope that the results presented here may contribute to the solution of some of these questions.

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## II. Methods and Results

**A. Computational Details: Models and Methods.** Vinylamine and vinylborane were taken as models for an electron-rich and an electron-poor alkene, respectively. Although more realistic a model than vinylborane, acrylonitrile has not been retained because the cyano group contains two heavy atoms and furthermore gives rise to computational difficulties. Indeed, the geometry of cyano compounds is quite sensitive to the method used (e.g., UHF or RHF-CI), and their energy requires CI calculations involving at least quadruple excitation terms.<sup>11</sup> Fluoroethylene has not been chosen for two reasons: (a) fluoro compounds generally require extended basis sets and (b) the comparison with vinylamine would be more delicate, the fluoro substituent being electron-withdrawing by inductive effect while the amino group is electron-releasing by conjugating effect.

*Ab initio* UHF calculations were carried out with the MONSTERGAUSS program<sup>12</sup> using a split-valence 3-21G basis set. A significant improvement was observed when the attacking H atom was described with added p functions (*vide infra*, section II-C). Equilibrium and transition structures were fully optimized by a gradient procedure. The effect of electron correlation on the potential energy barriers was estimated by performing, on these UHF/3-21G optimized geometries, RHF calculations followed by configuration interaction employing the CIPSI algorithm.<sup>13</sup> A subroutine adapted from the GAUSSIAN 80 program<sup>14</sup> was used for the calculation of zero-point energy and internal energy temperature corrections, as well as vibrational frequencies and entropy changes. Semiquantitative analysis of the influence of different factors is made at the UHF/3-21G level by partitioning, according to the Kitaura-Morokuma scheme,<sup>15</sup> the energy change (activation energy or reaction energy) into a sum of almost independent contributions: deformation energy DEF, intermolecular electron-exchange energy EX, electrostatic interaction ES, charge transfer CT and polarization PL of one reactant by its partner. A last contribution, termed MIX, takes into account an eventual coupling of these various effects.

**B. Geometries. Addition of H· to Ethylene.** The optimized structures of ethylene (1c), of the transition state 2c, and of ethyl radical 4c, being identical with those published by Schlegel,<sup>7d</sup> are therefore not reproduced here.

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(12) MONSTERGAUSS (June 1981); Peterson, M.; Poirier, R. Chemistry Department, University of Toronto, Ontario, Canada.

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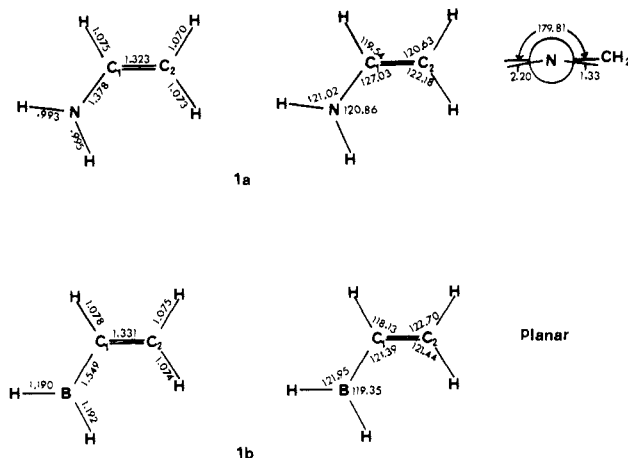


Figure 1. Fully optimized structures (UHF/3-21G) of vinylamine (**1a**) and vinylborane (**1b**).

**Addition of H· to Vinylamine.** The optimized structure of the substrate vinylamine (**1a**) is shown in Figure 1. (The structure optimized with the 6-31G\* basis set is slightly different from that calculated with the 3-21G basis set.<sup>16</sup>) Those of the products (primary and secondary aminoethyl radicals **4a** and **5a**) and of the corresponding transition states **2a** and **3a** are presented in Figure 2. For each structure, two Newman projections, along  $NC_1$  and  $C_1C_2$ , are also given.

Let us comment first on the structures of the product radicals. In the primary radical **4a**, the radical site is practically planar: the sum of the bond angles around  $C_2$  being  $358.55^\circ$ . (The radical site lacking a 3-fold axis of symmetry; its angle of pyramidalization cannot be unequivocally defined. We have therefore taken the sum of the three bond angles around this site as a crude measure of deviation from planarity: the larger the difference of this sum with  $360^\circ$ , the more pyramidalized the site.) The nitrogen atom is clearly pyramidalized ( $\sum\angle N = 338.33^\circ$ ). The conformation shown in Figure 2 has the nitrogen lone pair anti to a  $C_1H$  bond, as can be easily seen on the Newman projection along  $NC_1$ . The conformation of **4a** in which the lone pair is anti to the  $C_1C_2$  bond, when fully optimized, is only 0.04 kcal/mol lower in energy, an insignificant difference at this level of calculations (UHF/3-21G).

In the secondary aminoethyl radical **5a**, the nitrogen lone pair is conjugated with the singly occupied orbital, and it is well-known that a three-electron interaction is attractive for small values of the overlap but becomes repulsive when the overlap is too large.<sup>17</sup> It is interesting to note that the optimum overlap in **5a** has been obtained by a combination of two antagonistic effects: an increasing planarity of the nitrogen atom ( $\sum\angle N = 349.94^\circ$  vs.  $338.33^\circ$  in **4a**) which tends to augment the  $N-C_1$  overlap and an increasing pyramidalization of the radical site ( $\sum\angle C_1 = 349^\circ$  in **5a**, to be compared with  $\sum\angle C_2 = 358.55^\circ$  in **4a**) which tends to diminish the overlap. Finally, N and  $C_1$  are pyramidalized roughly to the same extent with the  $NC_1$  fragment in a staggered conformation.

Let us now turn to the transition states. In **2a**, when the hydrogen atom approaches  $C_1$  from the upper side, the latter starts to pyramidalize, bending  $H_1$  and N downward ( $\angle H_1C_1C_2 + \angle H_1C_1N + \angle NC_1C_2 = 356.63^\circ$ ). At the same time,  $C_2$  starts to pyramidalize upward, although the deviation from planarity is negligible ( $\sum\angle N = 359.84^\circ$ ). The amino group, practically planar in vinylamine, loses its planarity as conjugation is destroyed ( $\sum\angle N = 350.52^\circ$ ). The hydrogens linked to N are bent upwards and the  $NC_1$  bond rotates slightly so that the nitrogen lone pair becomes anti to the incipient  $HC_1$  bond. Therefore, in the transition state, the conformation is already staggered with respect to both the  $NC_1$  and  $C_1C_2$  bonds. Notice that the  $HC_1$  distance is large

Table I. Barrier Heights (in kcal/mol) at Different Computational Levels

level of calculation	addition to ethylene	addition to vinylamine		addition to vinylborane	
		on $C_1$	on $C_2$	on $C_1$	on $C_2$
UHF/3-21G	2.26	6.73	3.44	0.94	1.42
UHF/(3-21G+p) <sup>a</sup>	2.13	6.34	3.21	0.73	1.32
RHF/3-21G/CI <sup>b</sup>	7.6	8.87	6.13	3.79	6.07
RHF/3-21G + p/CI <sup>b</sup>	3.77	6.16	1.70	1.17	2.18

<sup>a</sup> The notation 3-21G + p means that the alkene has been calculated with the 3-21G basis set but that p functions have been added to the attacking hydrogen atom. <sup>b</sup> Configuration interaction has been performed with the CIPSI program.<sup>13</sup> All determinants with a coefficient higher than 0.02 have been incorporated in the S space.

(1.845 Å) and the  $C_1C_2$  bond lengthening rather small (0.05 Å, i.e., 28% of the total bond lengthening when going from **1a** to **4a**): **2a** may be considered as reactant-like.

The geometrical deformations in **3a** are even smaller: the deviation from planarity is nil for  $C_1$  ( $\sum\angle C_1 = 359.93^\circ$ ) and negligible for  $C_2$  and N ( $\sum\angle C_2 = 358.03^\circ$  and  $\sum\angle N = 358.96^\circ$ ). The  $HC_2$  distance in **3a** is 1.958 Å, greater than the  $HC_1$  distance in **2a**. The  $C_1C_2$  bond stretching is only 0.032 Å, which corresponds to 17% of the difference  $1.509 - 1.323$  Å (CC bond lengths in **1a** and **5a**). It seems then reasonable to suppose that **3a** is an earlier transition state than **2a**. To confirm this hypothesis, we must delve into the reaction energetics (vide infra, section III-A).

**Addition of H· to Vinylborane.** The optimized structure of vinylborane (**1b**) is shown in Figure 1; those of the transition states **2b** and **3b** and of the corresponding product radicals **4b** and **5b** are in Figure 3.

A major difference with the vinylamine case is that the radical site and the boron atom remain planar here. Even for the attacked site, pyramidalization is nil (**2b**:  $\sum\angle C_1 = 359.99^\circ$ ) or negligible (**3b**:  $\sum\angle C_2 = 359.54^\circ$ ). But the most striking feature comes from the comparison of the dihedral angles containing the incoming H atom:  $HC_1C_2N = 112.93^\circ$  in **2a** and  $HC_1C_2B = 75.17^\circ$  in **2b**. The H atom thus apparently behaves as a "nucleophilic" radical, being attracted by the vacant orbital on B and repelled by the N lone pair. The attraction by boron is so strong that in the transition state **2b**, the  $H\cdots B$  distance is shorter than the  $H\cdots C_1$  distance (2.15 vs. 2.21 Å). (Nevertheless, **2b** is the transition state for H addition to  $C_1$  and *not* the transition state for H addition to B, as can be shown by an analysis of the reaction coordinate.) Polar effects will be discussed in more details in section III-B.

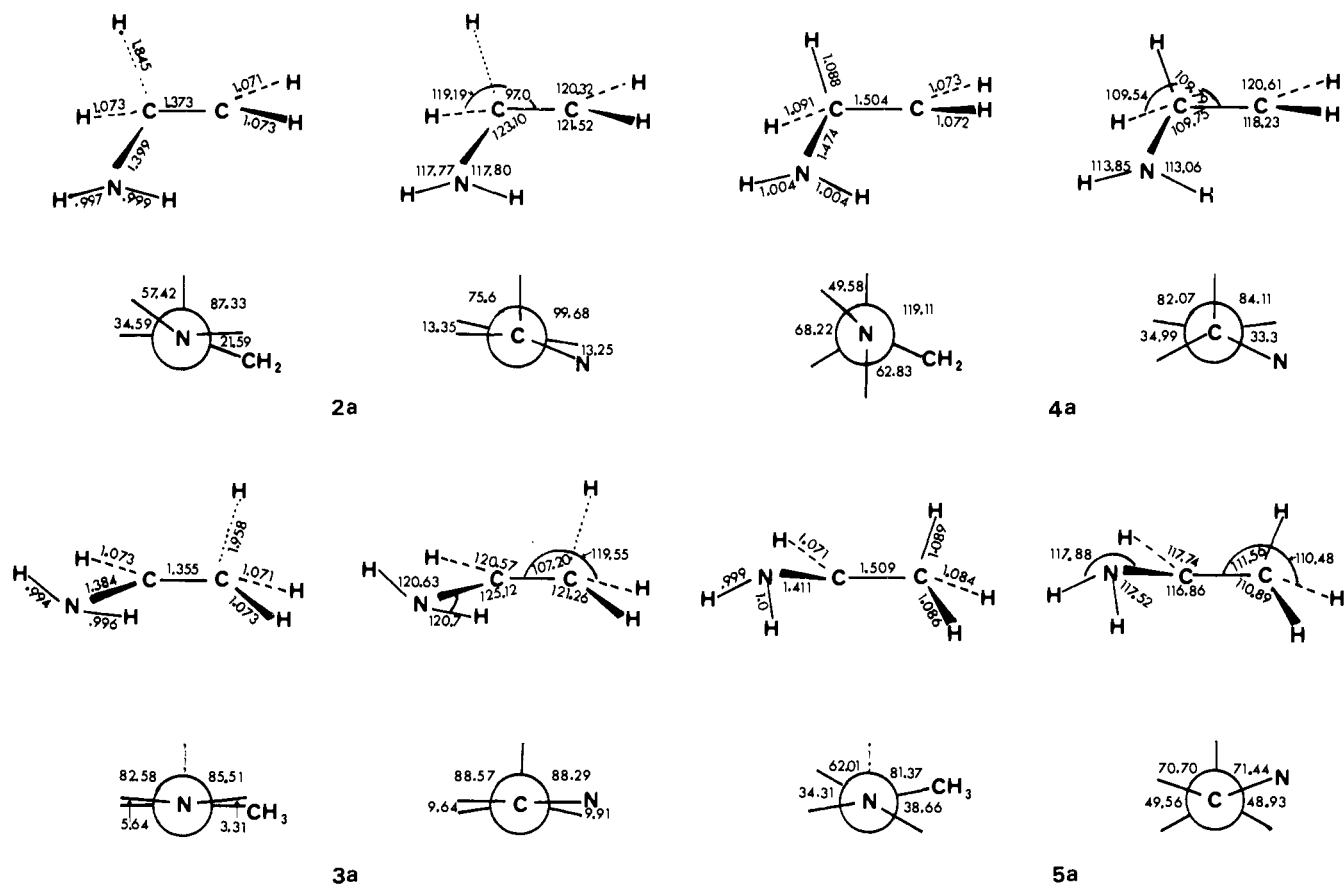
**C. Regioselectivity. Dependence of the Barrier Heights on the Computational Level.** Table I reports the changes of barrier heights (i.e., the differences between the HF or HF-CI energies of the transition states and of the starting compounds) with the computational level. This comparison has been triggered by Schlegel's intriguing observation<sup>7c</sup> that low barrier heights (2.27 or 2.9 kcal/mol) for the hydrogen addition to ethylene are obtained with the 3-21G or 6-31G\* basis sets only at the HF level. Inclusion of the Moller-Plesset correlation energy, up to the fourth order, shoots the barrier up to  $\sim 9$  kcal/mol. That the results are rather worse with the 6-31G\* than with the 3-21G basis set suggests that the former set is unbalanced: one of the reactants ( $H\cdot$ ) is not as well described as its partner ( $C_2H_4$ ). Transition states, where both the reactants intervene, should be particularly sensitive to such an effect, which explains why the barrier height increases when the basis set is "improved" from 3-21G to 6-31G\*. Configuration interaction lowers more the energy of the initial system and accentuates the difference.

If this interpretation is correct, a better  $H\cdot$  description should reduce the calculated barrier height. Indeed, Table I shows that addition of polarization functions to the attacking hydrogen atom gives, after CI, a barrier height of 3.77 kcal/mol which is in satisfactory agreement with experimental results ( $2.04 \pm 0.08$  kcal/mol) and compares excellently with the value of 3.7 kcal/mol obtained by Harding<sup>18</sup> with a large basis set and extensive CI.

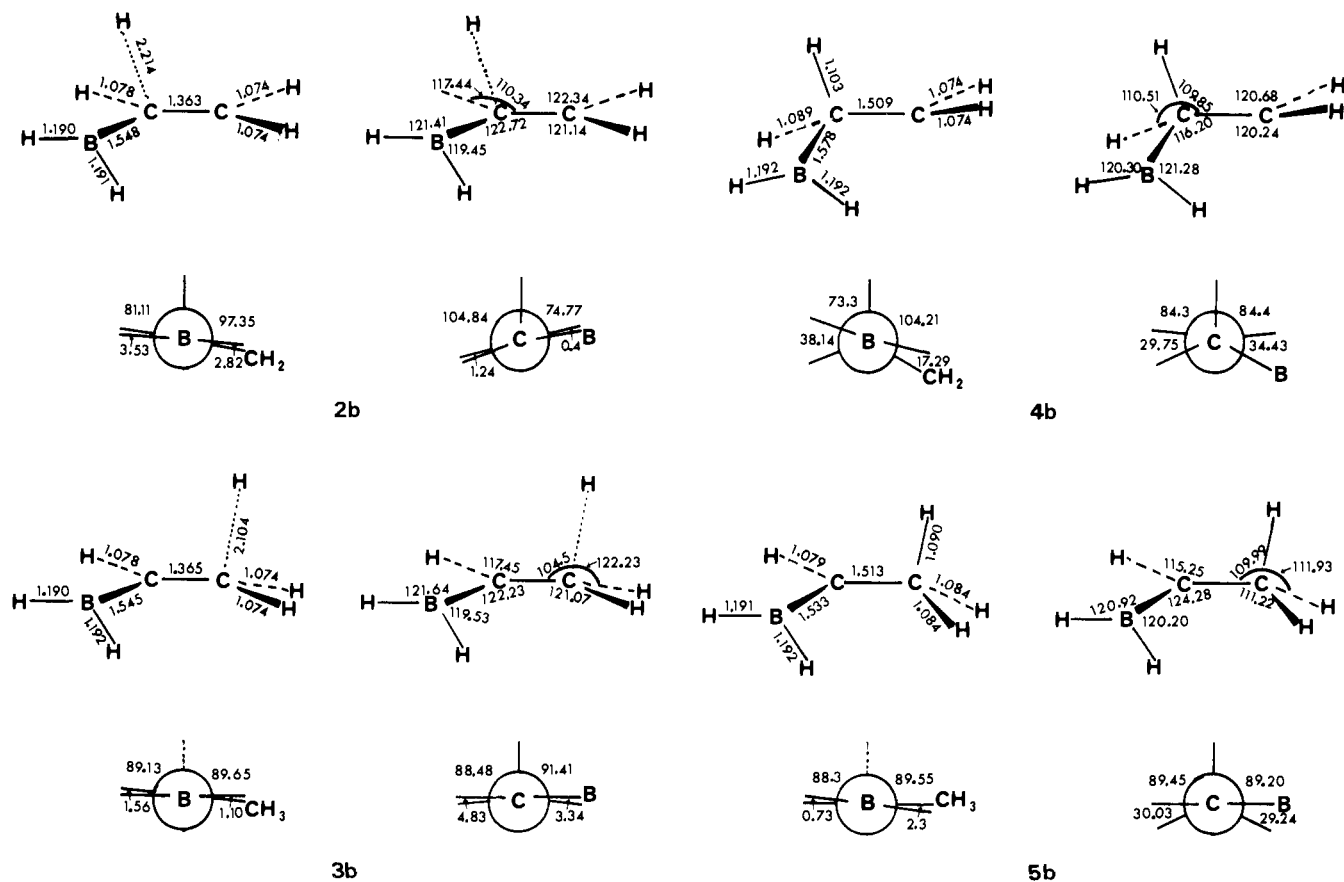
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(18) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469.



**Figure 2.** Addition of H $\cdot$  to vinylamine (1a). Fully optimized structures (UHF/3-21G) of the transition states 2a and 3a and of the final aminoethyl radicals 4a and 5a.



**Figure 3.** Addition of H $\cdot$  to vinylborane (1b). Fully optimized structures (UHF/3-21G) of the transition states 2b and 3b and of the product radicals 4b and 5b.

**Table II.** Calculated Partial Rate Constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for H Addition to Ethylene, Vinylamine, and Vinylborane

	198 K	298 K	398 K	498 K
Ethylene <sup>a</sup>				
$10^{13}k$	0.23	2.83	11.75	31.5
$10^{13}k_{\text{exptl}}^b$	2	11.3	31	44
Vinylamine				
$10^{13}k_1^c$	$7.3 \times 10^{-8}$	$5.8 \times 10^{-5}$	$1.9 \times 10^{-3}$	$1.7 \times 10^{-2}$
$10^{13}k_2$	$1.9 \times 10^{-9}$	$6.6 \times 10^{-2}$	$4.7 \times 10^{-1}$	1.7
$k_1/k_2$	$3.9 \times 10^{-5}k$	$8.7 \times 10^{-4}$	$3.9 \times 10^{-3}$	$1.0 \times 10^{-2}$
Vinylborane				
$10^{13}k_1^c$	8.1	33	81	159
$10^{13}k_2$	2.6	15	44	96
$k_1/k_2$	3.1	2.2	1.84	1.66

<sup>a</sup> The symmetry number has been omitted (see text). <sup>b</sup> Reference 20. <sup>c</sup>  $k_1$  and  $k_2$  refer to the rate constants for addition to  $C_1$  and  $C_2$ , respectively.

(Schlegel et al.<sup>7c</sup> have also suggested that "polarization functions on hydrogen and singly excited configurations may be important". See also ref 5k for another example of where the 6-31G\* gives worse results than the 3-21G basis set.)

Table I also shows that the regioselectivity trends are always the same: at any level of calculation, attack on  $C_2$  is preferred for addition to vinylamine, while attack on  $C_1$  is preferred for addition to vinylborane. For this reason and in order to avoid prohibitive costs, all the remaining calculations are performed with the 3-21G basis set.

**Rate Constants.** The vibrational frequencies, zero-point energy corrections, temperature corrections for internal energy, entropies, and Arrhenius parameters  $A$  and  $E_a$  for the various structures are reported in the Appendix section.

Table II shows the partial rate constants for H atom addition to ethylene, vinylamine, and vinylborane calculated at four different temperatures: 198, 298, 398, and 498 K. In these calculations, the symmetry number has been omitted. In other words, it is supposed that attack by the reagent leads to only one transition state. For comparison with experimental values, the rate constants of Table II have to be multiplied by a statistical factor which is the number of equivalent activated complexes that can be formed if all identical atoms in the reactants are labeled.<sup>19</sup> Thus, the rate constant  $k$  for addition to ethylene must be multiplied by 4. In the same way, the global rate which would be experimentally observed for addition to a substituted ethylene is equal to  $2k_1 + 2k_2$ , where  $k_1$  and  $k_2$  are, respectively, the calculated values for attack on  $C_1$  and  $C_2$ .

Comparison of the calculated and the experimental values<sup>20,21</sup> for ethylene indicates a good agreement only at 298 K (calculated  $k$ ,  $11.32 \times 10^{-13}$ ; experimental,  $11.3 \times 10^{-13}$ ). At 198 K the rate constant is underestimated while it is overestimated at 398 and 498 K. However, as the rate increases with the temperature, the general trend is correctly reproduced. With respect to ethylene, the rates of H addition to vinylamine are decreased whereas the rates for addition to vinylborane are increased, independently of the attacked site. The H atom thus behaves as a nucleophilic radical. The regioselectivity, as measured by the  $k_1/k_2$  ratio, is higher for vinylamine than for vinylborane and decreases when the temperature is raised.

### III. Discussion

**A. Steric Effects and Regioselectivity. Correlation with Early and Late Transition States.** Qualitatively, steric effects may be considered as describing the obvious observation that two solids cannot occupy the same space at the same time. Quantitative estimates of steric repulsion require a more precise definition. In order to use the Kitaura-Morokuma energy partition analysis,<sup>15</sup> we conventionally assimilate steric repulsions to exchange re-

pulsion and exchange repulsion only. Electrostatic repulsions are thus classified as polar, not steric, effects.

Our definition of steric effects is more restrictive than others found in the literature. In particular, Rüchardt<sup>10</sup> remarked that "any influence that tends to reduce the angle between orbitals or bonds will encounter strong resistance" because it will shorten the distance between nonbonded atoms. Tedder and Walton<sup>2b</sup> extended this idea further and wrote that "any radical addition to an olefin involves just such angle changes and, even though the reaction is exothermic and the transition state therefore early, nonetheless, the experimental evidence is that appreciable bond deformation occurs very early in the addition process".

Now it is interesting to note that in the Morokuma analysis, there is a DEF term which represents the energy required to bring, in the absence of the reagent, the substrate (ethylene, vinylamine, or vinylborane) from its initial geometry to its transition or final structure. This term, thus, much resembles the bond deformations considered by Tedder and Walton to be a manifestation of steric effects for early transition states where the reactants interact at large distances. Despite this resemblance, it is not deemed justified to treat DEF as a pure steric contribution. As a matter of fact, the molecular deformation in the transition state is a compromise between two antagonistic influences. The energetic cost of the deformation is compensated by a better interaction with the incoming reagent, leading to a greater stabilization. (Indeed, Morokuma has pointed out that the DEF term is the molecular analogue of the promotion energy of an atom from its ground state to its valence state.) If the bonding interactions are strong, the DEF term will be small. If they are feeble, the substrate must be "better prepared" and consequently the DEF term will be large. It seems therefore more reasonable to correlate DEF, not with steric repulsions but with the localization of the transition state on the reaction path: the smaller the DEF value, the earlier the transition state.

To check the consistency of this correlation, comparison with other criteria for earliness is made, using as examples the four transition states **2a**, **3a**, **2b**, and **3b**. As stated in section II-B, Figure 2 suggests that **3a** is an earlier transition state than **2a**: the angular deformations are smaller, as is the  $C_1C_2$  bond lengthening whereas the distance of approach of the H atom is larger. This agrees with the indications of Mulliken population analysis, the relative change in the  $C_1C_2$  overlap population being 28% for **3a** and 42% for **2a**. A glance at Table III shows that DEF is also smaller for **3a** than for **2a**, both in absolute values (1.86 vs. 5.28 kcal/mol) and in relative values (the ratios of the transition-state DEF to the corresponding product DEF being, respectively, 4.68% and 10.83%).

A similar comparison can be made with **2b** and **3b**. It is interesting to note that both the geometrical characteristics (Figure 3) and the DEF values point to an earlier character for **2b** compared to **3b**, although addition to  $C_1$  is less exothermic than addition to  $C_2$  (Table III). This may be attributed to the favorable interaction between the incoming H• and the boron atom, which renders the  $C_1H$  bond forming easier and displaces the transition state toward the reactants. This may be illustrated schematically by the Bell-Evans-Polanyi plot<sup>22</sup> shown in Figure 4. "Normal" bond breaking and bond forming are approximated by families of noncrossing curves (straight lines are used in Figure 4 for simplicity sake): in this case, the more exothermic the reaction, the earlier the transition state. However, the strongly attractive B...H interactions introduces a curvature and the  $C_1H$  bond forming corresponds to the solid curve and not the straight dotted line. The two BF lines then cross and **2b** is "earlier" than **3b** although the reaction is less exothermic.

Let us now analyze more closely the problem of regioselectivity with the help of the energy partition scheme (Table III). The first observation which can be made is that the EX (exchange

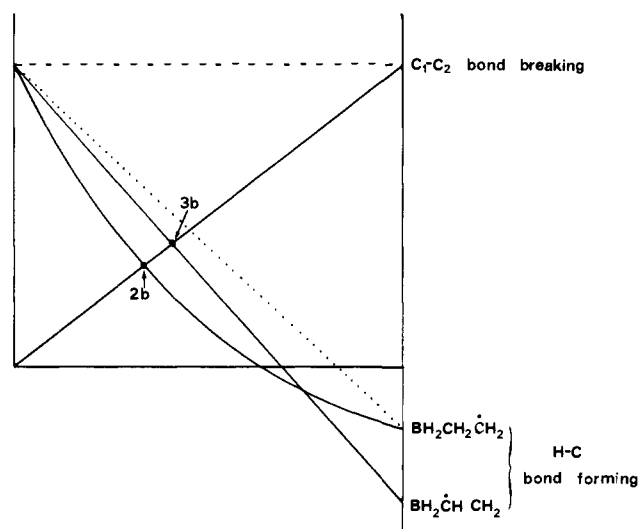
(19) Murrell, N. J.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371.  
 (20) Sugawara, K.; Okazaki, K.; Sato, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2872. The values given correspond in fact to 211, 297, 401, and 461 K.  
 (21) Nagase, S.; Morokuma, K. *J. Am. Chem. Soc.* **1978**, *100*, 1666.

(22) Evans, M. G.; Polyanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340. Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *A154*, 414. Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Press: New York, **1975**; p 212.

**Table III.** Energetics of Hydrogen Addition to Ethylene, Vinylamine, and Vinylborane, Obtained by UHF/3-21G Calculations: All Energies Are in kcal/mol

	alkene										
	ethylene, 1c		vinylamine, 1a				vinylborane, 1b				
	site of attack	heat of reaction	substituted carbon C <sub>1</sub>		unsubstituted carbon C <sub>2</sub>		substituted carbon C <sub>1</sub>		unsubstituted carbon C <sub>2</sub>		
barrier height	2.26	-41.7	-31.4	-39.8	-34.0	-46.6	2.26	6.73	3.44	0.94	1.42
Morokuma analysis	transition state	product <sup>a</sup>	transition state 2a	product 4a	transition state 3a	product 5a	transition state 2b	product 4b	transition state 3b	product 5b	
DEF	1.78	42.9	5.28	48.76	1.86	39.71	0.88	32.30	1.23	38.10	
INT <sup>b</sup>	0.48	-83.8	1.44	-80.18	1.57	-79.44	0.06	-66.30	0.19	-84.31	
EX	18.09	215.2	32.28	220.63	23.48	235.47	15.81	214.91	13.25	195.96	
CT	-5.24	-172.5	-10.17	-162.39	-7.96	-159.17	-4.74	-149.06	-4.02	-145.09	
ES	-7.05	-73.0	-12.71	-74.55	-9.98	-88.03	-5.64	-73.26	-5.04	-62.97	
PL	-0.28	-23.4	-0.85	-24.50	-0.50	-24.05	-0.28	-21.87	0.14	-23.16	
MIX	-5.04	-30.1	-7.10	-39.37	-3.48	-43.66	-5.10	-37.02	-3.86	-49.05	

<sup>a</sup>The Morokuma analysis for the ethyl radical is taken from ref 21 in which the 4-31G basis set is used. <sup>b</sup>The INT term is the sum EX + CT + ES + PL + MIX. The sum DEF + INT for the transition state (product) is equal to the barrier height (heat) of the reaction.

**Figure 4.** Bell-Evans-Polanyi plot for H• addition to vinylborane.

repulsion) term is, by far, the largest term in all cases. This confirms the importance of steric effects, even for early transition states. As a matter of fact, according to the rules given by Benson,<sup>23</sup> the sum of the van der Waals radii for H and C may be estimated to be  $1.3 + 1.7 = 3 \text{ \AA}$ , a value superior to the H...C distance in the transition states **2a**, **2b**, **3a**, and **3b**. It is therefore not surprising that the nonbonded interactions may be quite sizable.

In spite of the important steric effects, the preferential site of attack is *not* always the site with the smaller EX term (compare **2b** and **3b**). On the other hand, we may note that the DEF term correlates quite well with the barrier height  $V^*$  or the activation energy. The correlation is even better if we compare the difference for attacks on C<sub>1</sub> and C<sub>2</sub>, as shown in Table IV. Only  $\Delta\text{DEF}$  appears to be a good estimate for  $\Delta E_a$ , which, in turn, is a measure of the regioselectivity.

That DEF is a much better predictor for regioselectivity than EX may be expected. Indeed Tedder and Walton have emphasized that no simple property could be used to determine the orientation. Therefore, if we want to use just one reactivity index, this index must enclose, in a properly balanced manner, all the major factors, the attractive as well as the repulsive ones. As discussed above, this is exactly what the DEF terms are. (The INT term, by definition, is a combination of several factors. It contains all the attractive terms but excludes the repulsive DEF term: the combination is not well balanced and cannot approximate  $V^*$  or  $E_a$ ). As DEF also correlates with the early or late character of the

**Table IV.** Tentative Use of the Various Terms of the Energy Partition as Regioselectivity Predictors: All Values Are in kcal/mol

	addition to vinylamine	addition to vinylborane
$E_a^{(1)} - E_a^{(2)}$		
198 K	3.7	-0.4
298 K	3.6	-0.4
398 K	3.5	-0.4
498 K	3.5	-0.4
$V_1^* - V_2^*$	3.29	-0.48
$\text{DEF}_1 - \text{DEF}_2$	3.42	-0.35
$\text{EX}_1 - \text{EX}_2$	8.8	2.56
$\text{CT}_1 - \text{CT}_2$	-2.21	-0.72
$\text{ES}_1 - \text{ES}_2$	-2.73	-0.6
$\text{INT}_1 - \text{INT}_2$	-0.13	-0.13

transition state, this explains why the assumption of thermodynamic control (the preferred reaction is the more exothermic one) often gives good predictions. We can now furthermore specify the limitations of this hypothesis, using the language of the BEP treatment. If the curves describing the bond forming at the competitive sites do not cross, then thermodynamic control leads to good predictions. If, however, these curves do cross, then the rule no longer holds.

**B. Polar Effects.** Tedder's and Giese's rules indicate that the regioselectivity is mainly determined by steric effects, polar effects being the second most important factor. A rapid survey of the literature reveals that various criteria have been used for probing polar effects in radical reactions.

(1) The experimental evidence most frequently quoted is the influence of donor or attractor substituents on the rate of addition. Some radicals such as  $\text{CH}_3\cdot$  are termed "nucleophilic" because they add more easily to electron-poor alkenes than to electron-rich alkenes. The poorer the substrate, the higher the rate of reaction. The situation is reversed with the so-called "electrophilic" radicals, e.g.,  $\text{X}\cdot$  and  $\text{CX}_3\cdot$ .<sup>24</sup> In MO language, this amounts to saying that for nucleophilic (electrophilic) radicals, the SOMO-LUMO (SOMO-HOMO) interaction is predominant in the transition state.

(2) Charge-charge or dipole-dipole electrostatic interactions have also been invoked.<sup>25</sup> The orientation of radical addition to  $\text{CHF} = \text{CF}_2$  is often considered as a typical example, illustrating this type of interaction: the nucleophilic  $\text{CH}_3\cdot$  prefers to add to the more substituted end  $\text{CF}_2$ , while the electrophilic  $\text{CF}_3\cdot$  attacks preferentially at the  $\text{CHF}$  end. In MO calculations, the indexes corresponding to this criterion would be the electron-cloud distortion and/or the atomic charges.

(23) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 94.

(24) (a) Reference 2c, p 22. (b) Reference 3, p 407. (c) Reference 4, p 753. (d) Nonhebel, D. C.; Tedder, J. M.; Walton, J. C. "Radicals"; Cambridge University Press: New York, 1979; p 90. (e) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: New York, 1974; p 228, 278.

(25) Reference 24d, p 93. Reference 24e, p 166, 217.

(3) While most authors agree on the importance of polar effects, Abell, who focuses on solvent influences, states on the contrary that "polar effects have not been observed"! He concludes that "the lack of influence of solvent on the rate of many (addition) reactions indicates that the polarity effects probably enters into the polarizability of the transition state, with electron transfer and charge separation as the bond formation takes place".<sup>26</sup>

This apparent contradiction between Abell's and other authors' views is not completely unexpected. Although all the foregoing criteria (substituents effects on the rate, electrostatic interactions, solvent effects, etc.) are practically equivalent for the determination of polar effects in ionic reactions, they are not necessarily equivalent in radical reactions. The reactants having no net charges, polar effects are much smaller and some criteria become less well suited than others.

This point may be exemplified by the examination of the three transition states **2a**, **2b**, and **2c**. It has been mentioned earlier (section II-B) that in **2a** and **2b**, H· is respectively repelled by the N lone pair and attracted by the vacant orbital on the boron atom, thus behaving as a nucleophilic species. This structural criterion agrees with the kinetic data (Table II) which also point to a nucleophilic H·: the rate of addition being largest with vinylborane, intermediate with ethylene, and smallest with vinylamine.

If we look at the charge transfer between the substrate and reagent, it is found that electron density has been displaced from vinylamine and ethylene to H· in **2a** and **2c** (H net charges: -0.062e and -0.023e, respectively). In contrast, in **2b**, electron density is transferred from H· to vinylborane (H net charge: +0.014). In other words, H· appears to be nucleophilic with respect to vinylborane and electrophilic with respect to ethylene and vinylamine.

If we now try to determine the nature of the reagent observing the net charge at the site of attack, it is found that the preferential site of attack (i.e., C<sub>1</sub> in vinylborane and C<sub>2</sub> in vinylamine) is the one with the higher electron density. Thus, with the criterion, H· is always electrophilic! How can we explain that this criterion, which works quite well for ionic reactions, is much less satisfactory here? The reason is that the hydrogen SOMO, lying roughly at the nonbonding level, interacts about equally with the HOMO and LUMO of the substrate. Although the interaction with one frontier orbital may slightly predominate, the second interaction is not negligible. As the HOMO and LUMO are polarized in opposite senses, the influences of their electronic density partly cancel each other. The net result, being small, may be masked by "secondary" interactions with neighboring atoms, viz., N in vinylamine and B in vinylborane. An ancillary result follows: the apparent electronegativity of the attacked site should be a bad predictor for polar effects, being directly related to the net charge.

A semiquantitative estimate of the various polar factors magnitudes may be obtained with the help of the energy partition analysis. Table III shows that the contributions of the charge-transfer (CT) and electrostatic (ES) terms are similar, roughly one-third of the exchange repulsion (EX) and 1–2 times the barrier height. The polarization term (PL) is about 1 order of magnitude smaller. The ratio of "polar" to "steric" terms (ES + CT + PL)/EX is 69.5% in **2c** (ethylene), 74% and 78.5% in **2a** and **3a** (vinylamine), and 67.5% and 69.5% in **2b** and **3b** (vinylborane). It may seem surprising that this ratio is smaller for the reaction with vinylborane than for the reaction with ethylene. The reason is that the absolute value of each term depends on many parameters, among them the distance between the reactants and the extent of molecular deformation. Now polar factors favor the reaction with vinylborane and make the transition state earlier: the H...C distance being larger and the molecular deformation smaller, the absolute value decreases for all terms. As the law of dependence is not the same for EX than as for CT or ES, the (ES + CT + PL)/EX ratio appears to vary in an erratic way. However, when two reactions with completely different mechanisms are compared, then, of course, there is a clear change. For

example, the polar-to-steric ratio is ~100% for ionic additions<sup>21</sup> instead of the 70% obtained in radical additions. It is interesting to note that Nagase and Morokuma<sup>21</sup> found this ratio to be also ~100% in radical abstractions, which may reflect a tighter transition state for these reactions compared to homolytic additions.

**C. Perturbational Treatment of Regioselectivity: Successes and Limitations.** Perturbational treatment being quite successful for ionic reactions, it is tempting to apply it also to radical reactions. Several papers have been published,<sup>27</sup> but we shall discuss here only those of Canadell<sup>6</sup> and of Boldt<sup>9</sup> in light of the present work results.

Canadell and his co-workers pointed out that, assuming the dominance of the SOMO–HOMO interaction (i.e., assuming the radical to be always "electrophilic"), they can predict correctly in most cases the orientation of radical additions. That their simple model leaves place for exceptions is normal.

(1) The static index used ("the addition should preferentially occur at the carbon having the larger coefficient in the  $\pi$  orbital") naturally cannot account for the influence of the attacking radical.

(2) The SO–HO interaction describes essentially the charge transfer from the substrate to the radical. Again it must be emphasized with Tedder and Walton that one single property cannot suffice.

(3) Frontier orbital interactions give a good estimate of the attractive terms in the transition state, but it may be feared that the neglect of the repulsive components may give rise to some trouble. Indeed, Arnaud et al.<sup>28</sup> remarked that inclusion of overlap in the PMO treatment improves the results.

(4) If the substrate's LUMO never intervenes, it is impossible to explain why nucleophilic radicals react more rapidly with electron-poor alkenes than with electron-rich alkenes. The orientation reversal observed for addition of CH<sub>3</sub>· and CF<sub>3</sub>· to CHF = CF<sub>2</sub> cannot be explained either.

(5) Secondary interactions between nonbonded atoms are neglected, and we have seen, in the extreme case of vinylborane, that they may reverse the orientation.

However, the point to be cleared is not these obvious limitations of Canadell's hypothesis of the SO–HO dominance, but rather its amazing success, good predictions being obtained even with nucleophilic radicals like CH<sub>3</sub>·. Some interesting clues are given by the works of Fujimoto et al.<sup>6c</sup> and of Nagase et al.<sup>6d</sup> Fujimoto et al. found that the initial  $\alpha$ -spin electron transfer from the radical to the substrate is practically cancelled by the exchange repulsion. It follows that the forming of the incipient bond is due essentially to the  $\beta$  electrons transferred from the olefin to the reagent. This transfer is of course well described by the SO–HO interaction. Nagase et al. also suggested a three-stage mechanism involving successive  $\beta$ - and  $\alpha$ -spin electron transfer followed by spin polarization of the reactive bond. If the assumption that the initial  $\beta$  transfer justifies theoretically Canadell's rule is correct, then the following consequences can be predicted.

(1) This dissymmetrical behavior of  $\alpha$  and  $\beta$  electrons having been observed by Fujimoto et al. and Nagase et al. for substitutions as well as for additions, the SOMO–HOMO dominance, in Canadell's sense, should apply also to radical abstractions.

(2) Stressing the importance of the  $\beta$ -electron transfer amounts to putting the accent on the bond-forming process in the reaction. It follows that the "HOMO control" should suffer the same limitations as the "thermodynamic control" discussed in the previous section.

(3) "HOMO control" requires furthermore that the transition state be early: the later the TS, the more important the role of  $\alpha$  electrons.<sup>6c,d</sup> As a consequence, Canadell's rule will be violated when the two following conditions are simultaneously satisfied: (a) both termini of the olefin are substituted by substituents of the same electronic nature and (b) with respect to the substrate,

(26) Abell, P. I. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 66.

(27) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; Chapter 5.

(28) Arnaud, R.; Douady, J.; Subra, R. *Now. J. Chim.* **1981**, *5*, 181. Arnaud, R.; Subra, R.; Barone, V. *Ibid.* **1982**, *6*, 91.

**Table V.** Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Initial, Transition, and Final Structures Corresponding to the Addition of H· to Vinylamine

1a	2a	3a	4a	5a
210	774 <i>i</i>	640 <i>i</i>	263	44
410	331	238	300	236
462	431	281	391	352
689	463	362	463	496
881	509	417	649	644
955	555	440	819	838
997	606	704	864	947
1031	743	884	1019	1015
1236	912	896	1059	1117
1303	971	935	1118	1204
1449	1015	970	1281	1364
1627	1201	1212	1370	1396
1643	1231	1261	1403	1470
2922	1418	1420	1488	1479
3021	1480	1523	1643	1628
3066	1642	1621	2743	2759
3334	2936	2924	2763	2856
3551	2948	2958	2908	2893
	3040	3054	3059	2911
	3412	3333	3356	3270
	3516	3511	3441	3436
Internal Rotation Moments of Inertia, au				
30.87	47.65	44.45	49.85	42.87
178.89	191.56	203.17	189.95	200.52
209.14	217.90	224.19	221.16	229.45
ZPE, kcal/mol <sup>-1</sup>				
41.15	41.98	41.38	46.36	46.25

**Table VI.** Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Initial, Transition, and Final Structures Corresponding to the Addition of H· to Vinylborane

1b	2b	3b	4b	5b
268	331 <i>i</i>	436 <i>i</i>	124	188
378	165	223	193	305
553	278	275	347	330
805	369	334	423	637
889	420	351	549	756
978	540	612	746	835
1039	795	796	837	921
1069	881	862	969	991
1087	928	947	972	1055
1199	948	966	1050	1077
1298	981	985	1138	1198
1436	1073	1074	1195	1336
1594	1192	1190	1284	1393
2378	1209	1210	1406	1475
2498	1372	1371	1426	1476
2910	1486	1483	2385	2373
2988	2388	2377	2485	2475
3020	2501	2475	2638	2797
	2913	2883	2881	2864
2982	2931	2899	2872	
	3020	3047	3030	2968
Internal Rotation Moments of Inertia, au				
36.53	51.04	51.20	49.70	42.04
178.26	200.37	206.94	198.67	214.01
214.78	223.59	231.12	234.58	245.08
ZPE, kcal/mol <sup>-1</sup>				
37.72	37.80	37.73	41.43	43.35

the attacking radical is neither strongly electrophilic nor strongly nucleophilic.

As discussed in section III-A, repulsive interactions (attractive interactions) tend to displace the transition state toward the products (reactants). Now condition (a) implies that the exchange repulsion is increased for both attacks, making the TS later and Canadell's rule then not operable. Condition (b) is required to ensure that there are no strongly attractive interactions which tend to make the TS earlier and therefore cancel the effects of condition (a). Notice that although the SOMO-LUMO interaction has

**Table VII.** Temperature Corrections, Entropies, Activation Energies, and Preexponential Terms Calculated at Four Different Temperatures

	198 K	298 K	398 K	498 K
$\int C_p dT$ , kcal mol <sup>-1</sup>				
1a	1.49	2.67	4.21	6.06
2a	1.48	2.87	4.72	6.94
3a	1.67	3.17	5.08	7.33
4a	1.57	2.93	4.70	6.83
5a	1.82	3.22	4.98	7.0.
1b	1.43	2.58	4.10	5.9.
2b	1.70	3.18	5.11	7.41
3b	1.68	3.17	5.08	7.38
4b	1.80	3.31	5.23	7.53
5b	1.61	2.95	4.71	6.85
1c	1.19	1.91	2.83	3.98
2c	1.34	2.35	3.66	5.24
4c	1.53	2.57	3.84	5.36
$S$ , cal mol <sup>-1</sup> K <sup>-1a</sup>				
1a	57.82	63.42	68.42	73.01
2a	59.62	66.04	71.92	77.33
3a	61.12	67.99	74.06	79.55
4a	60.40	66.72	72.38	77.59
5a	64.03	70.51	76.16	81.32
1b	57.35	62.81	67.76	72.40
2b	61.44	68.26	74.36	79.95
3b	57.46	68.07	74.16	79.74
4b	62.61	69.53	75.63	81.21
5b	60.71	66.95	72.57	77.80
1c	51.30	54.99	58.22	61.25
2c	54.89	59.79	64.12	68.09
4c	56.76	61.78	66.02	69.87
$E_a$ , kcal mol <sup>-1</sup>				
2a	7.9	8.3	8.8	9.4
3a	4.2	4.7	5.3	5.9
2b	1.1	1.3	1.6	1.9
3b	1.5	1.7	2.0	2.3
2c	2.4	2.6	2.9	3.2
$A$ , cm <sup>3</sup> mol <sup>-1</sup>				
2a	$3.5 \times 10^{-12}$	$7.1 \times 10^{-12}$	$1.3 \times 10^{-11}$	$2.2 \times 10^{-11}$
3a	$8.3 \times 10^{-12}$	$1.9 \times 10^{-11}$	$3.8 \times 10^{-11}$	$6.7 \times 10^{-11}$
2b	$1.2 \times 10^{-11}$	$3 \times 10^{-11}$	$6.2 \times 10^{-11}$	$11.1 \times 10^{-11}$
3b	$1.1 \times 10^{-11}$	$2.7 \times 10^{-11}$	$5.6 \times 10^{-11}$	$10.0 \times 10^{-11}$
2c	$3.8 \times 10^{-11}$	$8.6 \times 10^{-11}$	$17.3 \times 10^{-11}$	$31.2 \times 10^{-11}$

<sup>a</sup> The symmetry numbers have been omitted in this table (see section C).

little effect on the initial electronic density of the bond being formed, it does diminish the total energy of the system.

Boldt and his co-workers used superdelocalizability indexes and found quite good correlation with experimental results for additions of  $(\text{NC})_2\text{CH}\cdot$  and  $\text{CF}_3\cdot$  radicals to olefins substituted by alkyl and vinyl groups.<sup>9</sup> In these calculations, steric interactions have not been explicitly introduced. However, in the compounds studied, steric and electronic effects (polarization of the electron cloud) go in the same direction: neglect of steric repulsion has then no serious consequence.

It is unfortunate that no direct comparison of  $(\text{NC})_2\text{CH}\cdot$  and  $\text{CH}_3\cdot$  has been made in Boldt's paper. However, Arnaud et al.<sup>28</sup> indicated that PMO treatment works well only for a family of similar reactions but fails to give the correct order of reactivity when two different reactions are compared. The reason is that the resonance integral is usually kept constant in a PMO treatment. This is justified only for a same family of reactions where the transition states may be assumed to have similar structures, in particular, to have about the same intermolecular distance.

#### IV. Conclusions

In this work, simplified models have been used to study the influence of donor and attractor substituents. Therefore, the results are not to be taken at their face values. In particular, the  $\text{BH}_2$  group is an extreme case contributing only a vacant orbital, while the usual attractor group (CO, CN, etc.) have vacant  $\pi^*$  and



occupied  $\pi$  orbitals. This may be one reason why our calculations predict a preferential attack on the substituted carbon of vinylborane, although, to the best of our knowledge, such orientation has never been experimentally observed for a monosubstituted olefin. However, even if the calculated effects are exaggerated, we believe that the general trends are correct. With this caveat in mind, the main results of the present work may be taken as the following.

(1) The importance of steric effects is confirmed, even for highly exothermic reactions with quite early transition states. The exchange repulsion is roughly 3–6 times the barrier height. But the preferential site of attack is not necessarily the site with the smaller steric repulsion.

(2) With our conventional definitions, "polar effects", as measured by ES + CT + PL, amount to  $\sim 70\%$  of "steric effects", as measured by EX. In spite of the sizable magnitude of polar effects, a nucleophilic (electrophilic) radical will not necessarily prefer to attack the site with the lower (the higher) electronic density. Also it must be emphasized that the nucleophilic or electrophilic character of a radical is only a relative property, depending on the substrate considered.

(3) The molecular deformation DEF term, which correlates with the early character of the transition state, appears to be a good regioselectivity predictor. How to predict simply the values of DEF remains the major problem which is currently investigated in our laboratory.

(4) Canadell's rule may be violated if the alkene is substituted on both termini by groups of the same (donor or attractor) character and if the attacking radical is neither strongly electrophilic nor strongly electrophilic with respect to the substrate.

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#### Appendix

The vibrational frequencies of the initial, transition, and final structures corresponding to the addition of H $\cdot$  to vinylamine and

vinylborane are reported in Tables V and VI. Those corresponding to the addition of H $\cdot$  to ethylene have already been published by Schlegel.<sup>7d</sup> Following Schlegel the calculated frequencies are multiplied by 0.89 in order to better reproduce the experimental results.

The entropies of the various species are calculated by the relation<sup>23</sup>

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} - R \log \sigma$$

where  $\sigma$  is the symmetry number. For radicals,  $R \log 2$  must be added to take the spin into account. The rate constants are calculated, using the activated complex theory.<sup>23,29</sup> For a bimolecular reaction

$$k = K \frac{kT}{k} e^{2\Delta S_c^*/R} e^{-E_a/RT} = A e^{-E_a/RT}$$

where  $K$  is the transmission coefficient (usually taken equal to 1),  $\Delta S_c^*$  the entropy in concentration units, and  $E_a$  the activation energy. These two latter terms are calculated by the following relations

$$\Delta S_c^* = \Delta S_p^* + R \log R'T$$

$$E_a = V^* + \Delta ZPE + \Delta \int C_v dT + RT$$

where  $\Delta S_p^*$  is the entropy (in pressure units),  $R'$  the ideal gas constant in liter inverse atmospheres (0.082),  $V^*$  the potential barrier (difference between the transition state and reactants energies),  $\Delta ZPE$  the zero-point energy correction, and  $\Delta \int C_v dT$  the temperature correction. The values computed for  $\int C_v dT$ ,  $S$ ,  $E_a$ , and  $A$  are reported in Table VII.

**Registry No.** Hydrogen atom, 12385-13-6; ethylene, 74-85-1; vinylamine, 593-67-9; vinylborane, 5856-70-2.