Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies of Radical Alternating Copolymerization. I. Quantitative Determination of the Relative Reactivities between Free Comonomers and a Complex between Them; A Theoretical Treatment in Terms of Frontier Molecular Orbital Interactions. Application to Radical Maleic Anhydride-Vinyl Acetate Alternating Copolymerization

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To cite this Article Arnaud, Roger , Caze, Claude and Fossey, Jacques(1980) 'Studies of Radical Alternating Copolymerization. I. Quantitative Determination of the Relative Reactivities between Free Comonomers and a Complex between Them; A Theoretical Treatment in Terms of Frontier Molecular Orbital Interactions. Application to Radical Maleic Anhydride-Vinyl Acetate Alternating Copolymerization', Journal of Macromolecular Science, Part A, 14: 8, 1269 — 1284

To link to this Article: DOI: 10.1080/00222338008056745
URL: http://dx.doi.org/10.1080/00222338008056745

J. MACROMOL. SCI.–CHEM., A14(8), pp. 1269-1284 (1980)

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ABSTRACT

A simple quantitative determination of the ratio β_i of rate constants k_{ij} corresponding to the addition of a complex or a free monomer on a same growing chain in alternating copolymerization was determined. The application of this method to the case of alternating maleic anhydride (A)-vinyl acetate (D) copolymerization give for $\beta_1 = k_{AC}/k_{AD}$ and for $\beta_2 = k_{DC}/k_{DA}$ (C refers to the complex) the respective values of 7 and 0. A complex was more reactive than A but less reactive than D toward a growing chain. In order to explain these reactivities, a frontier molecular orbital treatment was proposed. A good qualitative correlation with experimental results was obtained.

INTRODUCTION

The mechanism of radical alternating copolymerization has attracted much attention [1-5]. In most cases the two comonomers form a complex and the propagation steps of the copolymerization involve the participation of both free monomers and complex. Some methods are proposed to determine the relative participation of the complex in the propagation steps [4, 5]. These methods are based on the kinetic results of the copolymerization process with varying experimental conditions (relative concentration of both comonomers, total concentration of comonomers, temperature, solvent, etc.). Shirota et al. [4] suggest separation of the overall copolymerization rate into two parts due, respectively, to the complex and to the free monomers. Zubov et al. [5] have developed a method to determine the ratios

$$\beta_1 = \frac{k_{AC}}{k_{AD}}, \qquad \beta_2 = \frac{k_{DC}}{k_{DA}}, \qquad \alpha = \frac{k_{AD}}{k_{DA}}$$

where k_{ij} is the propagation rate constant for the addition of species j on a growing chain (radical) terminated by an i unit; and A, D, and C refer, respectively, to acceptor monomer, donor monomer, and the complex between them. This method gives the relative reactivities of the complex and of each monomeric molecule toward the same growing chain. Starting from the α, β_1, and β_2 ratios, we can determine the probabilities of propagation by a complex. The knowledge of the equilibrium constant K (defined by Relation 1) in the experimental conditions used in the copolymerization process (solvent, temperature) is required to determine the α, β_1 and β_2 values.

$$A + D \rightleftharpoons C, \qquad K = \frac{[C]}{[A][D]} \tag{1}$$

K values are generally determined in an inert solvent and at 25°C [6]. Extrapolation of the experimental conditions used in the copolymerization process is quite hazardous. In this paper we propose a method to determine $\beta_1 K$ and $\beta_2 K$ values. These values are used to calculate the probabilities of propagation by a complex. The estimate of K under experimental conditions gives a range of β_1 and β_2 values. This method is applied to results obtained in the case of maleic anhydride (A) and vinyl acetate (D) radical alternating copolymerization [3]. In the complex the two molecules are specific (HOMO and LUMO of the complex largely located, respectively, on the VA and MA molecules), but atomic coefficients and energies of molecular orbitals are different for free molecules and the complex. In another paper [6] we have suggested that these modifications were the origin of the differences of the reactivities observed.

The present paper tries to give a qualitative interpretation in terms of frontier molecular orbital interactions.

RESULTS AND DISCUSSION

Kinetics Aspects

When the alternating copolymerization process involves the participation of free and complexed molecules, we have four propagation steps:

$$\sim A^{\cdot} + D \xrightarrow{k_{AD}} \sim D^{\cdot} \tag{2}$$

$$\sim A^{\cdot} + C \xrightarrow{k_{AC}} \sim A^{\cdot} \tag{3}$$

$$\sim D^{\cdot} + A \xrightarrow{k_{DA}} \sim A^{\cdot} \tag{4}$$

$$\sim D^{\cdot} + C \xrightarrow{k_{DC}} \sim D^{\cdot} \tag{5}$$

Reactions (3) and (5) include two steps:

1. Addition of the first molecule of the complex (either D or A)
2. Very rapid addition of the second molecule of the complex (either A or D).

The overall rate of copolymerization R_p was defined as

$$R_p = -\frac{d}{dt}([A] + [D])$$

Experimentally we plotted R_p vs F_A (molar fraction of monomer A in the feeding mixture) for a given total concentration of comonomers (2)-(5). These curves show a maximum, depending on the total concentration of comonomers M (2)-(3). Starting from this type of experimental results, we can make some approximations:

1. k_{DA}, $k_{DC} \gg k_{AD}$, k_{AC}. This approximation is based on the fact that the rate of copolymerization is greater than the rate of homopolymerization of monomer D.
2. The position of the maximum of R_p is considered as independent of a possible variation of the initiation rate (RI) vs F_A. The variation of R_p vs F_A is very important.
3. Termination steps defined by Relations (6)-(8) are diffusion controlled [5]:

$$\sim A\cdot + \sim A\cdot \xrightarrow{k_{tAA}} P \tag{6}$$

$$\sim A\cdot + \sim D\cdot \xrightarrow{k_{tAD}} P \tag{7}$$

$$\sim D\cdot + \sim D\cdot \xrightarrow{k_{tDD}} P \tag{8}$$

4. K is small and the concentration of the complex is given by Eq. (9) where $[A]_0$ and $[D]_0$ are the initial concentrations of monomers A and D:

$$[C] = K[A]_0[D]_0 \tag{9}$$

Approximation 1 is applied when monomer A does not homopolymerize. Approximations 2 and 3 are general. Approximation 4 depends on the experimental value of K.

When applying these approximations, R_p is given by

$$R_p = k_{AD}\left(\frac{RI}{kt_0}\right)^{0.5}\Bigg[(1 - F_A)M + 2\beta_1 K(1 - F_A)F_A M^2 + \frac{1 - F_A}{F_A}(F_A M + 2\beta_2 K(1 - F_A)F_A M^2)\Bigg] \tag{10}$$

where

$$k_{t_0} = \frac{1}{4}(k_{tAA} + k_{tAD} + k_{tDD}), \tag{5}$$

and

$$\beta_1 = k_{AC}/k_{AD}, \qquad \beta_2 = k_{DC}/k_{DA}$$

The position of the maximum rate defined by $(F_A)_{max}$ and obtained by $\partial R_p/\partial F_A = 0$ is given by

$$(F_A)_{max} = \frac{\beta_1 - 2\beta_2}{2(\beta_1 - \beta_2)} - \frac{1}{\beta_1 - \beta_2}\,\frac{1}{2K}\,\frac{1}{M} \tag{11}$$

β_1 and β_2 can be determined by the linear equations

$$\frac{1}{2}M(0.5 - (F_A)_{max}) = \beta_1 K - \beta_2 K\left(\frac{1 - (F_A)_{max}}{0.5 - (F_A)_{max}}\right) \tag{12}$$

$$\frac{1}{2}M(1 - (F_A)_{max}) = \beta_1 K\left(\frac{0.5 - (F_A)_{max}}{1 - (F_A)_{max}}\right) - \beta_2 K \tag{13}$$

$\beta_1 K$ and $\beta_2 K$ are obtained from the slopes of linear equations (12) and (13). Starting from these values, we can determine the probabilities of propagation by a complex. These probabilities are given by [5]

$$P(C/A) = \beta_1 K[A]/\beta_1 K[A] + 1 \tag{14}$$

TABLE 1. Values of $(F_A)_{max}$ vs M

$(F_A)_{max}$	M
0.21	1
0.32	1.5
0.37	2

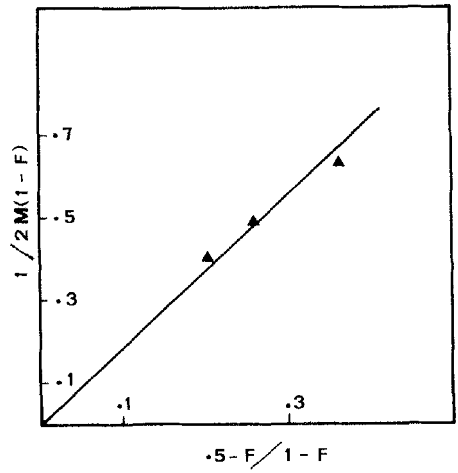


FIG. 1. Linear determination of β_1K.

$$P(C/D) = \beta_2K[D]/\beta_2K[D] + 1 \tag{15}$$

where P(C/X) is the probability of adding the complex for a growing chain terminated by an X unit. We applied this method to the results obtained in the case of radical alternating copolymerization of maleic anhydride (A) and vinyl acetate (D). Data of Ref. 3 are reported in Table 1. Starting from these values, the linear determination of β_1K and β_2K reported in Figs. 1 and 2 gave 1.8 and 0, respectively. The value of K in cyclohexane can be taken as 0.56 at 25°C [6]. In benzene at 60°C we evaluate K as 0.25 (order of magnitude of ΔH: 10 kcal/mole [2]); thus $\beta_1 \simeq 7$. A growing chain terminated by a D unit does not add the complex, and the addition of the complex to a growing chain terminated by an A unit is faster than the addition of a free D molecule. The propagation steps of this alternating copolymerization

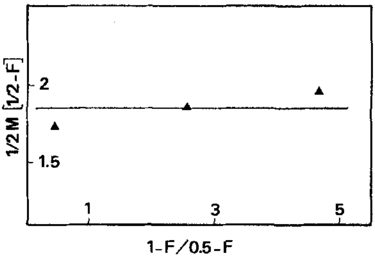


FIG. 2. Linear Determination of β_2K.

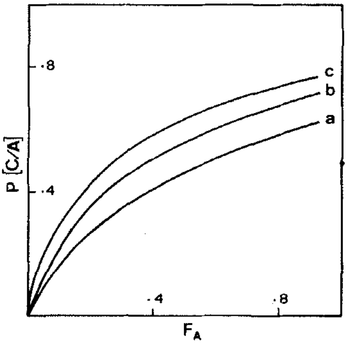


FIG. 3. Probabilities of adding the complex for a growing chain terminated by an A unit vs F_A. (a) M = 1 mole/L. (b) M = 1.5 mole/L. (c) M = 2 mole/L.

are (2), (3), and (4). P(C/A) and P(C) (probability of propagation by a complex) are reported vs F_A for different values of M in Figs. 3 and 4. These probabilities increase with M.

FRONTIER MOLECULAR ORBITAL INTERPRETATION OF THE DIFFERENCE OF REACTIVITY BETWEEN FREE AND COMPLEX MOLECULES

Data upon Free Radical Addition Reactions

Experimental evidence seems to suggest that the optimum mode of approach of alkyl radicals is along a line through one of the terminal atoms of the double and perpendicular, or almost perpendicular to the

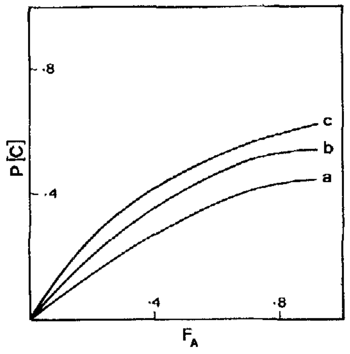


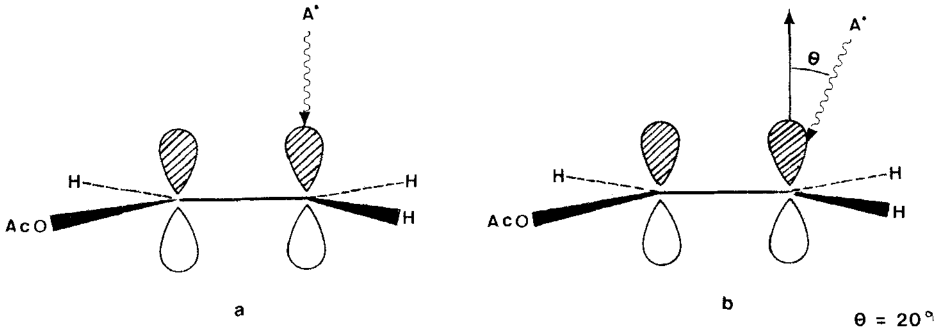
FIG. 4. Probabilities of adding the complex in the copolymerization process. (a) M = 1 mole/L. (b) M = 1.5 mole/L. (c) M = 2 mole/L.

nodal plane of the π MO involved in the reaction [7]. This has been recently confirmed by theoretical studies. First, Salem et al. [8] showed that the triangular approach of the radical to the olefinic plane directly above the middle of the double bond should be spin symmetry forbidden. Then Dewar et al. [9] studied the addition of a methyl free radical to various olefins; this work suggests that an intermediate approach between end-on attack and perpendicular attack is likely. This mode would be more favorable for nucleophilic radicals where the dominant orbital interaction involves the lowest unoccupied molecular orbital of the double bond [10].

When a free radical reacts upon a double bond, it formally has the choice between two sites. It turns out that generally (except for cyclization [7]) the most stable free radical is formed. On the other hand, according to Salem [8]: "addition of a free radical to a double bond tends to occur at that position for which the incipient bond has maximum ionic character."

Consequently, we assumed the geometries of approach shown on page 1277 (illustrated for the case where A adds to the double bond of vinyl acetate). The distance between the radical center and the carbon C_1 is fixed at 2 Å. For a VA substrate, Sites 1 and 2 are not the same; the acetyl substituent polarizes the double bond with a net π charge transfer from C_2 to C_1 ($\Delta q\pi$ = 0.14). The attacking free radical A, being an electrophile (vide infra), accepts more a negative charge and hence forms a more polar bond with the electron-rich center C_1. Then A should add initially to the unsubstituted carbon.

Addition of alkyl free radicals to double bonds is generally an exothermic process [11] and the transition state should be near the reagents [12]; in these conditions the reactivity can be analyzed in terms of orbital interactions between the free radicals and the



substrates taken in the initial state [13]. For free radical reactions, in terms of frontier orbitals the SOMO (single occupied molecular orbital) of the reagent interacts with both the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) of the substrate. The resultant energy of interaction E_{int} can be evaluated by a perturbation treatment applied to the reactivity [14]. We consider the reaction shown in the following scheme:

$$\underset{\text{free or complexed substrate}}{>C{=}C<} + R^{\bullet} \longrightarrow \underset{\text{transition state}}{\left[>C{=}C<\cdot\ {\cdot}R\right]^{\ddagger}} \longrightarrow \text{intermediate} \longrightarrow$$

If formation of the intermediate is rate determining, then the rate of the reaction will depend on the relative stabilization of the transition state, i.e., the stabilization of the free radical R· by the olefin [15]. If we assume that the mechanism of the addition is the same in the case of free and complexed molecules for a given reagent, knowledge of E_{int} at the beginning of the reaction for the system R•-"free" substrate and R•-"complexed" substrate gives information about the difference of reactivity of these systems.

Method of Evaluating Interaction Energies

Recently, Bernardi et al. [15, 16] have shown that the SOMO-HOMO interaction is not always a stabilizing one; the inclusion of overlap in the theoretical analysis can lead to a better understanding of the nature of the two orbital-three electron interaction. In a general way, the interaction energy E_{int} resulting from the interaction of two nondegenerate MO's Φ_i and Φ_j is obtained by solving the secular determinant

$$\begin{vmatrix} E_i - E & H_{ij} - ES_{ij} \\ H_{ij} - ES_{ij} & E_j - E \end{vmatrix} = 0$$

Here E_i and E_j are the unperturbed energies of Φ_i and Φ_j, respectively, H_{ij} is the resonance integral, and S_{ij} is the overlap integral between Φ_i and Φ_j. Eigenvalues E^+ and E^- are given by the relation

$$E^+ \text{ or } E^- = (E_i - E_j + 2H_{ij}S_{ij} + \text{or} - D)/2(1 - S_{ij}^2)$$

with

$$D = [(E_i - E_j)^2 + 4(H_{ij} - E_iS_{ij})(H_{ij} - E_jS_{ij})]^{1/2}$$

The interaction energies are then given by

$$\text{SOMO}(\Phi_i) - \text{HOMO}(\Phi_j) \text{ interaction: } E_{int} = 2(E^- - E_j) + (E^+ - E_i) \tag{16a}$$

$$\text{SOMO}(\Phi_i) - \text{LUMO}(\Phi_j) \text{ interaction: } E_{int} = E^- - E_i \tag{16b}$$

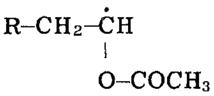
A negative value of E_{int} indicates a stabilizing interaction whereas a positive one indicates a destabilizing one. In order to solve (16a) and (16b), we have to know E_i, E_j, H_{ij}, and S_{ij}.

For frontier orbital energies of the substrates (HOMO and LUMO), the following procedure is adopted [16]: By application of Koopmans' theorem [17] the HOMO energies are taken as the negative value of the ionization potentials, IP (9.85 eV for VA [18] and 12 eV for MA [19]). The energies ϵ_{HOMO}^{VA} and ϵ_{HOMO}^{MA} obtained from CNDO/2 calculations for complexed substrates are connected by the quantities $(IP^{VA} - \epsilon_{HOMO}^{VA})$ and $(IP^{MA} - \epsilon_{HOMO}^{MA})$, respectively ($\epsilon$ is CNDO/2 energy for "free" substrates); the LUMO energy of MA can be equated to the negative of its affinity EA ($EA^{MA} = -1.4$ eV) [20]. For the other substrates, calculated ϵ_{LUMO}'s are corrected by the quantity $(EA^{MA} - \epsilon_{LUMO}^{MA})$. (Geometries used in CNDO/2 calculations are given by Refs. 21-23 in the case of free reagents and by PCILO calculations in the case of the complex [6]).

TABLE 2. Unperturbed Molecular Orbital Energies (eV)

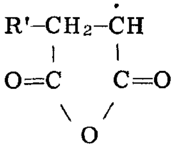
Orbital energies	$D^{\bullet}$	$A^{\bullet}$	VA Free	VA Complexed	MA Free	MA Complexed
SOMO	-6.50	-9.03				
HOMO			-9.85	-8.45	-12	-11.42
LUMO			1.87	1.46	-1.4	-1.22

Concerning the SOMO energies of radicals $D^{\bullet}$ and $A^{\bullet}$:



$$R{-}CH_2{-}\overset{\bullet}{C}H{-}O{-}COCH_3$$

$D^{\bullet}$



$A^{\bullet}$

The model selected is the ethyl free radical with its geometry [24] and IP [25] known; the ϵ_{SOMO}'s calculated for D and A are corrected by the quantity ($IP^{ethyl} - \epsilon^{ethyl}_{SOMO}$). These "adjusted" values are listed in Table 2. The SOMO energies of free radicals are in good agreement with the expected substituent effects: the SOMO of D is raised (α-effect) while the SOMO of A is lowered (C flanked by a Z-substituent).

The matrix elements H_{ij} are calculated using the Mulliken approximation [26]: $H_{ij} = kS_{ij}$. Assuming planar geometries of radicals D and A, the overlap integrals S_{ij} are evaluated by

$$S_{ij} = \langle \Phi_i | \Phi_j \rangle$$

with

$$\Phi_i = c_{ip_z} \chi_{z'}, \qquad \Phi_j = \sum_{\mu} c_{j\mu} \chi_u$$

therefore

$$S_{ij} = c_{ip_z} \sum c_{j\mu} \langle \chi_{pz} | \chi_{\mu} \rangle$$

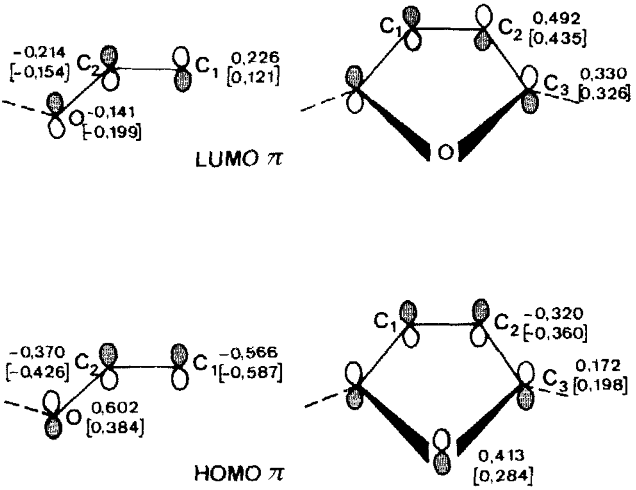


FIG. 5. AO's coefficients of frontier orbital values in brackets are relative to complexed molecules.

The AO coefficients c_{ipz} and $c_{j\mu}$ in the frontier molecular orbitals are given by CNDO/2 calculations; the values of $c_{j\mu}$ are summarized in Fig. 5. The calculated overlap integrals S_{ij} for geometries a and b are given in Tables 3A and 3B.

RESULTS AND DISCUSSION

The calculated interaction energies are reported in Tables 4A and 4B; E_{int}^{free} and E_{int}^{comp} are the interaction energies involving a frontier MO of free and complexed substrates, respectively. For each interaction we give the values $\Delta E = E_{int}^{free} - E_{int}^{comp}$. A negative ΔE indicates preferential attack of the free substrates.

We can see that in the case of addition of free radical A to vinyl acetate (propagation steps 2 and 3), the SOMO-HOMO interaction is prevalent; A acts toward VA like an electrophilic free radical. On the other hand (propagation steps 4 and 5), D acts like a nucleophilic free radical toward MA (strong SOMO-LUMO interaction).

The interaction between SOMO of D and HOMO of MA becomes destabilizing ($E_{int} > 0$, see Table 4B); the corresponding E_{int} has approximately the same value for the free or complexed MA molecule.

TABLE 3A. Overlap Integrals for the Addition of Radical A$^{\bullet}$ to the Double Bond of Vinyl Acetate

	Geometry a		Geometry b	
Overlap integrals	"Free" VA	Complexed VA	"Free" VA	Complexed VA
SOMO-HOMO	0.1304	0.1398	0.1182	0.1246
SOMO-LUMO	0.0279	0.012	0.0308	0.0147

TABLE 3B. Overlap Integrals for the Addition of Radical D$^{\bullet}$ to the Double Bond of Maleic Anhydride

	Geometry a		Geometry b	
Overlap integrals	"Free" VA	Complexed VA	"Free" VA	Complexed VA
SOMO-HOMO	0.0728	0.0782	0.0619	0.0657
SOMO-LUMO	0.0785	0.0766	0.0876	0.0848

The energy gap between frontier MO's decreases for MA complexed (see Table 2) whereas the overlap integral S_{ij} increases (see Table 3B). These effects act in opposite directions and explain the almost constant values for interaction energies. These results are in accord with the recent work of Bernardi et al. [16]; for a given value of S_{ij} the interaction energy becomes less stabilizing or destabilizing as the energy gap between frontier MO's increases, and, for a destabilizing interaction the system is increasingly destabilized as S_{ij} increases. It is interesting to note that the neglect of overlap in the theoretical treatment leads to opposite conclusions; thus E_{int} corresponding to the interaction between SOMO of D and HOMO are, respectively, -1.4 and -1.26 eV for free and complexed MA. The value corresponding to the interaction between SOMO of D and LUMO of free and complexed MA are, respectively, -0.44 and -0.41 eV (in the case of geometry a, the same tendency is obtained for geometry b). If overlap is not taken in account, the interaction SOMO-HOMO is prevalent and the total ΔE_D has a positive value.

TABLE 4A. Interaction Energies (eV) for the Addition of Radical A$^\bullet$ to the Double Bond of Vinyl Acetate

Orbital interactions	Geometry a			Geometry b		
	E_{int}^{free}	E_{int}^{comp}	ΔE_A	E_{int}^{free}	E_{int}^{comp}	ΔE_A
SOMO-HOMO	-0.5026	-1.2498	+0.7472	-0.4726	-1.2120	+0.7394
SOMO-LUMO	-0.0085	-0.0007	-0.0078	-0.0320	-0.0248	+0.0072

TABLE 4B. Interaction Energies (eV) for the Addition of Radical D$^\bullet$ to the Double Bond of Maleic Anhydride

Orbital interactions	Geometry a			Geometry b		
	E_{int}^{free}	E_{int}^{comp}	ΔE_D	E_{int}^{free}	E_{int}^{comp}	ΔE_D
SOMO-HOMO	0.0545	0.0503	+0.0042	0.0389	0.0328	+0.0061
SOMO-LUMO	-0.2053	-0.1900	-0.0153	-0.2537	-0.2218	-0.0319

For nucleophilic radicals, our results show that geometry b is favorable; for this geometry, destabilizing interaction is reduced while stabilizing interaction is increased.

We admit, at the beginning of the reaction, a linear relationship between E_{int} and the activation energy: the interaction energy is greater and the transition state is lower. Then, if k_{AD} and k_{AC} are the rate constants of the addition of A$^\bullet$ to free and complexed VA, and $\Delta E_A{}^T$ is the total interaction energy, we arrive at

$$\ln \frac{k_{AC}}{k_{AD}} = \ln \beta_1 \propto \Delta E_A{}^T$$

and similarly

$$\ln \frac{k_{DC}}{k_{DA}} = \ln \beta_2 \propto \Delta E_D{}^T$$

$\Delta E_A{}^T = +\,0.7394$ eV for geometry a, and free radical A adds a complexed VA molecule faster. $\Delta E_D{}^T = -0.0257$ eV for geometry b, and free radical D adds a complexed MA molecule slowly.

A qualitative treatment in terms of frontier orbital interactions permits an interpretation of the experimental trend.

Experimentally, growing free radical A also adds the free VA molecule and, from a theoretical point of view, propagation step (5) is probable. In fact, in the mixture $[C] \ll [D]$ and $[C] \ll [A]$. In our opinion, this explains the presence in the kinetic scheme of step (2) and the absence of step (5).

In conclusion, we point out that our treatment is a qualitative one. In this work we have used the same level of approximation, particularly for energies of frontier molecular orbitals. Hence we think that the information given by our results is qualitatively correct. This viewpoint is supported by the fact that for a given substrate, only one type of interaction occurs or dominates in the problem under investigation. However, it must be borne in mind that these calculated energy interaction values are only information of a general trend; numerical values are dependent to one particular choice of approximating the interaction matrix element H_{ij}. In our opinion, this treatment only permits comparison of similar systems; application to different systems is quite hazardous.

ACKNOWLEDGMENT

One of the authors (R.A.) is sincerely grateful to Prof. J. M. Bonnier for his constant interest and encouragement.

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Accepted by editor August 13, 1979
Received for publication September 20, 1979