Calculations on the Polymerization Process of Some 1,1-Disubstituted Cyclopropanes: I. The Initiation Step

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Ab initio calculations on the initial steps of the polymerization process of 1,1-dicyano-, -difluoro- and -dimethyl-substituted cyclopropanes are presented. Polymerization enthalpies determined by model calculations show the thermodynamic feasibility of the process. The reaction mechanism of the first step is further discussed by considering initiation by various species such as H^q, OH^q, and CH_3^q (q = +, 0, –). Transition structures and energy barriers are obtained for all species, allowing discussion of the reaction mechanism and an estimation of the kinetic feasibility. The Hartree–Fock structures at the 6-31+G(d,p) level have been fully optimized and electron correlation has been introduced at the MP2 level for some selected reaction mechanisms.

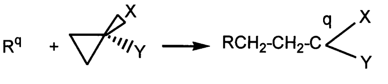
I. Introduction

An understanding of the various steps that take place in polymerization processes remains a challenge for the chemist. The importance of this field in material sciences is one of the underlying reasons for the large amount of literature devoted to such matters.

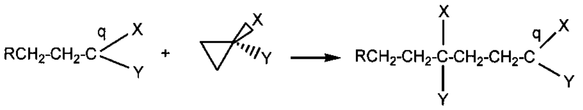
From an experimental point of view, there is an interest in synthesizing polymeric material substituted at every third carbon atom. To realize this aim, 1,1-disubstituted cyclopropanes seem to be good candidates, in that they are amenable to a ring-opening polymerization reaction. Radical, cationic and anionic polymerizations can be envisaged. In particular, when the cyclopropane is activated by a vinyl group at the 2-position, high polymers can be produced by a radical initiation[1], although in this case the substituents are attached at every fifth carbon atom. Cationic polymerization of such species gives poor yields, and most often non-ring-opened products are formed. Polymers can be obtained by anionic polymerization when strongly electron-withdrawing 1,1-substituents are present[2]. However, it is widely accepted that even though polymers may be obtained, the overall reactions are difficult and the yields are poor.

From a theoretical point of view, modelling of such processes is quite interesting. One of us[3] has proposed a simple model for calculating the thermochemical parameters of polymerization reactions. This model has been applied to a wide variety of polymerization reactions, giving a general assessment of the thermochemical feasibility of the overall reaction in question[4]. This global information is independent of the way in which the polymerization takes place, i.e. whether it is an ionic or a radical process. Such an analysis has also been carried out in the current work. It is presented in brief below and leads to the conclusion that the polymerization of 1,1-disubstituted cyclopropanes is thermochemically favored. Unquestionably, the release of ring strain in the ring-opening reaction favors the propagation step. Nonetheless, this thermochemical approach must be complemented by an analysis of the kinetic feasibility of such processes, since the activation barrier associated with the cleavage of a C−C bond is invariably high.

In the work reported herein, our aim was to acquire information concerning the mechanism of the polymerization of *gem*-disubstituted cyclopropanes, specifically with regard to the initial steps. We set out to delineate the reaction pathway of the initiation step, and to locate the transition states obtained using various initiators. The initiators H^0, H^+, H^-, CH_3^0, CH_3^+, CH_3^-, OH^- were considered to interact with some substituted cyclopropanes (X = Y = H, F, CN, CH_3), leading to the various familiar steps of the polymerization process: Initiation step (I), initial propagation step (II), further propagation step (III), termination step (IV).



(I)



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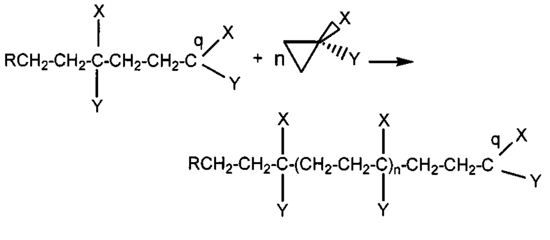
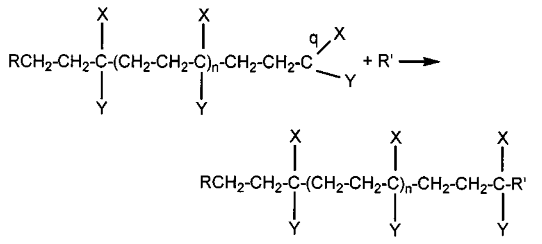


(III)

1434−193X/98/0707−1397 $ 17.50+.50/0



(IV)

q = +, 0, −.

II. Methodological Approach

Most calculations have been performed by the Hartree−Fock method using the GAUSSIAN series of programs[5]. The choice of the basis set is crucial to obtain a suitable balance between the quality and the cost.

For the thermochemical approach to the problem, only neutral molecules are required. As the latter are subsequently used in isodesmic reactions[6], all calculations may be performed at the 6-31G(d,p) polarized level. Geometries and energies were calculated. The structures obtained after a full geometry optimization were checked by computation of the second-order derivatives at all the obtained equilibrium structures. This ensures the correct curvature of the local potential surface and allows further computation of the vibrational frequencies as well as of the required thermodynamic functions. It should be mentioned at this point that the vibrational frequencies needed to evaluate the ZPE and thermal corrections (TC) have been scaled to adjust theoretical frequencies to experimental ones (1).

$$\nu\ (\mathrm{sc}) = 0.9\ \nu\ (\mathrm{th})\ [\mathrm{cm}^{-1}] \qquad \text{(I)}$$

For the mechanistic approach, as sp-diffuse functions are known to be of great importance for ionic and radical species, the previous basis set has been augmented and a 6-31+G(d,p) level has been considered in the analysis of the initiation step. Minima and transition structures were fully optimized at that level using the Hartree−Fock-restricted or unrestricted method, respectively, for closed- and open-shell species. A check at the second-order derivatives guarantees the quality of the results.

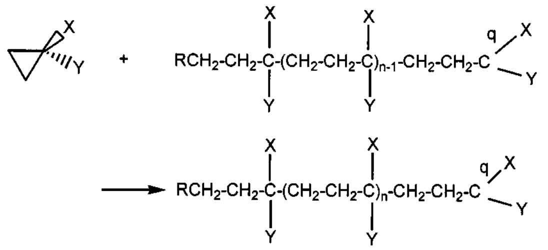
To confirm these results, for some selected reactions, the study has been completed by the introduction of some electron correlation at the MP2 level. Starting from the Hartree−Fock structures and their analytical force constant matrix, we reoptimized the structures. The modification of the geometries, especially for transition structures, has been extensively examined in order to obtain the best description of the reaction mechanism.

III. Thermochemical Model of Polymerization

Let us briefly recall the model of polymerization that we have used to confirm the thermochemical feasibility of the ring-opening polymerization reaction. The polymerization reaction may be represented by (V), leading to the reaction enthalpy (2).

$$\mathrm{M(onomer)} + \mathrm{P(olymer)}_{n-1} \rightarrow \mathrm{P(olymer)}_n \qquad \text{(V)}$$

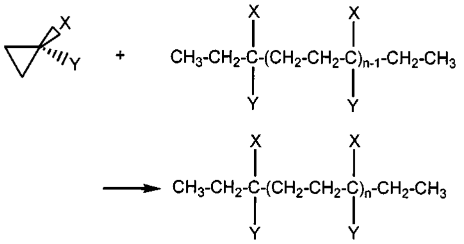
$$\Delta H_p^0 = \Delta H_f(\mathrm{P}_n) - \Delta H_f(\mathrm{M}) - \Delta H_f(\mathrm{P}_{n-1}) \qquad (2)$$



(VI)

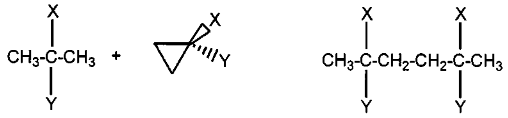
In the considered reaction, we may write as in (VI).

Globally, as the $CH_2{-}CH_2{-}CXY^q$ tail remains unaffected by the propagation step, one arrives at the conclusion that the polymerization enthalpy is independent of the charge carried by the terminal CXY^q group. This same polymerization enthalpy will thus be obtained in the reaction (VII).



(VII)

Replacing the ethyl substituent by a methyl group and setting $n = 1$, a good approximation of the polymerization enthalpy will be obtained by computing the reaction enthalpy of (VIII).



(VIII)

Such reaction enthalpy may be estimated with good precision by theoretical means using isodesmic reactions[6]. After correction for ZPE as well as thermal corrections, one obtains the standard 298 K reaction energy. For instance, in the case of dicyano compounds, one obtains at our level of methodology [kcal/mol]:

$\mathit{cyclo}\text{-}[C_3H_4(CN)_2] + CH_3{-}CH_2{-}CH_3 \rightarrow \mathit{cyclo}\text{-}(C_3H_6) + CH_3{-}C(CN)_2{-}CH_3\ \Delta H_r = 2.76$

$CH_3{-}C(CN)_2{-}CH_3 + CH_3{-}CH_3 \rightarrow CH_3{-}CH_2{-}CN + CH_3{-}CH(CN){-}CH_3\ \Delta H_r = -8.56$

$CH_3{-}C(CN)_2{-}(CH_2)_2{-}C(CN)_2{-}CH_3 + 2\ CH_3{-}CH_3 \rightarrow 2\ CH_3{-}C(CN)_2{-}CH_3 + CH_3{-}(CH_2)_2{-}CH_3\ \Delta H_r = -2.86$

With knowledge of the experimental ΔH_f[7] for all but one species, the latter may be obtained, and furthermore, the polymerization enthalpy may be estimated. Knowledge of the geometry and of the vibrational frequencies allows the further computation of Gibbs free energies through the use of statistical thermodynamic relations.

In Table 1, we have collected the total energy, the global thermal corrections, as well as the computed entropy, for each molecule considered in the polymerization process. The right-hand column gives the formation enthalpies deduced from the isodesmic processes. Polymerization data presented in Table 2 clearly show the thermochemical feasibility of polymerization reactions of 1,1-disubstituted cyclopropanes.

Table 1. Thermodynamic properties of the studied compounds [6-31G(d,p)]

Molecule	E [a. u.]	ZPE + T. C. [kcal/mol]	S [cal/mol K]	ΔH_f (theor.) [kcal/mol]
cyclo-[$C_3H_4(CN)_2$]	−300.52407	52.79	79.43	82.11
$CH_3-C(CN)_2-CH_3$	−301.72673	66.54	82.78	46.81
$C_6H_{10}(CN)_4$	−602.28642	121.54	122.93	106.91
cyclo-[$C_3H_4(F)_2$]	−314.77145	43.39	67.74	−79.29
$CH_3-C(F)_2-CH_3$	−315.99903	57.25	72.51	−133.40
$C_6H_{10}(F)_4$	−630.83609	103.10	103.12	−249.96
cyclo-[$C_3H_4(CH_3)_2$]	−195.14901	87.08	73.14	−4.64
$CH_3-C(CH_3)_2-CH_3$	−196.35246	100.77	73.48	−39.02
$C_6H_{10}(CH_3)_4$	−391.53291	190.28	113.39	−68.51

Table 2. Thermodynamic data of the polymerization reaction of the cyclopropanes

Polymerization reaction	ΔHp [kcal/mol]	ΔSp [cal/mol K]	ΔGp [kcal/mol]
$CH_3-CH_2-CH_3$ + *cyclo*-(C_3H_6) → $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$	−27.65	−34.63	−17.32
$CH_3-C(CN)_2-CH_3$ + *cyclo*-[$C_3H_4(CN)_2$] → $CH_3-C(CN)_2-(CH_2)_2-C(CN)_2-CH_3$	−22.01	−39.28	−10.30
$CH_3-C(F)_2-CH_3$ + *cyclo*-[$C_3H_4(F)_2$] → $CH_3-C(F)_2-(CH_2)_2-C(F)_2-CH_3$	−37.27	−37.14	−26.20
$CH_3-C(CH_3)_2-CH_3$ + *cyclo*-[$C_3H_4(CH_3)_2$] → $CH_3-C(CH_3)_2-(CH_2)_2-C(CH_3)_2-CH_3$	−24.85	−33.23	−14.94

IV. The Initiation Reaction

Having accepted the thermochemical feasibility of the polymerization process, one has to verify the kinetic feasibility of the process, starting with the initiation reaction. Thus, we examined the influence of the nature of the initiator through an analysis of the reaction mechanism. This involved the three steps suggested by Figure 1:

(i) Obtaining the global reaction energy ΔE_R.

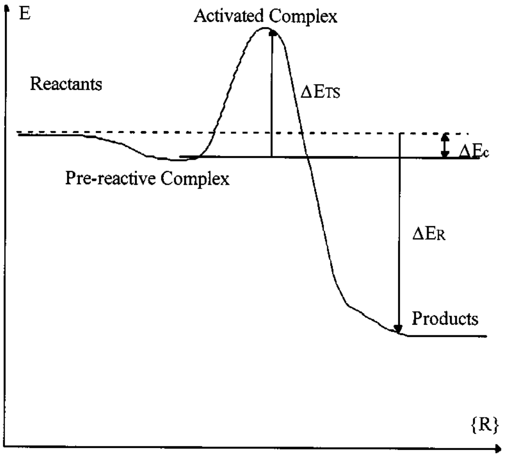
(ii) Searching for the pre-reactive complexes that appear along the reaction path and which are characterized by a complexation energy ΔE_C.

(iii) Localizing the activated complex which connects this pre-reactive van der Waals complex to the product; starting from the complex, the transition state presents an activation barrier of ΔE_{TS}.

IV. 1. Global Reaction Energy

In Table 3, we present the results obtained for the global initiation reaction between the considered cyclopropanes and the various initiators. The data show that most reactions are fairly exothermic, except when OH^- reacts with cyclopropane or alkylcyclopropanes. The latter observation can be attributed to the high thermodynamic stability of the hydroxyl anion, which is lost upon charge transfer to a carbon center. This loss of stability is not compensated by the formation of a new C−O bond, nor by a release of ring strain. Since the presence of strongly electron-withdrawing groups stabilizes the carbanion, the reaction energy becomes exothermic when cyano groups or fluorine atoms are present.

Figure 1. Schematic reaction path of the initiation reaction



We note that the exothermicity becomes particularly impressive for the protonation process of cyclopropane and the substituted cyclopropanes.

Table 3. Reaction energy and free energy of the studied initiation steps [kcal/mol]

X = Y	ΔE_R			$\Delta G_R{}^0$		
	H^0	H^+	H^-	H^0	H^+	H^-
H	−47.69	−202.65	−55.28	−39.05	−193.64	−47.38
F	−54.22	−195.79	−84.61	−43.93	−183.98	−75.15
CN	−62.26	−150.16	−137.89	−53.02	−139.81	−127.50
CH_3	−48.93	−218.47	−50.32	−39.33	−209.29	−41.82

X = Y	ΔE_R			$\Delta G_R{}^0$		
	$CH_3{}^0$	$CH_3{}^+$	$CH_3{}^-$	$CH_3{}^0$	$CH_3{}^+$	$CH_3{}^-$
H	−28.46	−67.18	−24.24	−17.08	−54.69	−12.72
F	−35.17	−73.63	−53.37	−20.99	−60.26	−40.25
CN	−43.45	−28.64	−106.75	−31.24	−16.88	−92.64
CH_3	−29.86	−95.26	−19.15	−17.40	−83.63	−6.97

X = Y	ΔE_R		$\Delta G_R{}^0$	
	OH^0	OH^-	OH^0	OH^-
H	−23.79	6.27	−14.57	15.18
F	−29.43	−21.50	−17.34	−11.15
CN	−37.40	−74.76	−27.36	−65.17
CH_3	−25.01	12.91	−14.65	22.34

IV. 2. Formation of van der Waals Pre-reactive Complexes

The initiators were allowed to approach the cyclopropanes through four channels, as depicted in Figure 2 (limited to 1 and 2 in the case of cyclopropane). Some of the results are presented in Table 4. This table contains the energies obtained for the most stable complex. The approach channel of the initiators is denoted by the number in parentheses, in accordance with Figure 2.

Figure 2. The studied approaches of the initiator

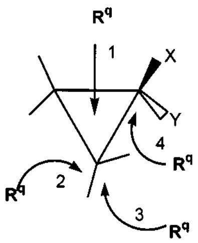


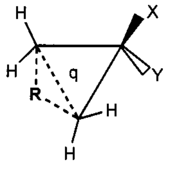
Table 4. Complexation energies between cyclopropanes and some selected initiators [kcal/mol]

X = Y	H^0	H^+	H^-
H	−0.14 (1, 2)	–	−28.97 (2)
F	−0.17 (2)	[−163.59]	−38.00 (2)
CN	−0.21 (2)	[−143.83]	−50.41 (2)
CH_3	−0.15 (2)	–	−30.58 (2)
X = Y	CH_3^0	CH_3^+	CH_3^-
H	−0.11 (1, 2)	–	−3.27 (2)
F	−0.36 (2)	[1.22]	−8.69 (2)
CN	−0.69 (2)	[2.28]	−17.76 (2)
CH_3	−0.15 (2)	–	−4.03 (2)
X = Y	OH^0	OH^-	
H	−0.41 (1)	−7.91 (1)	
F	–	−15.00 (2)	
CN	–	−27.23 (2)	
CH_3	–	−10.22 (2)	

To summarize the results, one may point out that:

1. *The cationic initiators* do not lead to complexes, but give reactions. Many channels are open for reaction and, among these, a product may be formed without any barrier. This product is most often an alkyl cation as opposed to an alkene. The case of methyl interacting with cyclopropane leads to the ethyl cation and ethylene along one channel, or straight to a butenyl cation along another channel. The initially formed ion, being a secondary cation, is less stable, and spontaneously rearranges on the energy surface to its secondary isomer. Generation of a cyclopropyl cation was also encountered. Four entries are included in the table pertaining to structures which resemble complexes, i.e. like that shown schematically in Figure 3, and which should be associated with transfer reactions.

Figure 3. Complexes obtained between cationic initiators and cyclopropanes



These stable structures are very exothermic with a proton, and are slightly endothermic with the methyl cation. The strong exothermic character is related to the proton affinity of these substituted cyclopropanes. The experimental proton affinity reported for cyclopropane[8] is 179.8 kcal/mol.

2. *The radical initiators* show a very low affinity for the cyclopropanes throughout. The reported data show that this affinity is well below 1 kcal/mol. We should mention here that, as the complexes with an OH radical hardly converge, cyclopropane was the only system studied.

3. *The anionic initiators* show affinity for the cyclopropanes. The complexes obtained are strong and are located along the reaction path. The strongest complexes are obtained with H^- but, irrespective of the initiator, their stability follows the order: CN > F > CH_3 > H.

From this analysis, it would appear that the anions are good candidates for initiating the polymerization reaction by surmounting the activation barrier. As the H^- species is not a common initiator, only CH_3^- and OH^- will be further considered in this paper with regard to obtaining the activated complex.

IV. 3. Activated Complex and Reaction Mechanism

The search for the transition state follows the same strategy as that used throughout this work. The maximum along the curve connecting the van der Waals complex to the product in the $3N - 6$ dimensional space is localized. The reaction coordinate contains principally the "initiator/reaction site" distances, as well as the corresponding ring-opening valence angle. The values of these parameters at the maximum correspond to the activated complex structure. Energy results are presented in Table 5 for CH_3^- and OH^- as initiators.

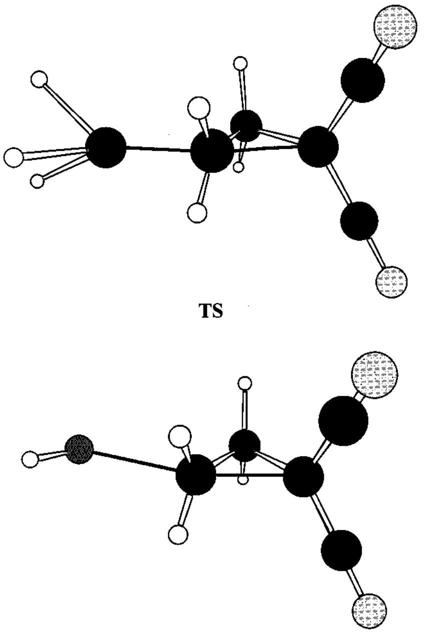
Table 5. Thermodynamic properties of the transition states [kcal/mol]

	ΔE_{TS}		ΔG_{TS}	
	CH_3^-	OH^-	CH_3^-	OH^-
H	40.51	44.97	42.97	45.17
F	38.28	42.36	40.91	42.97
CN	27.40	10.86	20.05	10.18
CH3	45.18	51.22	46.62	50.88

At this point, it should be mentioned that the transition states obtained with H^- are different from those obtained with CH_3^- and OH^- and will be presented later for the sake of completeness.

From a general point of view, the obtained transition states share a common feature. Figure 4 shows the transition structures obtained when CH_3^- or OH^- initiators react with dicyanocyclopropane. One concludes that the initiator attacks along path 2 (Figure 2), interacting with the CH_2 group opposite to the substituted carbon atom. This is an S_N2-like transition state in which the leaving group remains bound to the molecule through a cyclic bond. That this structure is observed throughout suggests a specific reaction mechanism. A similar transition structure has indeed been reported in the case of oxirane[9] and methyloxirane or thiirane ring-opening reactions with nucleophiles[10]. The various reactions are differentiated only by their energies. Dimethylcyclopropane presents a huge activation barrier, but when a stabilized carbanion such as dicyanocyclopropane is formed, a considerable reduction of the barrier is obtained. This effect, even though not negligible with CH_3^-, is remarkably high with OH^-. Difluoro compounds appear in between these two limiting situations.

Figure 4. Transition state structures of the reaction between 1,1-dicyanocyclopropane and the selected CH_3^- or OH^- initiators



Considering the interaction of cyclopropane with any H^q, the transition state corresponds to a C_{2v}-symmetric structure, where H^q takes up a position between two CH_2 groups. Even though one obtains a first-order minimax, the reaction coordinate describes a hydrogen-transfer reaction and does not connect a van der Waals complex to an activated propyl species. Furthermore, an extensive scan of the quadratic energy hypersurface did not lead to a "correct" transition state located along the reaction pathway. One may suppose that a bifurcation point obtained at a higher level description of the surface could explain this behavior. The nature of the substituents does not affect the transition structure obtained when H^q attacks between CH_2 groups, rendering further studies of this reaction path unnecessary.

IV. 4. The Influence of Correlation Energy

It is known that these reactions are sensitive to electron correlation. This is why a maximum of flexibility was given to the wavefunction at Hartree−Fock level. As a continuation of this study, we have introduced some electron correlation at the MP2 level. The reactions (except those with dimethylcyclopropane) initiated by anionic species were submitted to a full geometry optimization starting with the Hartree−Fock analytical Hessian. Reaction partners, van der Waals complexes, and transition states were calculated and the resulting data are collected in Table 6. For the sake of clarity and easy comparison, the corresponding Hartree−Fock results are given in parentheses.

Table 6. Effect of MP2 electron correlation on the reaction properties compared to RHF results [kcal/mol]

	CH_3^-		OH^-	
X = Y = H	MP2	(RHF)	MP2	(RHF)
ΔE_R	−28.51	(−24.24)	10.66	(6.27)
ΔE_C	−6.18	(−3.27)	−10.99	(−7.91)
ΔE_{TS}	31.41	(40.51)	40.48	(44.97)

	CH_3^-		OH^-	
X = Y = H	MP2	(RHF)	MP2	(RHF)
ΔE_R	−58.77	(−53.37)	−17.97	(−21.50)
ΔE_C	−12.30	(−8.69)	−18.49	(−15.00)
ΔE_{TS}	29.20	(38.28)	37.63	(42.36)

	CH_3^-		OH^-	
X = Y = H	MP2	(RHF)	MP2	(RHF)
ΔE_R	−105.50	(−106.75)	−64.40	(−74.76)
ΔE_C	−22.24	(−17.76)	−24.26	(−27.23)
ΔE_{TS}	5.84	(27.40)	4.78	(10.86)

As far as the structures are concerned, the results obtained are close to those at the Hartree−Fock level for all the species. On the other hand, the potential energy hypersurface changes its local shape and is flattened considerably. As a consequence, the transition states present lower barriers and the number of secondary reaction channels increases. In other words, one may stress that although the initiation step corresponds to the same mechanism and becomes more easy to fulfil, as more and more secondary reactions appear, its global yield diminishes.

As a final conclusion of this section, comparing the various substituents, one finds that the reaction barrier decreases with more electron-withdrawing substituents, while the complexation and reaction energies become more exothermic. This leads to a situation where cyano substituents present barriers that fall below the complexation energies. This could explain why the polymerization process of such species is favored.

V. Conclusion

In this paper, we have examined the initiation step of the polymerization process of 1,1-disubstituted cyclopropanes. We are aware that many reacting channels may be available during the initiation process and that some of these may be preferred to the one focussed on herein. Some specific channels may also be favored by the influence of the medium and by the nature of the solvent, which are very important in these reactions. Nevertheless, to study the possible polymerization process, which is experimentally observed under defined conditions, we have limited our investigation to the elementary reaction that takes place between single molecular species in the sole initiation process. Calculations aimed at elucidating the reaction pathway lead to interesting thermodynamic data. The location of the transition state shows that the anionic process is easily attainable through an S_N2-like direct addition of the incoming initiator to a methylene unit of the ring, with the CX_2 group acting as the leaving group.

An OH^- initiator seems to be interesting only when the released energy is sufficient to overcome the strong stabilization energy of the anion. This is the case when the formed carbanion is stabilized by strongly electron-withdrawing groups such as CN. On the other hand, the reaction barrier itself is lowered when the product is stabilized, rendering the reaction kinetically feasible.

With CH_3^- as the initiator, the reactions are slightly more exothermic, but activation barriers are increased in such cases. In the case of alkylcyclopropanes, one can envisage that the obtained activation barriers are approximately transferable from the initiation step to the propagation steps, and thus offer further information on the kinetics of these steps. This idea is currently being explored with a view to studying the mechanism of the subsequent steps of the polymerization process, keeping in mind that the nature of the initiator and of the substituents remain critical parameters with regard to the kinetics and thermodynamics of the polymerization reaction.

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