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A R T I C L E S

Lithium Cation as Radical-Polymerization Catalyst

Timothy Clark

Contribution from the Computer-Chemie-Centrum der Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25, 91052 Erlangen, Germany

Received May 8, 2006; E-mail: clark@chemie.uni-erlangen.de

Abstract: Density-functional theory (DFT) and ab initio (QCISD and CBS-RAD) calculations suggest that complexation of "naked" lithium cations to olefins favors the addition of alkyl radicals to the double bond over abstraction of an allylic hydrogen atom. Thus, "naked" lithium cations in nonpolar solvents can catalyze the radical polymerization of olefins by favoring the chain-lengthening reaction over the competing hydrogen-atom extraction, which is competitive in the absence of metal ions. One putative initiation reaction, addition of triplet dioxygen to the double bond, is thermoneutral and has a very low barrier when the oxygen molecule is complexed to a lithium cation. An alternative process, abstraction of an allylic hydrogen atom to generate the allyl and hydroperoxy radicals, is also strongly favored by complexation of the oxygen to the lithium cation but is less favorable than addition. These results support Michl's recent interpretation of experimentally observed alkene polymerization in the presence of lithium salts of hydrophobic carborane anions.

Introduction

Twenty years ago, ab initio calculations suggested that the addition of alkyl radicals to olefins can be catalyzed by complexing the olefin to a lithium cation.[1] This prediction was long held to be unlikely to have experimental consequences in solution because polar solvents compete with the olefin to complex lithium cations. However, recently Michl et al. first observed that exposure to air initiates polymerization of the alkene side chains of the lithium salts (and only the lithium salts) of ω-(undecamethylcarba-*closo*-dodecaboran-1′-yl)alk-1-enes.[2] The same authors also demonstrated that "naked" lithium cations, present in solutions of lithium salts of such hydrophobic carborane anions, catalyze the radical polymerization of propene and other terminal olefins and that triplet dioxygen or conventional radical starters can initiate the polymerization.[3] Although it had been suggested[4] that complexation of Li^+ to olefins is unlikely under more usual experimental conditions, the active sites of enzymes or the cavities of zeolites also provide suitable conditions for olefin complexation to Li^+. Thus, our recent work on the effect of complexation of metal ions[5] or fluoride anions[6] to radical-clock systems suggests that the rates of the clock rearrangements can be influenced by complexation with ions and this phenomenon might falsify conclusions about the mechanisms of enzyme reactions. We have now returned to the original subject of radical addition to olefins in order to consider the main competition reaction in a potential polymerization reaction, hydrogen-atom abstraction from the allyl position. If this competing reaction enjoys less transition-state stabilization through complexation with Li^+ than addition, Michl's results can be rationalized purely in terms of the effect of Li^+-complexation to the olefins. We also showed earlier[7] that addition of triplet dioxygen to ethylene is catalyzed by complexation of the oxygen with a lithium cation. We have reinvestigated this reaction as a candidate for the initiation of radical polymerization in the presence of "naked" Li^+.

Methods

All calculations used Gaussian03.[8] Initial geometry optimizations were performed with the Becke three-parameter/Lee−Yang−Parr (B3LYP)[9] hybrid density-functional technique as implemented in Gaussian03[8] with the 6-31G(d) basis set.[10] Stationary points thus found were refined by QCISD[11] geometry optimization using the same basis set, and for radicals, the results of these two sets of calculations were used with further single-point calculations to calculate CBS-RAD-(QCISD,B3-LYP) energies, as defined and recommended by Radom and co-workers.[12] CBS-RAD(QCISD,B3-LYP) extrapolated energies use the QCISD-optimized geometries for further single-point calculations but the B3LYP-calculated vibrational frequencies.[12]

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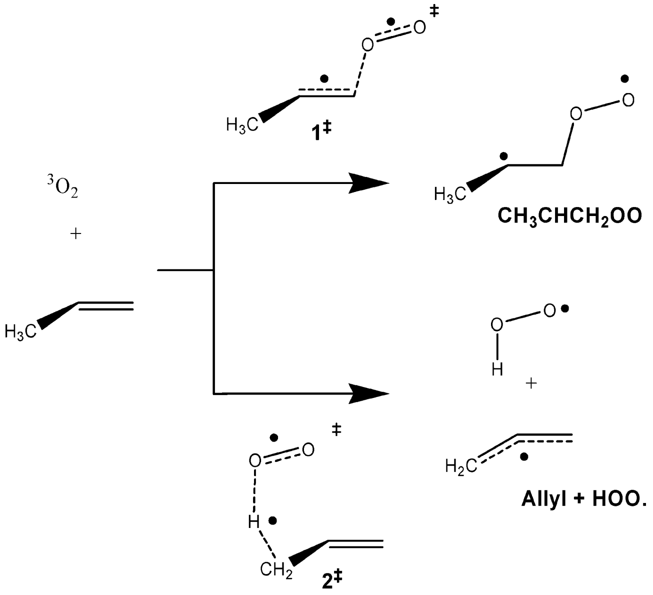
10.1021/ja063204+ CCC: $33.50

Results

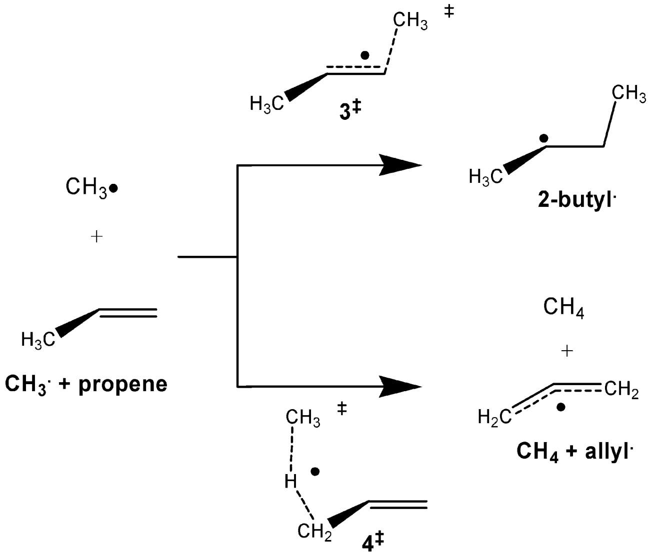
The calculated energies at the different calculational levels are shown in Table 1.

Two initiation reactions between propene and triplet dioxygen, addition and abstraction of an allyl hydrogen atom, were considered:



The uncatalyzed addition of triplet dioxygen to propene is calculated (QCISD/6-31G(d)) to be endothermic by 30.8 kcal mol^{-1} with an activation energy of 36.9 kcal mol^{-1}, whereas the alternative abstraction of an allyl hydrogen atom by $^3O_2$ is even less favorable with a heat of reaction of +37.4 kcal mol^{-1} and an activation energy of 49.1 kcal mol^{-1}.

The competing reactions of alkyl radicals with propene are addition and abstraction of an allyl hydrogen atom:



The unperturbed reactions of the methyl radical (used as a model alkyl radical in this study) with propene occur with calculated (CBS-RAD) activation energies of 5.8 and 8.7 kcal mol^{-1} for hydrogen-atom abstraction and addition to the double bond, respectively. The different calculational levels disagree as to which of the two reactions is the more facile. B3LYP and CBS-RAD prefer hydrogen-atom abstraction, whereas QCISD favors addition. In any case, the activation energies for the two competing processes are calculated to be close.

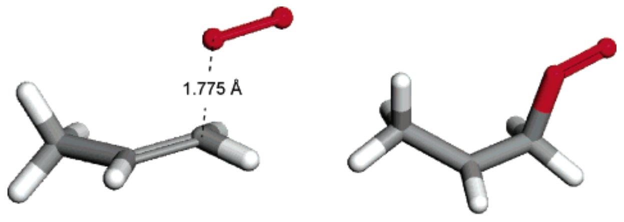
Table 1. Calculated Relative Energies (kcal mol^{-1}) for the Species Discussed in the Text

species	B3LYP/6-31G(d)	QCISD/6-31G(d)	CBS-RAD (QCISD,B3-LYP)
$^3O_2$ + Propene			
$^3O_2$ + propene	0.0	0.0	
1‡	29.0	36.9	
CH_3CHCH_2OO	28.7	30.8	
2‡	36.1	49.1	
allyl + HOO•	36.4	37.4	
$CH_3^\bullet$ + Propene			
$CH_3^\bullet$ + propene	**0.0**	**0.0**	**0.0**
3‡	6.5	9.8	8.7
2-butyl•	−24.0	−22.9	−17.8
4‡	4.1	11.9	5.8
CH_4 + allyl•	−19.6	−17.0	−16.5
$^3O_2$ + Li^+:Propene			
$^3O_2Li^+$ + propene	**0.0**	**0.0**	
5	−25.7	−25.1	
6‡	3.7	0.8	
7	−3.9	0.1	
8‡	**no Ts**	14.9[c]	
9	**optimizes to 5**	10.0[c]	
$HOOLi^{+\bullet}$ + allyl•	20.5	18.8	
$CH_3^\bullet$ + Li^+:Propene			
$CH_3^\bullet$ + Li^+:propene	**0.0**	**0.0**	**0.0**
10	−13.5	−13.5	−10.7
11‡	12.1	19.2	13.3
12‡	2.9	11.9	5.5
13	−30.2	−28.6	−27.8
CH_4 + allyl:Li^+	−20.5	−18.3	−23.3
14‡	0.4	5.4	1.4
15‡	2.2	7.2	2.8
16	−24.5	−23.3	−24.7
Li^+:$CH_3^\bullet$ + Propene			
CH_3•••Li^+ + propene	11.2	10.5	9.3
17	3.3	8.3	5.1
18‡	10.6	21.4	13.1
CH_4•••Li^+ + allyl•	**optimizes to 13**	**optimizes to 13**	
19‡	4.5	12.2	6.5
20	−13.4	−14.9	−15.1

[a] B3LYP/6-31G(d) relative energies include the unscaled zero-point energy correction. [b] QCISD/6-31G(d) relative energies are corrected with the unscaled B3LYP/6-31G(d) zero-point vibrational energies. [c] Using an estimated B3LYP/6-31G(d) zero-point energy of 52.0 kcal mol^{-1}.

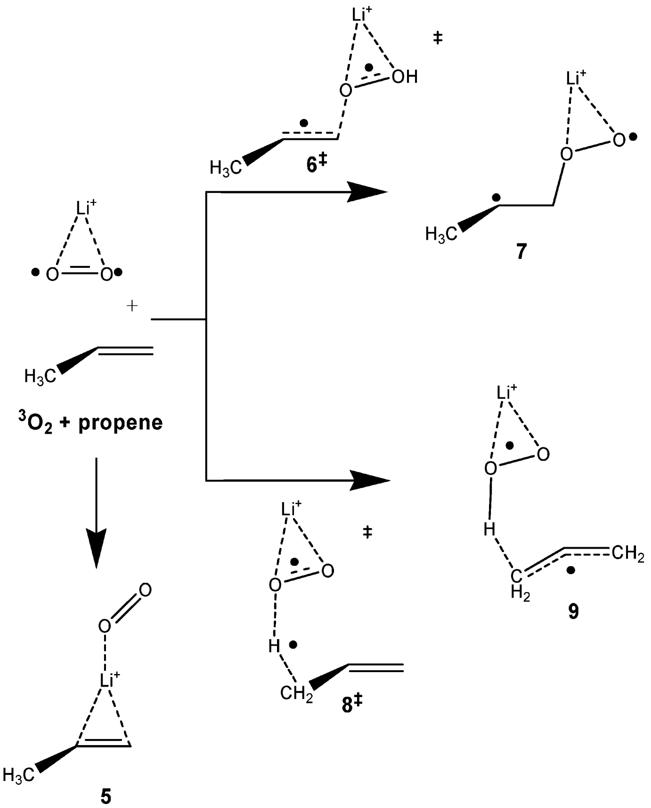
In the following, the structures shown in the charts are the QCISD/6-31G* optimized ones, which are also the basis of the CBS-RAD calculations.

Lithium-Ion Catalyzed Reactions. Addition of $^3O_2$:Li^+ to Propene. The unperturbed addition of triplet dioxygen to propene is very unfavorable. Triplet dioxygen reacts via transition state **1**‡ to give the triplet CH_3CHCH_2OO diradical. As outlined above, this reaction is both kinetically and thermodynamically unfavorable.

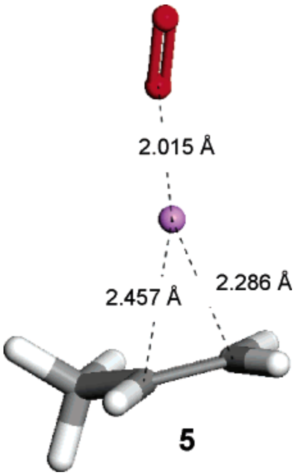


1‡ **CH_3CHCH_2OO**

The Li^+-catalyzed reaction was calculated, as in our previous work,[6] as the addition of the $LiO_2^{+\bullet}$ complex to propene:



The alternative addition of $^3O_2$ to Li^+:propene is unfavorable. The most stable structure found for the reactants is the complex **5**, which is 22 kcal mol^{-1} more stable than the separated reactants. We regard this structure as a propene-solvated Li^+ complex of triplet dioxygen. Thus, additional propene molecules act as solvent, so that we can use $^3O_2$:Li^+ as a computational model for propene-solvated Li^+ complexed to $^3O_2$.



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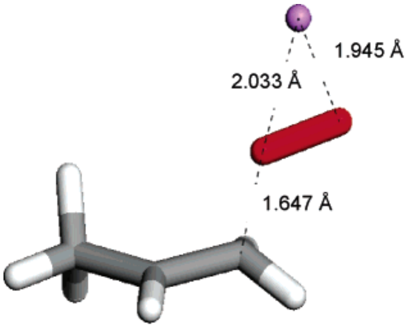
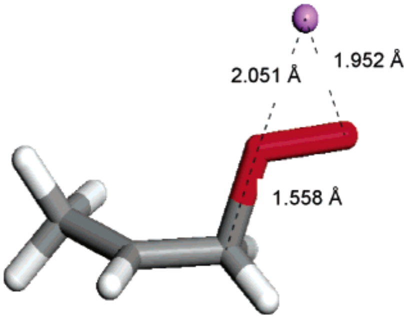
$^3O_2$:Li^+ adds to propene via the transition state **6**‡ to give the addition product **7**. The addition transition state **6**‡ lies both energetically and geometrically very close to the product **7**. The forming C−O bond in the transition states has a calculated (QCISD) length of 1.647 Å, compared with 1.558 Å for the product. The calculated activation energy is 0.8 kcal mol^{-1} and the heat of reaction +0.1 kcal mol^{-1}, so that the Li^+-complexation favors the addition of dioxygen to propene thermodynamically by almost 31 kcal mol^{-1} (relative to the unperturbed reaction) and stabilizes the transition state by 36 kcal mol^{-1}. This stabilization is explained by the increasing polarity of the O−O unit as the new C−O is formed.[7]



6‡



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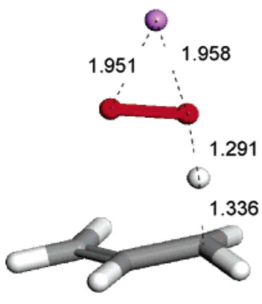
Thus, the addition of triplet dioxygen to propene is calculated to be favored strongly, both thermodynamically and kinetically, by complexation with the lithium cation. These results confirm that complexation of triplet dioxygen to "naked" lithium cations in solution can activate it as a radical initiator. It is gratifying that Michl's experimental work has also helped support our theoretical prediction of this effect, which was published 16 years ago.[7]

Abstraction of an Allyl Hydrogen by $^3O_2$. With no Li^+ present, the alternative initiation reaction between propene and triplet dioxygen, the hydrogen abstraction outlined in eq 2, is thermodynamically and kinetically even less favorable than addition for the unperturbed reaction, as outlined above. The calculated complexation energy of the hydroperoxy radical to Li^+ is 12 kcal mol^{-1} more negative than that to $^3O_2$ because of the polarity effect, so that even the hydrogen abstraction reaction to give separated Li^+:OOH and the allyl radical is favored thermodynamically by this amount. Neither a hydrogen-transfer transition state nor a triplet Li^+:OOH complex with the allyl radical could be found at the B3LYP/6-31G(d) level, but at the QCISD/6-31G(d) level the reaction proceeds via transition state **8**‡ to give the product complex **9**.

This reaction is also calculated to be more endothermic (heat of reaction = 10.0 kcal mol^{-1}) than the Li^+-complexed addition reaction and to have an activation barrier of 14.9 kcal mol^{-1}. Thus, our calculations indicate that the addition reaction is more likely to occur, in accord with Michl's observation of OH end groups in the $^3O_2$-initiated polymerizations.[3]



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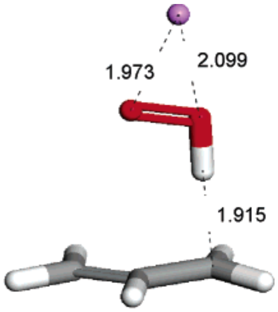

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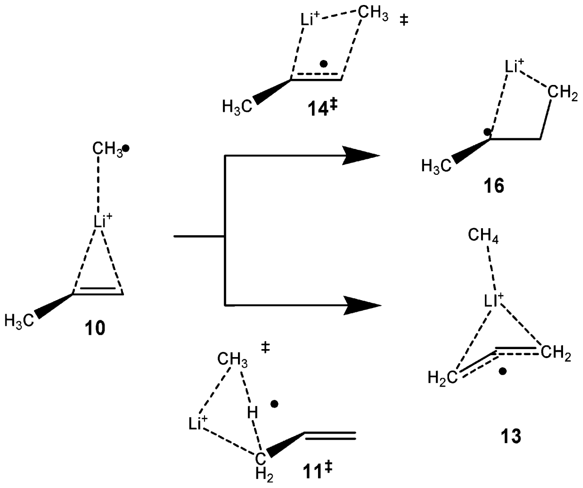
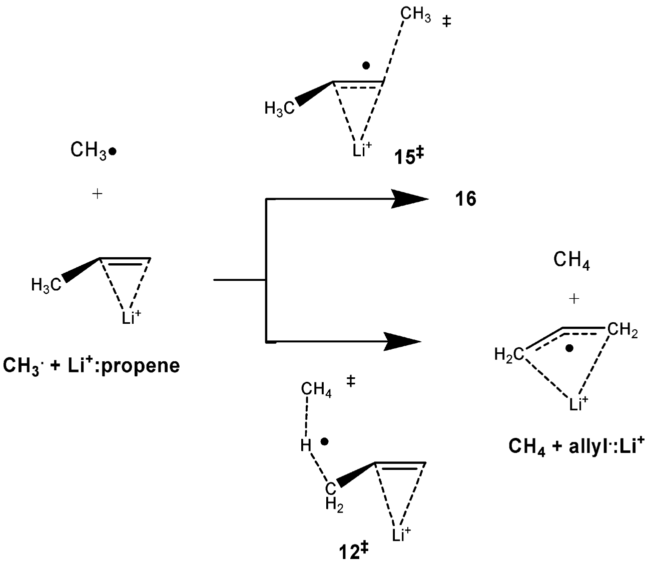
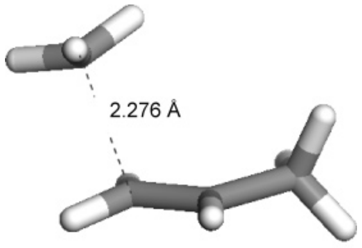
Figure 1 shows a schematic comparison of the addition and abstraction reactions of $^3O_2$ with propene both with and without the lithium cation.

H-Atom Abstraction from Propene:Li+ by the Methyl Radical. The relative energies of the transition states for addition ($\mathbf{3}^‡$) and H-atom abstraction ($\mathbf{4}^‡$) for the unperturbed reactions of the methyl radical with propene serve as comparisons for the Li^+-catalyzed reaction of the methyl radical with propene: Li^+. However, this reaction can take several alternative paths. The initial step for the Li^+-catalyzed reaction is the formation of the stable propene:Li^+:methyl complex **10**. This complex is bound by 11 kcal mol^{-1} relative to the methyl radical and propene:Li^+, an energy attributable to the C−Li one-electron bond.[11] However, the direct path from this complex to the allyl radical plus methane passes over the higher of the two H-atom-abstraction transition states $\mathbf{11}^‡$, in which the methyl radical attacks from the side syn to the lithium cation. The calculated activation energy for this abstraction is 13.3 kcal mol^{-1}, 7.5 kcal mol^{-1} higher than that for the corresponding reaction in the unperturbed system. The alternative process in which the methyl attacks the face anti to that on which the lithium cation is complexed via transition state $\mathbf{12}^‡$ has a calculated activation energy of 5.5 kcal mol^{-1} relative to the methyl radical plus the propene:Li^+ complex. Thus, in the most favorable case, lithium-ion complexation to propene hardly changes the barrier to H-abstraction relative to the unperturbed reaction ($\Delta E^‡ = 5.8$ kcal mol^{-1}).

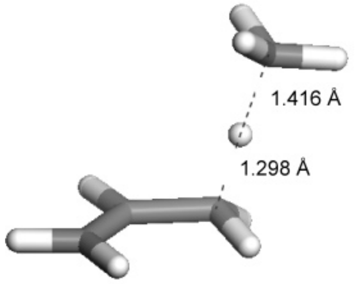
This unchanged barrier to H-atom abstraction is consistent with the geometrical nature of the transition state. The allyl-H bond in $\mathbf{4}^‡$ is slightly shorter (1.292 Å compared with 1.298 Å) in the Li^+-complexed case ($\mathbf{12}^‡$), and the CH_3−H distance is correspondingly slightly longer (1.418 Å compared to 1.416 Å).







$\mathbf{3}^‡$



$\mathbf{4}^‡$

These changes are consistent with a more exothermic process for the Li^+-complexed case (−27.8 compared with −16.5 kcal mol^{-1} for the unperturbed system). The methane:Li^+:allyl complex **13**, which is the direct product of the syn H-atom abstraction reaction, is stabilized by 4.5 kcal mol^{-1} relative to methane + Li^+:allyl. This stabilization is the result of three Li−H−C agostic interactions to the methane moiety.

Addition of the Methyl Radical to Propene:Li$^+$. As for the H-atom abstraction, there are two transition states for the addition of the methyl radical to propene:Li^+, with the CH_3 radical syn and anti to the face to which the lithium cation is complexed. For the addition reaction, however, the syn addition transition state $\mathbf{14}^‡$ is found to be the more stable, so that the most favorable addition path leads directly from the complex **10** via $\mathbf{14}^‡$ to the 2-butyl radical:Li^+ complex **16**. Transition state $\mathbf{14}^‡$ lies 1.4 kcal mol^{-1} higher in energy than the methyl

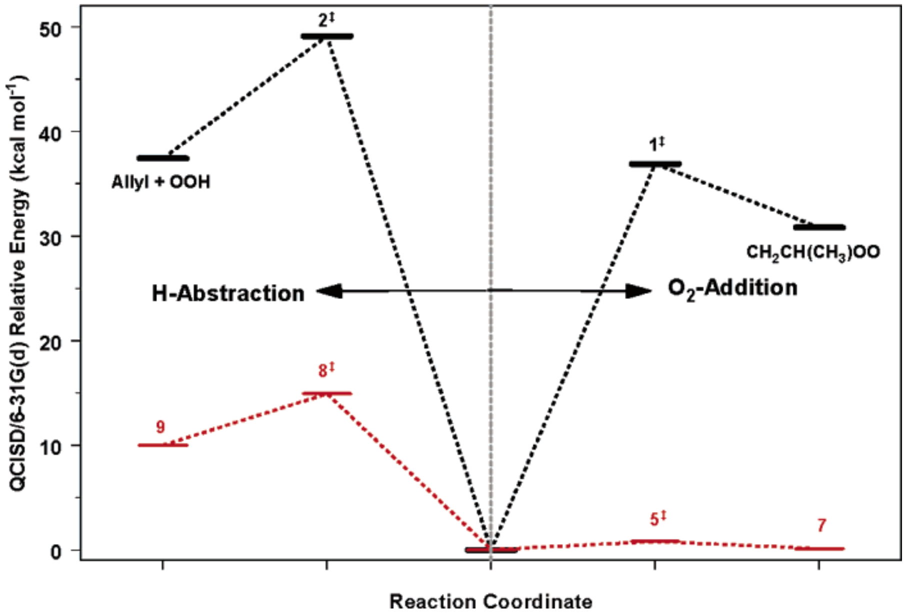
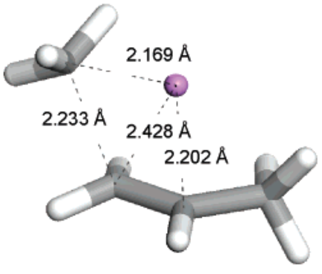
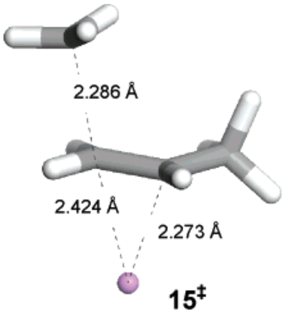


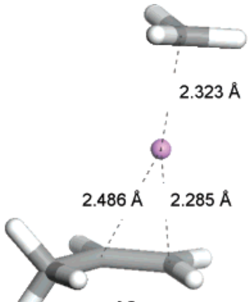
Figure 1. Schematic diagram of the reaction profiles (QCISD/6-3G(d) with B3LYP/6-31G(d) ZPE-correction) for the reactions of $^3O_2$ with propene with (red) and without (black) complexation to the lithium cation.



14‡



15‡



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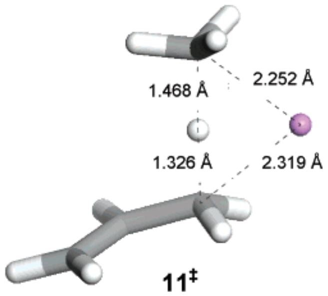
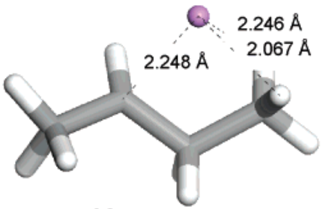


11‡



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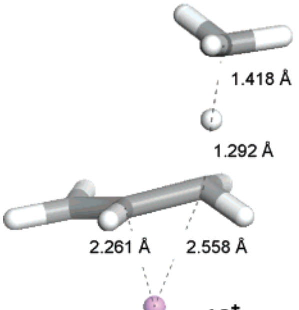
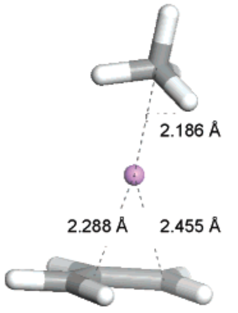


12‡



13

radical + Li^+:propene, which gives an addition barrier of 12.1 kcal mol^{-1} relative to the initial complex **10**. **14‡** also lies 11.9 and 4.1 kcal mol^{-1} lower in energy than the syn and anti H-abstraction transition states **11‡** and **12‡**, respectively. Addition via the anti transition state **15‡** has a 1.4 kcal mol^{-1} higher barrier than the syn addition but is still more favorable kinetically than the alternative H-atom abstraction, both for the syn and anti processes.

Transition state **15‡** shows a longer distance for the forming C−C bond than in the unperturbed case (2.286 vs 2.276 Å), as would be expected for a slightly more exothermic (−26.4 vs −23.5 kcal mol^{-1}) reaction. However, the syn addition transition state **14‡** is clearly stabilized by a template effect of the lithium cation, which is within bonding distance of the radical center and the double bond being attacked. This sort of interaction is not possible for the abstraction reaction, which requires a more or less linear C−H−C linkage, ruling out effective complexation of the reacting centers to the metal ion.

Reaction of $CH_3Li^{+\bullet}$ with Propene. An alternative to the reaction of the free radical with the olefin:Li^+ complex is that of a methyl radical complexed to Li^+ with the free olefin. We will not consider the case of radical and olefin reacting with each other when they are both complexed to Li^+ as this would be very unfavorable because of the Coulomb repulsion between the two complexes. $CH_3\cdots Li^{+\bullet}$ is a one-electron bonded complex[13] with a calculated C−Li bond-dissociation energy of 12.8 kcal mol^{-1}.[14] The complexation energy of Li^+ with propene at the same level is −22.2 kcal mol^{-1}, suggesting that complex-

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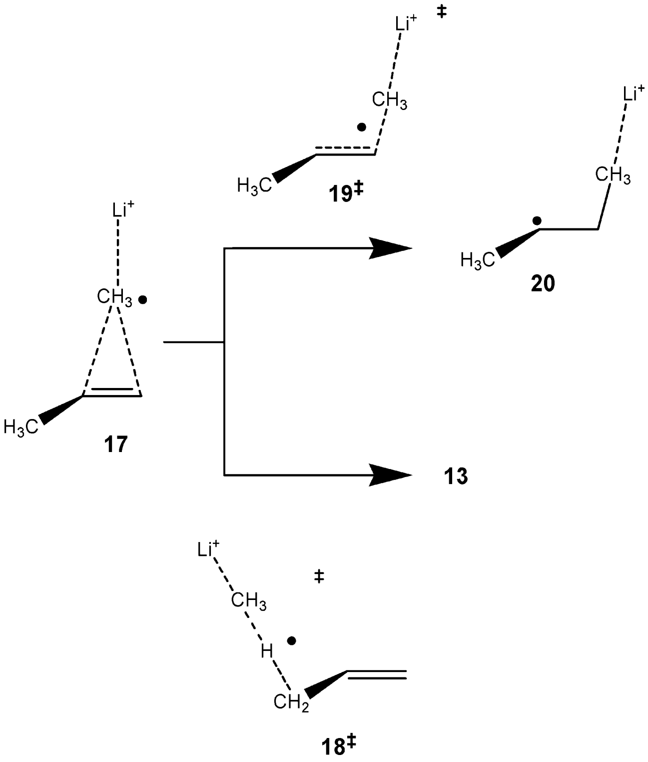
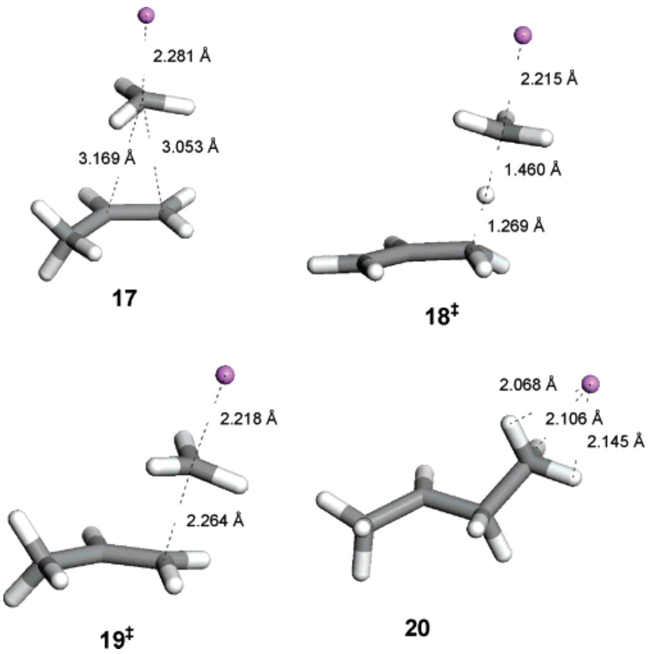
(13) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672.
(14) QCISD//6-311+G(d,p) optimized value with correction for zero-point vibrational energy at the same level; Clark, T. Unpublished results.

ation with a free radical is not competitive. Nonetheless, radical: Li^+ complexes may be formed directly by an addition reaction and react further with olefins. Thus, we have also investigated the reactions of $CH_3\cdots Li^{+\bullet}$ with propene.

The $Li^+\cdots CH_3^\bullet$:propene complex **17** is 15.8 kcal mol^{-1} less stable than the alternative complex **10**, as would be expected from the complexation energies of the methyl radical and propene to Li^+. Hydrogen-atom abstraction starting from this complex proceeds via transition state **18**‡, which lies 11.7 kcal mol^{-1} higher in energy than the lowest Li^+-catalyzed abstraction transition state **14**‡ (syn) and 10.3 kcal mol^{-1} higher than its anti equivalent **15**‡. The activation energy starting from immediate precursor, the complex **17**, is 8.0 kcal mol^{-1}, slightly higher than the 5.8 kcal mol^{-1} found for the unperturbed system.



The addition transition state **19**‡, for which the length of the forming C−C bond (2.264 Å) lies between those found in **11**‡ and **12**‡, is calculated to lie 1.4 kcal mol^{-1} higher in energy than **17** at the CBS-RAD(QCISD, B3-LYP) level. B3LYP and QCISD give barriers of 7.3 and 13.1 kcal mol^{-1}, respectively, relative to **17**. The product of this addition is the alternative agostically bound complex **20**, which lies 9.6 kcal mol^{-1} higher in energy than the odd-electron bonded complex **16**, in accord with the expected one-electron binding energy between the 2-butyl radical and Li^+. Therefore, reaction of Li^+:CH_3 with propene is less likely than reaction of Li^+:propene with CH_3.



Discussion

Comparison of the Calculational Levels. As pointed out by Radom et al.,[12] and confirmed in this work, QCISD/6-31G(d) reaction barriers for radical reactions are consistently too high compared to both B3LYP/6-31G(d) and CBS-RAD-(QCISD,B3-LYP), of which the density-functional method usually gives slightly higher barriers. Generally, as found previously,[4,5,12] B3LYP/6-31G(d) gives results quite close to those from CBS-RAD. In this case, it is pleasing to note that all three methods give the same order of activation energies except that QCISD finds no Li^+-stabilization of the H-atom abstraction transition state. The calculated QCISD activation barriers for the unperturbed reaction (via **4**‡) and the more favorable anti process with Li^+ (via **12**‡) are both 11.9 kcal mol^{-1}. Li^+ favors this reaction by 1.2 and 4.2 kcal mol^{-1} at the B3LYP and CBS-RAD levels, respectively. The alternative addition reaction (via **19**‡) is favored by Li^+ at all three levels (by 5.1, 4.4, and 6.7 kcal mol^{-1} at B3LYP, QCISD, and CBS-RAD, respectively).

More recently, Radom et al.[15] have used the G3- and W1-type techniques for reactions of the type discussed here. Their experience suggests that the CBS-RAD barriers reported here are systematically about 1.9 kcal mol^{-1} too low, although comparison with experiment for the unperturbed addition reaction (see above) suggests that CBS-RAD(QCISD,B3-LYP) is accurate at least for this reaction. Therefore, we can conclude that the barriers calculated here are reliable, although perhaps a little low. The agreement of the three calculational methods as to the ordering of the activation energies gives us confidence that the effects discussed below are not computational artifacts.

Origin of the Barrier Lowering. The original theory of odd-electron bond strengths[13] was refined by Hiberty et al.[16] in terms of valence-bond theory to give the following expression for the odd-electron bond energy D_{AB} between the moieties A and B:

$$D_{AB} = \frac{D_{AA} + D_{BB}}{2}\exp(-\Delta IP/2\sqrt{D^{AA}D^{BB}}) \qquad (1)$$

where D_{AA} and D_{BB} are the dissociation energies of the symmetrical odd-electron bonds between two moieties A and B, respectively, and ΔIP is the absolute value of the difference between their ionization potentials. Although this expression has since been improved to account for the stability[17] of some

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Table 2. ΔIP Values and Calculated (CBS-RAD(QCISD,B3-LYP)) Activation Energies (kcal mol^{-1})

	$CH_3^{\bullet}$ + propene	$CH_3^{\bullet}$ + propene:Li^+	$CH_3^{\bullet}$:Li^+ + propene
ΔIP according to (eq no.)	224[a] (2a) 273[a] (2b)	122[b] (3)	56[b] (4)

Activation Energies

		$CH_3^{\bullet}$ + propene	$CH_3^{\bullet}$ + propene:Li^+	$CH_3^{\bullet}$:Li^+ + propene
relative to the separated reactants	abstraction	5.8	5.5	5.1
	addition	8.7	1.4	6.7
relative to the precursor complex	abstraction		16.2	8.0
	addition		13.1	1.4

[a] Calculated assuming that the electron affinity of the methyl radical is zero and using the experimental[22] ionization potentials of propene and the methyl radical plus the spectroscopic electron affinity of propene.[23] [b] B3LYP/6-31G(d) values, which are generally reliable for ionization potentials.[24]

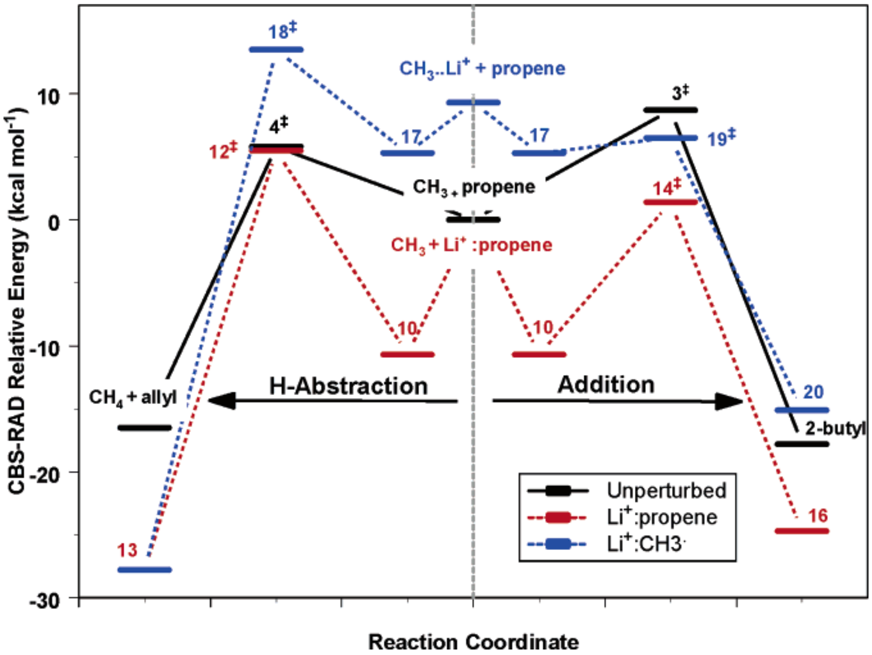

Figure 2. Schematic energy diagram of the competing addition and H-atom abstraction reactions (all energies are CBS-RAD(QCISD, B3-LYP)).

neutral odd-electron bonded complexes,[18] the conclusion[19] that singly charged (either positive or negative) odd-electron bonded species should be more strongly bound than neutral ones remains valid.

Equation 1 predicts that the odd-electron bond energy should decrease exponentially with increasing ΔIP. As ΔIP in a neutral odd-electron bonded complex represents the difference between an ionization potential and an electron affinity, it is necessarily large (i.e., it is the energy required to separate the charges). This is the basic principle behind electrostatic catalysis,[19] which has been demonstrated calculationally for a variety of open-shell reactions.[1,7,20,21] Electrostatic catalysis occurs because odd-electron interactions are usually present in the transition states for radical or triplet reactions but not in the starting materials or products.

Normally, complexation to a metal ion would be expected to increase the electrophilicity of a reagent, so that for a conventional closed-shell reaction complexation to the electrophilic reaction partner should lead to a lower barrier, whereas complexation to the nucleophilic partner should slow the reaction down. This is, however, not necessarily the case for electrostatic catalysis of radical reactions. Introducing a single positive charge will reduce ΔIP independently of the position of complexation. Thus, for the three pairs of reactions considered above, ΔIP is defined by eqs 2−4:

$$CH_3^{\bullet} + CH_3CH{=}CH_2 \rightarrow CH_3^{-} + CH_3CH{=}CH_2^{+\bullet} \quad (2a)$$

or

$$H_3^{\bullet} + CH_3CH{=}CH_2 \rightarrow CH_3^{+} + CH_3CH{=}CH_2^{-\bullet} \quad (2b)$$

$$CH_3^{\bullet} + CH_3CH{=}CH_2{:}Li^{+} \rightarrow CH_3^{+} + CH_3CH{=}CH_2{:}Li^{\bullet} \quad (3)$$

$$CH_3{:}Li^{+\bullet} + CH_3CH{=}CH_2 \rightarrow CH_3Li + CH_3CH{=}CH_2^{+\bullet} \quad (4)$$

Thus, complexing Li^+ to either reaction partner results in a charge shift, rather than a charge separation, as the defining reaction for ΔIP. Table 2 shows a summary of the Δ*IP* values and calculated activation energies relative to both the separated reactants and the precursor complexes.

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Table 2 shows that the simple expectations based on eq 1 are largely correct. The magnitudes of the barriers increase in each case in the expected order with the addition barriers usually lower than those for H-atom abstraction. These barriers are increased by the complexation energies for the precursor complexes **10** and **17**, but even so the barriers relative to the precursor complexes for the $Li^+\cdots CH_3^\bullet$ reactions are lower than those for propene:Li^+. This is perhaps surprising because $Li^+\cdots CH_3^\bullet$ itself exhibits a one-electron bond, so that the change in barrier must be attributed to the difference between two odd-electron bonds, rather than to the existence of an odd-electron bond solely in the transition state. Note that because of the higher complexation energy for **10** than for **17**, the propene:Li^+ transition states have lower absolute energies than those for $Li^+\cdots CH_3^\bullet$, although the activation energies starting from **17** are lower than those from **10**. The most favorable reaction paths are summarized in Figure 2, from which this effect can be seen.

The effect of Li^+-complexation on the addition reactions is far stronger than that on the hydrogen abstractions, which remain remarkably unaffected. This can be understood from the orbital interactions involved. Whereas addition to a double bond involves a clear odd-electron interaction with the π-bond that is complexed with the lithium cation, the abstraction involves interactions of the radical with σ_{CH} and σ^*_{CH} orbitals of the allyl CH_3 group, which are only affected inductively by complexation with the Li^+.

Li^+ as a Polymerization Catalyst. We must consider competition between the reaction system and solvent as solvating ligands for Li^+, even in alkane or chloroalkane solutions. Alkanes complex to Li^+ via agostic bonds of the type found, for instance, in **20**. This suggests that agostic bonding to Li^+ in alkane solution is roughly 10 kcal mol^{-1} less favorable than complexation to double bonds. This means that the latter should dominate in solutions containing alkenes. Thus, the processes to be compared in order to judge the effect of Li^+ ions in solution are the unperturbed radical reaction (black Figure 2) and that between the methyl radical and propene:Li^+ (red in Figure 2). The difference in activation energies between the H-atom abstraction and addition reactions changes from 2.9 kcal mol^{-1} in favor of H-atom abstraction in the unperturbed system to 4.1 kcal mol^{-1} in favor of addition for the reaction with propene:Li^+. Thus, the calculations provide support and rationalization for Michl's results and indicate that simple electrostatic catalysis provided by complexation with Li^+ is responsible for the remarkable effect of $LiCB_{11}(CH_3)_{12}$ on the polymerization of simple terminal olefins.[3]

Acknowledgment. I thank Josef Michl for fruitful discussions and for providing me with his experimental results before publication and Naomi Haworth for suggestions for improving the manuscript. This work was supported by the *Deutsche Forschungsgemeinschaft* under Grant No. Cl85/16-1 and -2.

Supporting Information Available: The full version of ref 8 together with Table S1 and the Gaussian 03 archive entries for the QCISD optimizations of structures **1** to **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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