Theoretical Study of Diels−Alder Cycloadditions of Butadiene to C₇₀. An Insight into the Chemical Reactivity of C₇₀ as Compared to C₆₀

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Received: January 31, 1996[⊗]

The eight unique Diels−Alder cycloadditions of butadiene to C_{70} are analyzed theoretically and compared with the well-established, two possible Diels−Alder cycloadditions of butadiene to C_{60}. Full geometry optimizations of reactants, adducts, and transition states are performed using the AM1 semiempirical method followed by single-point *ab initio* energy calculations. The results show that the cycloaddition of butadiene to the C_{70} fullerene in the gas phase is slightly more reactive than that to C_{60}. However, in toluene solution calculations yield that the different solvent effects on C_{60} and C_{70} cause a significant decrease of the energy barrier in the C_{60} cycloaddition, thus predicting a larger reactivity for C_{60} as compared to the C_{70} fullerene.

Introduction

The fascinating structure and properties of fullerenes have attracted much attention since their discovery 10 years ago.[1] Much is now known concerning their reactivity,[2] especially in reactions involving additions to C_{60}.[3,4] Among them, particularly appealing are the thermally allowed Diels−Alder cycloadditions to the C_{60} fullerene,[4] which take place readily through the shorter 6−6 bond rather than the 6−5 ring junction. On the contrary, studies involving Diels−Alder cycloadditions to the C_{70} fullerene are more scarce.[5,6] Loss of symmetry when going from I_h symmetry in C_{60} to D_{5h} symmetry in C_{70} increases the number of different carbon atoms in the fullerene (from 1 to 5) and the number of chemically different C−C bonds (from 2 to 8). Nevertheless, and as found for C_{60}, in addition to C_{70}[7,8] the attack to the 6−6 bond is preferred to the attack to the 6−5 bond; this is especially true for the so-called a−b and c−c bonds of C_{70}.[2b] In the present work, the widely accepted nomenclature employed by Balch *et al.*[7] for naming the five different carbon atoms and the eight distinct C−C bonds in C_{70} is used (see Scheme 1).

To our knowledge, a number of theoretical studies on the electronic structure of C_{70} have been appearing lately,[9] although only few calculations concerning the reactivity of C_{70} have been reported to date. A theoretical study by Henderson *et al.*[10] on the $C_{70}H_2$ isomers has shown that, at the semiempirical PM3 level, the c−c isomer is more stable than the a−b isomer by 1.1 kcal/mol, whereas at the Hartree−Fock 3-21G level the a−b isomer is the most stable by 0.2 kcal/mol, in agreement with experiment. In another work, Karfunkel and Hirsch[11] have carried out AM1 calculations which predict that the most probable products in nucleophilic additions to C_{70} are the c−c adducts, followed usually by the a−b isomers. Besides the appealing results of these papers, they are limited to thermodynamic considerations, and no transition states are located and characterized.

Even more interestingly, it is nowadays unclear whether C_{70} is more reactive than C_{60}; for instance, C_{60} reacts with cyclopentadiene *ca.* 7 times faster than C_{70} at 293 K in toluene,[6a] although an analogous behavior has not been established for the gas phase yet. Likewise, Becker *et al.*[12] have found that $C_{60}{}^{•+}$ reacts 5 times faster than $C_{70}{}^{•+}$ does with 1,3-cyclopenta-

SCHEME 1
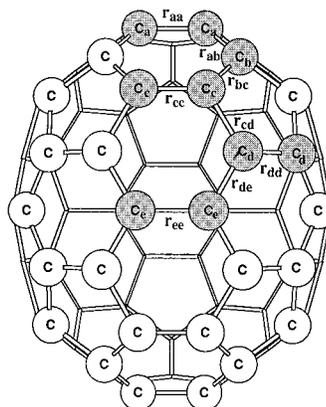
diene in the gas phase. Moreover, some authors[5b] have suggested that the larger aromaticity of C_{70} could result in lower reactivity. Furthermore, it could also be argued that the large stability of C_{70} as compared to that of C_{60} should decrease its reactivity. However, on the other hand, the dominant driving force in Diels−Alder cycloadditions involving fullerenes is the HOMO−LUMO interaction.[14] Given that experimental work[15] and theoretical calculations[9c,f,14] predict lower LUMO energies for C_{70} than for C_{60}, from this point of view one should also expect an increased reactivity of C_{70} as compared to C_{60}.[2a,14]

The lack of calculated data on transition states and the controversy on C_{60} *vs* C_{70} reactivity have led us to carry out a combined semiempirical AM1 and *ab initio* study of the Diels−Alder cycloadditions to butadiene to C_{60} and C_{70}. This work has thus two main purposes: first, to perform a gas phase analysis of the thermodynamic and kinetic factors that govern the regiochemistry of Diels−Alder cycloadditions to C_{70} and second to compare the reactivity of C_{70} to that of C_{60} for this kind of reactions in the gas phase and in solution.

Computational Details

The size of the systems studied prevents the use of *ab initio* molecular quantum mechanical methods to perform optimizations. Therefore, full geometry optimizations have been carried out with the AM1 semiempirical method[16] as implemented in the AMPAC 5.0, a quantum chemistry program from Semichem, Inc.[17] The AM1 method has been preferred over other semi-

TABLE 1: Main AM1 Geometrical Parameters of Reactants, Transition States, and Adducts in the Diels–Alder Processes Studied[a]

dienophile	attack	reactant				transition state				adduct			
		r_i	r_i^{Exp}	Pyr(1)[e]	Pyr(2)[e]	r_i	r_{DA}	r'_{DA}	$\nu^{\ddagger}$	r_i	r_{DA}	r'_{DA}	Δr_i[g]
C_{60}	6–6	1.385	1.401(10)[c]	11.64	11.64	1.433	2.167	2.167	687i	1.573	1.539	1.539	0.188
	6–5	1.464	1.458(6)[c]	11.64	11.64					1.617	1.535	1.535	0.153
C_{70}	c–c[b]	1.375	1.376(7)[d]	10.57	10.57	1.421	2.180	2.180	640i	1.557	1.540	1.541	0.182
	a–b[b]	1.387	1.385(7)[d]	11.91	11.93	1.434	2.154[f]	2.184	690i	1.576	1.538	1.539	0.189
	d–e[b]	1.414	1.417(6)[d]	9.75	8.64					1.587	1.552	1.541	0.173
	d–d	1.434	1.438(4)[d]	9.75	9.75	1.474	2.159	2.159	770i	1.620	1.538	1.538	0.186
	b–c	1.461	1.449(6)[d]	11.93	10.57					1.613	1.533	1.533	0.152
	a–a	1.464	1.459(4)[d]	11.91	11.91					1.618	1.533	1.533	0.154
	c–d	1.467	1.46(1)[d]	10.57	9.75					1.606	1.539	1.534	0.139
	e–e[b]	1.465	1.479(7)[d]	8.64	8.64					1.635	1.552	1.552	0.170

[a] r_i is the C–C distance between the two attacked carbon atoms of the fullerene, while r_{DA} and r'_{DA} are the two forming C–C single bond lengths in the cycloaddition. Pyr(1) and Pyr(2) are the pyramidalization angles of the two attacked carbons in the initial fullerene. $\nu^{\ddagger}$ is the imaginary frequency in the saddle point. Distances are given in angstroms, angles in degrees, and frequencies in cm^{-1}. [b] 6–6 bonds in C_{70}. [c] Reference 33. [d] Reference 34a. [e] Reference 35. [f] C–C bond length for the attack to atom labeled a. [g] $\Delta r_i = r_i^{adduct} - r_i^{reactant}$.

empirical methods due to four main reasons: first, it yields reliable results for the geometries of C_{60}[18] and C_{70} (*vide infra*) and also for the Diels–Alder adducts;[18] second, it reproduces high-level *ab initio* calculations and experimental results for a number of Diels–Alder cycloadditions;[19] third, for the ethylene + butadiene cycloaddition, this method yields better energy barriers as compared to experiment than some correlated *ab initio* or density functional methods;[20] and fourth, Dewar's group encourages the use of the AM1 method among other semi-empirical methods for the study of pericyclic reactions.[21] All zero-gradient structures have been optimized using the eigenvector following algorithm, continued by a vibrational analysis to characterize the stationary points. For the most relevant stationary points, single-point *ab initio* Hartree–Fock (HF) energy calculations in the gas phase and in solution have been performed at the AM1-optimized geometries employing the 3-21G basis set[22] (HF/3-21G//AM1) and with the help of the Gaussian-94 program.[23] Solvent effects have been considered through the self-consistent reaction field (SCRF) method developed by Tomasi and co-workers,[27] as implemented in the Gaussian-94 package. A dielectric constant of 2.4 has been taken as being representative of a toluene solution. Cartesian coordinates for all reactants, transition states, and adducts are available from the authors upon request.

Results and Discussion

The main AM1-optimized parameters of C_{60}, C_{70}, transition states (TS), and adducts are gathered in Table 1. The results reveal a good agreement between the AM1-optimized and the experimental C–C bond lengths in the two fullerenes studied, thus providing confidence on the reliability of the AM1 method to reproduce geometries for fullerenes. The computed bond distances differ by less than 0.012 Å from those obtained using the PM3 method.[25] It is noteworthy that for C_{70} the bond length order found experimentally is correctly reproduced by theory, except for the c–d bond which is computed to be larger than the e–e bond by 0.002 Å. However, these two bonds are not specially relevant for the discussion of regioselectivity of Diels–Alder cycloadditions to C_{70}, given that, from a thermodynamic point of view, they are the less reactive (*vide infra*).

According to the different number of C–C bonds in C_{60} and C_{70}, two and eight unique adducts exist for C_{60} and C_{70}, respectively. As found experimentally in a similar reaction,[4a] the adducts adopt a stable boat conformation. Among the two possible 6–5 adducts for the C_{60} cycloaddition, corresponding to the usual exo and endo attacks,[18] only the so-called 6–5/5 isomer has been located, since it has been shown in a previous

study of a Diels–Alder cycloaddition to be the most stable adduct.[18] In this isomer the boat structure faces the pentagonal cycle instead of the hexagonal ring of the 6–5 bond being attacked. The same criterion has been adopted for the 6–5 adducts of C_{70}.

From the set of r_i values of reactants and r_i, r_{DA}, r'_{DA}, and Δr_i values of adducts collected in Table 1, some similarities can be recognized between the nature of bonds in C_{60} and C_{70}. If the two types of C–C bonds in C_{60} are taken as reference bonds, in C_{70} the a–b and c–c bonds show typical 6–6 bond structural parameters, and the a–a and b–c bonds can be considered as regular 6–5 bonds. The nature of the rest of C–C bonds present in C_{70} could be contemplated as follows: d–e and e–e are 6–6 bonds longer than the 6–6 bond in C_{60}, while d–d is a shorter 6–5 bond and c–d is a longer 6–5 bond, both compared to the 6–5 bond in C_{60}. This bonding nature will have direct consequences on the chemical reactivity of C_{70}: for a given bond type, longer bonds are less reactive and shorter bonds become more reactive, as compared to the reactivity of the same bond types in C_{60} (*vide infra*). The same ordering was found from *ab initio* calculations by Scuseria,[9c] who classify the nature of the bonds in C_{70} as double bonds (the a–b, c–c, and d–d), intermediate (d–e), and single bonds (the a–a, b–c, e–e, and c–d).

Furthermore, a good qualitative agreement is found between the theoretically calculated r_i values in c–c and a–b adducts (1.557 and 1.576 Å) and those reported experimentally by X-ray crystallography (1.584 and 1.603 Å, respectively) for a Diels–Alder addition of o-quinodimethane to C_{70}.[6b] Moreover, the tendency followed by the Δr_i values for the c–c and a–b attacks is fairly well reproduced; while AM1 calculations result in bond lengthening of 0.182 and 0.189 Å, a X-ray analysis[6b] reported values of 0.203 and 0.211 Å, respectively.

Only those TSs connecting the thermodynamically most stable adducts have been located (see Tables 2 and 3 for energetics), because in light of the Hammond postulate[26] the lowest TSs are likely to be found for the most stable adducts. For this reason only three out of eight TSs in C_{70} have been analyzed (Figure 1): two of them corresponding to a 6–6 attack (the so-called a–b and c–c) and one associated to a 6–5 attack (the so-called d–d). For the sake of comparison, the TS corresponding to the 6–6 attack to C_{60} (Figure 2) has been also optimized. Interestingly, among the studied TSs, the forming C–C single bond lengths are remarkably constant, lying in the usual range of 2.0–2.3 Å found in most cycloaddition reactions.[19] It must be noted here that both RHF/AM1 and high-level *ab initio* calculations predict concerted and synchronous

TABLE 2: AM1 Standard Enthalpy of Formation ($\Delta H_f°$), Reaction Enthalpy (ΔH_r), Enthalpy Barriers for the Diels−Alder ($\Delta H^{\ddagger}_{DA}$) and retro-Diels−Alder ($\Delta H^{\ddagger}_{rDA}$), Distortion Enthalpies of Reactants ($\Delta H_{dis}^{butadiene}$, ΔH_{dis}^{C70}), and Interaction Enthalpy between Distorted Butadiene and C₇₀ (ΔH_{int})[a]

| complex	label	$\Delta H_f°$	ΔH_r	$\Delta H^{\ddagger}_{DA}$	$\Delta H^{\ddagger}_{rDA}$	$\Delta H_{def}^{butadiene}$	ΔH_{def}^{C70}	ΔH_{int}
reactant	butadiene	30.69						
	C₇₀	1061.97						
TS	c−c	1107.57		14.91	67.46	11.33	5.45	−1.87
				(23.39)	(59.83)			
	a−b	1108.54		15.88	67.58	11.81	5.60	−1.53
				(24.15)	(61.34)			
	d−d	1113.08		20.42	66.23	13.08	7.37	−0.03
				(29.77)	(59.21)			
adduct	c−c	1040.11	−52.55			99.78	52.05	−204.38
			(−36.44)					
	a−b	1049.96	−51.70			99.41	51.89	−203.00
			(−37.20)					
	d−e	1061.91	−30.75			98.31	59.50	−188.56
	d−d	1046.85	−45.81			101.10	57.45	−204.36
			(−29.44)					
	b−c	1057.08	−35.58			101.79	58.46	−195.83
	a−a	1056.20	−36.46			101.52	58.29	−196.27
	c−d	1073.19	−19.47			101.00	62.42	−182.89
	e−e	1095.09	2.43			95.59	66.14	−159.30

[a] All values are given in kcal/mol. Values in parentheses have been recalculated at the *ab initio* HF/3-21G//AM1 level.

TABLE 3: AM1 Standard Enthalpy of Formation ($\Delta H_f°$), Reaction Enthalpy (ΔH_r) Enthalpy Barriers for the Diels−Alder ($\Delta H^{\ddagger}_{DA}$) and retro-Diels−Alder ($\Delta H^{\ddagger}_{rDA}$), Distortion Enthalpies of Reactants ($\Delta H_{dis}^{butadiene}$, ΔH_{dis}^{C60}), and Interaction Enthalpy between Distorted Butadiene and C₆₀ (ΔH_{int})[a]

complex	label	$\Delta H_f°$	ΔH_r	$\Delta H^{\ddagger}_{DA}$	$\Delta H^{\ddagger}_{rDA}$	$\Delta H_{dis}^{butadiene}$	ΔH_{dis}^{C60}	ΔH_{int}
reactant	butadiene	30.69						
	C₆₀	973.34						
TS	6−6	1020.27		16.24[b]	67.07	12.02	5.77	−1.55
				(25.70)	(60.74)			
adduct	6−6	953.20	−50.83			99.30	52.56	−202.69
			(−35.04)					
	6−5	970.98	−33.05			99.71	58.91	−191.67

[a] All values are given in kcal/mol. Values in parentheses have been recalculated at the *ab initio* HF/3-21G//AM1 level. [b] The STO-3G value, reported in ref 28, is 29.1 kcal/mol.
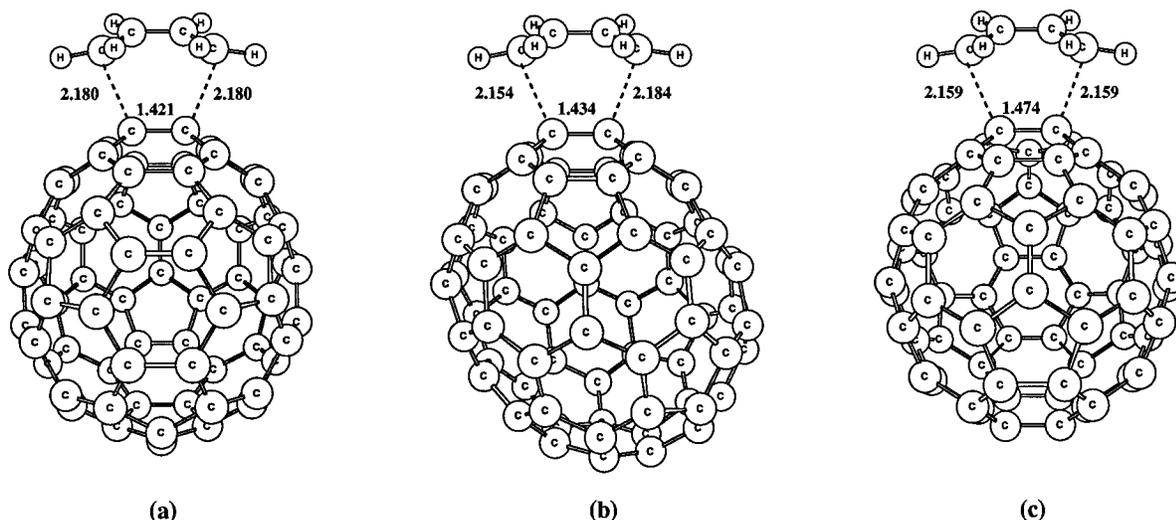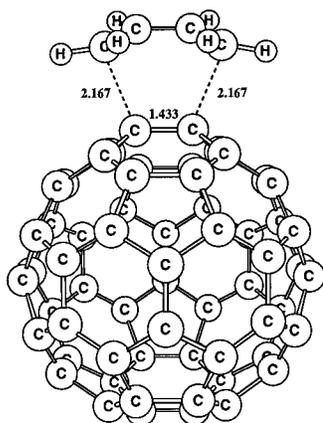

Figure 1. AM1 transition states corresponding to three studied attacks in the Diels−Alder cycloaddition of butadiene to C₇₀: (a) the c−c attack, (b) the a−b attack, and (c) the d−d attack.

TSs for Diels−Alder cycloadditions between unsubstituted dienes and dienophiles.[19] The c−c and d−d TSs located in this work preserve the C_s symmetry, confirming the concerted, synchronous nature of these TSs. The only exception corresponds to the a−b TS (Figure 1b). The reason must be found in the fact that the perpendicular plane dividing the a−b bond in the initial C₇₀ fullerene was not actually a symmetry plane. Table 1 collects also the imaginary frequency corresponding to the unique negative eigenvalue[27] of the mass-weighted energy second-derivative matrix of each optimized TS, which corre-

sponds to the expected normal mode showing the approach of the atoms involved.

The standard enthalpies of formation of reactants, TSs, and adducts are collected in Tables 2 and 3, together with reaction enthalpies and enthalpy barriers for the Diels−Alder and retro-Diels−Alder reactions. The different Diels−Alder enthalpy values (ΔH_r, $\Delta H^{\ddagger}_{DA}$, and $\Delta H^{\ddagger}_{rDA}$) of each complex have been divided into the enthalpy contributions due to distortion and interaction. The distortion enthalpy is the enthalpy needed to modify the geometry of the reactants to that they have in the

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Figure 2. AM1 transition state corresponding to the 6−6 attack in the Diels−Alder cycloaddition of butadiene to C_{60}.

complex and is in turn split into the distortion enthalpy of butadiene ($\Delta H_{\text{def}}^{\text{butadiene}}$) and that of the fullerene ($\Delta H_{\text{def}}^{\text{fullerene}}$). Likewise, the interaction enthalpy is the enthalpy stabilization due to the interaction between the two deformed fragments (ΔH_{int}).

As regards to the Diels−Alder cycloaddition of butadiene to C_{70}, and as found previously in related experimental[6b,8] and theoretical[10,11] studies of C_{70} reactivity, the c−c and a−b adducts are those most stable from a thermodynamic point of view. AM1 results in Table 2 favor the c−c over the a−b adduct by 0.85 kcal/mol, while the *ab initio* HF/3-21G//AM1 calculations yield the a−b adduct to be more stable by 0.77 kcal/mol. The fact that semiempirical methods favor the c−c adduct was already pointed out by Henderson *et al.*,[10] who, on the basis of experimental results, concluded that the HF/3-21G ordering of the adducts was superior to that provided by semiempirical methods. From such a result, one is led to infer that the a−b adduct is likely to be thermodynamically the most stable. With regard to enthalpy barriers, the AM1 method also favors the c−c adduct over the a−b adduct by 0.97 kcal/mol. It must be pointed out that AM1 enthalpy barriers in Diels−Alder reactions are usually better when compared to experiment than that obtained by means of the *ab initio* Hartree−Fock methodology.[20] Further, for enthalpy barriers the qualitative ordering given in Table 2 by the AM1 and the *ab initio* HF/3-21G//AM1 methods coincides, so it seems reasonable to conclude that whereas a−b is thermodynamically favored, c−c is probably preferred from a kinetic point of view. Since differences in enthalpies are relatively small, both attacks should be experimentally observed. Apart from the a−b and c−c adducts, the next most stable adduct is d−d, which is thermodynamically and kinetically destabilized by as much as *ca.* 6 kcal/mol with respect to the a−b and c−c adducts. It is interesting to observe that, from a thermodynamic point of view, in C_{70} a particular 6−5 attack (d−d) is found to be preferred over two types of 6−6 attacks (d−e and e−e).

As found in C_{60},[18,28] the a−b and c−c 6−6 ring fusions in C_{70} are far more reactive than the d−d 6−5 bonds. Noteworthy, in C_{70} the c−c bond is the shortest 6−6 bond, and although a−b is not the shortest 6−6 bond, its constituting atoms possess the largest pyramidalization angles followed by atom c (see values in Table 1). This result agrees with the fact that the regioselectivity for additions to fullerenes correlates with the degree of pyramidalization of the attacked carbon atoms, as proposed by Haddon.[29] In addition, Hawkins *et al.*[30] found that osmylation of C_{70} takes place regioselectively at sites of greater curvature like the a−b bond. On the other hand, among the 6−5 bonds, the d−d bond is both the shortest 6−5 bond and

the one which has the smallest curvature. Thus, as far as chemical reactivity is concerned, two characteristics appear to be determining. First, regardless of the bond type, short bond lengths (which mean larger π-bond orders and higher π-density) are preferred, and second, additions to 6−6 bond types are favored by larger pyramidalization angles,[29,30] while the reverse effect is observed for 6−5 bond types.

Interestingly, all pyramidalization angles of the C_{70} carbon atoms being attacked are almost constant in TSs and adducts, ranging from 11.8° to 12.2°. In the TSs the carbon atoms possess almost the same pyramidalization angle as in the adducts where carbon atoms are tetrahedrally coordinated. Thus, attacked carbon atoms pyramidalize to about 12° in the TSs when the diene is added. Therefore, those bonds with atoms having large pyramidalization angles in the C_{70} fullerene are the most reactive, basically because the local strain in these carbons is larger[29] and also because the loss of aromaticity when achieving the appropriate pyramidalization angle in the TS is smaller. Further, the average in the pyramidalization angles of all carbon atoms in the C_{70} cage takes values from 10.7° to 10.8° for C_{70}, TSs, and adducts. This confirms that hybridization and strain are approximately conserved in fullerenes during reactions, as pointed out by Haddon.[29]

Tables 2 and 3 show that the sum of distortion enthalpies of the butadiene and C_{60} or C_{70} accounts for almost all the enthalpy barriers of the reactions studied. Interaction enthalpies are always smaller than 2 kcal/mol. Thus, once the reactants are distorted to their geometries in the TS, the reaction proceeds without barrier. Remarkably, for the TSs studied, distortion enthalpies of C_{60} and C_{70} are quite small, their initial geometry remaining almost unchanged in the TS. In fact, the distance between the two attacked carbons of the fullerene changes by only 0.04−0.05 Å when going from the isolated fullerenes to their geometries in the TSs. The most relevant changes take place in the geometry of the butadiene, which shows larger distortion enthalpies with the reduction of the bond lengths of the two forming C−C bonds. Noticeably, the c carbon atoms involved in the c−c bond (which possesses the largest bond lengths for the two forming C−C bonds in the TS) bear also large LUMO coefficients (with an orbital energy of −3.28 eV). This allows butadiene (with an HOMO orbital energy of −9.37 eV) to interact favorably with the c−c bond of C_{70} at long distances, thus reducing both Pauli repulsions and distortion enthalpies, hence leading to a smaller enthalpy barrier. On the contrary, the a and b carbon atoms exhibit almost zero LUMO coefficients, although, on the other hand, they have a large coefficient for the LUMO+1 orbital (orbital energy equals −3.18 eV). The interaction of the HOMO of butadiene with the LUMO+1 orbital of C_{70} is somewhat less favorable than the interaction with its LUMO orbital, which results in a meaningfully smaller charge transfer in the a−b TS as compared to the c−c TS and to a slightly larger enthalpy barrier for the a−b TS. Noteworthy, the adducts corresponding to the TSs analyzed have also the largest interaction enthalpies.

It must be remarked here that the Diels−Alder cycloadditions studied have a normal electronic demand,[31] *i.e.*, an electron transfer from butadiene to fullerene. The charge transfer to C_{60} and C_{70} in the TSs studied is almost the same (*ca.* 0.25 au), which is quite large for unsubstituted Diels−Alder cycloadditions, yet somewhat larger for TSs concerning C_{70}, as expected from the fact that the LUMO orbital is more stabilized in this fullerene.[14,15]

AM1 enthalpy barriers for the studied retro-Diels−Alder cycloreversions ($\Delta H_{\text{rDA}}^{\ddagger}$) are systematically larger than those obtained at the *ab initio* HF/3-21G//AM1 level. This is not at

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all surprising since it is well-known that AM1 $\Delta H^{\ddagger}_{rDA}$ are usually larger (*ca.* 10 kcal/mol) than those found experimentally.[32] The retro-DielsAlder enthalpy barriers remain almost unchanged for the two fullerenes analyzed and for the different attacks studied.

AM1 reaction enthalpies (−52.6 *vs* −50.8) and enthalpy barriers (14.9 *vs* 16.2) of Tables 2 and 3 as well as *ab initio* energy results show that in the gas phase C$_{70}$ is slightly more reactive than C$_{60}$. However, for the Diels–Alder cycloaddition of C$_{60}$ and C$_{70}$ to cyclopentadiene in toluene solution,[6a] it was found that C$_{60}$ is 7 times more reactive than C$_{70}$. This might be caused by a larger solvent stabilization of the C$_{70}$ fullerene as compared to C$_{60}$. Moreover, Burba *et al.*[15a] have shown that the electron affinity difference between C$_{70}$ and C$_{60}$ in the gas phase is reduced in a solution of *n*-hexane from 0.073 to 0.025 eV.

To investigate how the combination of these two effects may affect the relative reactivities of the C$_{60}$ and C$_{70}$ fullerenes in the gas phase and in solution, we have undertaken the study of the Diels–Alder cycloadditions in toluene solution by means of a SCRF method. In particular, we have compared the 6–6 addition of butadiene to C$_{60}$ and the a–b attack to C$_{70}$ at the HF/3-21G//AM1 level using a dielectric constant of 2.4. We have found that whereas the free C$_{70}$ molecule is stabilized in solution by −3.7 kcal/mol, the C$_{60}$ is destabilized by 5.1 kcal/mol. As a result, the energy barrier of the C$_{60}$ cycloaddition in toluene solution becomes 20.8 kcal/mol, and the reaction enthalpy decreases to −40.5 kcal/mol. For the a–b attack to the C$_{70}$ molecule the effect is the opposite: both the enthalpy barrier and the reaction enthalpy increase to 28.5 and −33.8 kcal/mol, respectively. Thus, the different solvent effects in the C$_{60}$ and C$_{70}$ cycloadditions lead to a change in the relative reactivities in the gas phase and in solution. Therefore, the present results show that, in toluene solution, the cycloaddition to C$_{60}$ is, both kinetically and thermodynamically, more favorable than cycloaddition to C$_{70}$, which is in agreement with the experimental result found in the cycloaddition of cyclopentadiene to C$_{60}$ and C$_{70}$.[6a]

The model used in the present work to introduce solvent effects exhibits obvious limitations such as the level of calculation, the representation of the solvent by a continuous polarizable dielectric, and the lack of reoptimized geometries at the *ab initio* level, both in the gas phase and in solution. Despite these restrictions, the results yielded by this model should offer a fair indication of the main effects caused by the solvent in the studied cycloadditions.

Conclusions

In this work we have analyzed the Diels–Alder cycloadditions of butadiene to C$_{70}$. We have concluded that the most probable additions to C$_{70}$ take place at the a–b and c–c 6–6 bond types. While the a–b attack has been shown to be preferred from a thermodynamic point of view, the c–c attack seems to be kinetically favored. Additions to other bonds are thermodynamically unfavored by at least 6 kcal/mol. Comparison of the Diels–Alder chemical reactivity of C$_{60}$ and C$_{70}$ shows that in the gas phase the cycloaddition of butadiene to the 6–6 bond of the C$_{60}$ fullerene has a larger enthalpy barrier and a lower exothermicity than cycloadditions to the a–b and c–c bonds of C$_{70}$. However, in toluene solution the relative chemical reactivities of C$_{60}$ and C$_{70}$ interchange, C$_{60}$ becoming more reactive than C$_{70}$, mainly as a result of the different stabilization of the C$_{60}$ and C$_{70}$ fullerenes in solution.

We have not studied here the possibility of multiple additions to the fullerenes. The particular spatial disposition of the reactive bond sites in C$_{60}$ (30 symmetrically distributed 6–6 bonds) and in C$_{70}$ (10 a–b and 10 c–c 6–6 bonds concentrated at the poles) results in different patterns for the multiple additions to C$_{60}$ and C$_{70}$. For instance, in the Diels–Alder cycloaddition with benzyne it has been found[5d] that C$_{60}$ adds up to 6 equiv of the diene and C$_{70}$ reacts with 10 equiv. As a result, the relative reactivity of C$_{60}$ with respect to C$_{70}$ may also change as multiple addition proceeds. Research in this direction is currently under way in our laboratory.[36]

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