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Kinetics of the Diels–Alder reaction between C_{60} and acenes

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Abstract

The kinetics of the Diels–Alder reactions between C_{60} and the linear acenes anthracene and tetracene are studied in toluene, in the temperature range 22–63 °C. It is observed that tetracene reacts much more readily with C_{60} than does anthracene. The different reactivities of anthracene and tetracene towards C_{60} correlate with the respective aromaticity loss upon cycloaddition, as previously predicted theoretically. The two monoadducts also display different kinetics as regards the dissociation back to the reagents. In the studied temperature range, tetracene monoadduct decomposition by retro-Diels–Alder reaction is negligible, while the anthracene monoadduct is unstable above room temperature.

1. Introduction

The electron-deficient character of C_{60} determines its high reactivity as a dienophile in Diels–Alder ([4 + 2] cycloaddition) reactions [1–3]. For this reason, mono- and multiple C_{60} functionalization by the Diels–Alder reaction is a common synthetic procedure in fullerene chemistry [1–3]. Although numerous derivatives of C_{60} have been obtained by Diels–Alder cycloaddition [1–3], almost no experimental kinetic data is available for this important fullerene reaction. The only exception is the reaction of C_{60} with cyclopentadiene, for which the kinetics of both the direct [4] and the reverse Diels–Alder [5] reactions were studied. The energetics of the Diels–Alder cycloaddition of quinodimethanes to C_{60} was recently addressed theoretically [6]. A factor that can determine both the rates and the thermodynamics of a Diels–Alder reaction is the overall gain or loss of aromaticity when going from the reactants to the addition product [6]. These aromaticity changes may occur in the dienophile and/or in the diene. In the case of C_{60}, both a strain release (owing to pyramidalization) and aromaticity loss occur upon addition to a 6–6 bond [6]. As for the diene, an aromaticity gain (e.g., quinodimethanes [6]), no aromaticity change (e.g., cyclopentadiene), or an aromaticity loss (e.g., anthracene and other acenes [7]) can occur. The role of aromaticity loss in the relative reactivity of linear acenes (naphthalene, anthracene, tetracene, etc.) in Diels–Alder reactions was recently studied theoretically with ab initio and DFT quantum-chemical methods [7,8].

In this work, the kinetics of the Diels–Alder reactions of C_{60} with anthracene and tetracene are investigated experimentally, and the results compared to theoretical predictions.

2. Experimental

C_{60} (99.5%) was purchased from Sigma–Aldrich and used as received. Anthracene (>99.0%) and tetracene (>97.0%) were from Fluka. Toluene (Merck) was of spectroscopic grade. Absorption spectra were recorded on a Shimadzu UV 3101PC UV–VIS–NIR spectrophotometer using 1.0 cm path length cells, and a thermostated cell holder. The temperature was controlled to within ±0.5 °C, and the reactions carried out in the dark.

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All spectra were run against toluene as a blank. In order to avoid a competing Diels–Alder reaction (with singlet oxygen as the dienophile) [9], the tetracene reactions were carried out in sealed and degassed cells (4 freeze–pump–thaw cycles of the C_{60} solution in toluene, prior to mixing with tetracene under vacuum). No precaution of this kind was necessary for the aerated anthracene solutions, that for the concentration used were stable at all temperatures in the absence of fullerene.

3. Method of data analysis

The Diels–Alder reaction between acenes and C_{60} is described by a concerted mechanism [10],

$$F + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} FA, \tag{1}$$

where F is the fullerene, A is the acene, and FA is the monoadduct. The rate equation for the monoadduct is

$$\frac{d[FA]}{dt} = k_1[A][F] - k_{-1}[FA] \tag{2}$$

If the deviation to equilibrium is defined as $x = [FA]_e - [FA]$, Eq. (2) becomes

$$\frac{dx}{dt} = -\Gamma x - k_1 x^2 \tag{3}$$

with

$$\Gamma = [k_1([A]_e + [F]_e) + k_{-1}], \tag{4}$$

Γ being the inverse of the relaxation time of the system [11]. Integration of Eq. (3) yields

$$x = \frac{x_0}{(1+\alpha)e^{\Gamma t} - \alpha}, \tag{5}$$

where $x_0 = x(0)$ and

$$\alpha = \frac{k_1 x_0}{\Gamma} = \frac{K([FA]_e - [FA]_0)}{1 + K([A]_e + [F]_e)}, \tag{6}$$

where K is the equilibrium constant,

$$K = \frac{k_1}{k_{-1}}. \tag{7}$$

For small x_0, $\alpha \ll 1$ and Eq. (5) reduces to the well-known relaxation equation [11]. In the described experiments, however, $[FA]_0 = 0$, and α is not always small.

If the absorbance A of the system is measured at a wavelength, where only the addition product FA absorbs, then

$$A = \varepsilon_{FA} l([FA]_e - x), \tag{8}$$

where ε_{FA} is the absorption coefficient and l is the optical pathlength. Finally,

$$A(t) = A_\infty \frac{1 - e^{-\Gamma t}}{1 - \beta e^{-\Gamma t}}, \tag{9}$$

where

$$A_\infty = \varepsilon_{FA} l [FA]_e \tag{10}$$

and the parameter β, with $\beta \leqslant 1$, is

$$\beta = \frac{\alpha}{1+\alpha} = \frac{K([FA]_e - [FA]_0)}{1 + K([A]_e + [F]_e + [FA]_e - [FA]_0)}. \tag{11}$$

From a fit of Eq. (9) to experimental data, it is in principle possible to obtain the parameters Γ, β and A_∞. Then $[FA]_e$ is computed from A_∞ provided the absorption coefficient ε_{FA} is known. Next, the equilibrium constant is obtained from

$$K = \frac{[FA]_e}{([A]_0 - [FA]_e)([F]_0 - [FA]_e)}. \tag{12}$$

On the other hand, the parameter Γ allows the calculation of k_1,

$$k_1 = \frac{\Gamma}{[A]_e + [F]_e + \frac{1}{K}} \tag{13}$$

and k_{-1} is finally computed from K and k_1. The parameter β is redundant, and not always obtainable with satisfactory precision, as it can be much smaller than unity. Furthermore, it is correlated with A_∞, and it is preferable to write explicitly the dependence of parameter β on $[FA]_e$ and perform the fit with only two parameters, Γ and $[FA]_e$. In the two systems studied, particular cases of Eq. (9) apply, as will be discussed.

4. Results

4.1. Reaction with anthracene

The reaction of C_{60} with anthracene in toluene was studied in the temperature range 22–63 °C. The initial concentration of anthracene was 1.1×10^{-2} M while the C_{60} concentration was kept fixed at 2.1×10^{-4} M. After mixing C_{60} and anthracene, four prominent absorption features appear at 436 nm (sharp band), 486 nm (broad band), 640 nm (shoulder) and 706 nm (weak band), Fig. 1, their intensity progressively increasing with time. These absorption bands are characteristic of the mono-adduct of C_{60} and anthracene [12–14], formed upon [4 + 2] cycloaddition, Scheme 1.

The addition occurs at one of the 30 equivalent 6–6 bonds of C_{60}, and the reaction is regioselective from the point of view of anthracene, taking place at the central ring, across the 9, 10 positions. The existence of isosbestic points at 586 and 612 nm, see Fig. 1, confirms that multiple addition [15] is negligible for the experimental conditions and observation time window used, in spite of the relatively large excess of anthracene. Identical results were obtained for all the other temperatures.

Since the acene was always in large excess in the experiments, it results from Eq. (11) that

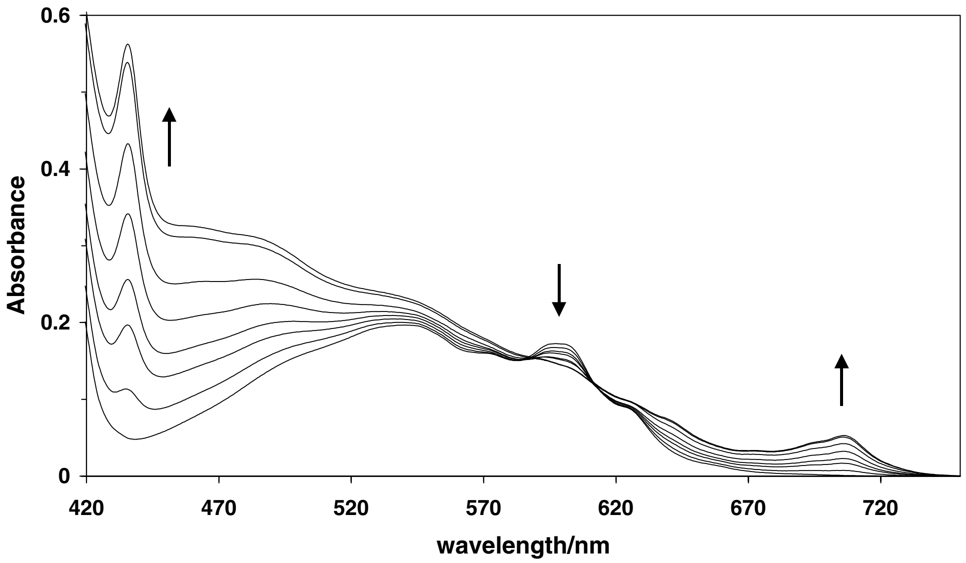
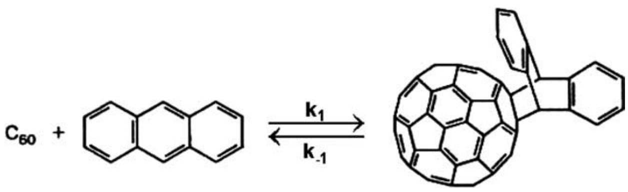


Fig. 1. Electronic absorption spectra of the reaction mixture C_{60}–anthracene as a function of time, for a temperature of 63 °C. The absorption spectrum with the lowest 436 nm absorption corresponds to the starting C_{60}–anthracene mixture. The remaining spectra correspond to reaction times of 60, 130, 185, 295, 482, 1523 and 2343 min.



Scheme 1.

$$\beta = \frac{K[FA]_e}{1+K[A]_0} < \frac{K[F]_0}{1+K[A]_0} < \frac{[F]_0}{[A]_0} = 0.02. \qquad (14)$$

Hence, Eq. (9) reduces to

$$A(t) = A_\infty(1 - e^{-\Gamma t}) \qquad (15)$$

The fitted values of Γ and A_∞ for several temperatures are given in Table 1 (see also Fig. 2). It is seen from Table 1 that there is a progressive decrease of A_∞ from its maximum possible value (corresponding to an irreversible reaction) as the temperature is increased. This shows that the reversibility of the reaction is non-negligible for temperatures higher than ambient. The decrease of the computed equilibrium constant with temperature shows that the reaction is exothermic, as expected for a Diels–Alder reaction. Values of K, k_1 and k_{-1} were estimated as described, using the determined A_∞ and Γ, and an absorption coefficient ε_{FA} for the monoadduct of 324 M^{-1} cm^{-1} at 706 nm [14]. The results are summarized in Table 1.

4.2. Reaction with tetracene

The reaction of C_{60} with tetracene in toluene was studied in the temperature range 25–59 °C. Owing to the faster rates for this reaction, and to the low solubility of tetracene in toluene, tetracene was not in large excess in the experiments, as was the case with anthracene. Instead, a molar ratio C_{60}:tetracene of 10:13 was used. The initial concentration of tetracene was 2.3×10^{-4} M while the C_{60} concentration was kept fixed at 1.8×10^{-4} M. After mixing C_{60} and tetracene, two prominent absorption features appear at 640 nm (shoulder) and 706 nm (weak band), Fig. 3, their intensity progressively increasing with time. The absorption features observed with anthracene at shorter wavelengths are in this case masked by the intrinsic absorption of tetracene, whose onset occurs at approximately 500 nm. Nevertheless,

Table 1
Fitted parameters and calculated rate constants and equilibrium constant for the reaction between C_{60} and anthracene

T (°C)	A_∞	Γ (10^{-6} s^{-1})	K (M^{-1})	k_1 (10^{-4} M^{-1} s^{-1})	k_{-1} (10^{-6} s^{-1})
22	0.068[a]	1.8	14300[a]	1.6	0.013[a]
39	0.066	8.9	3000	7.8	0.26
49	0.062	20	950	16	1.7
57	0.057	40	480	31	6.4
63	0.053	53	330	38	12

[a] Extrapolated.

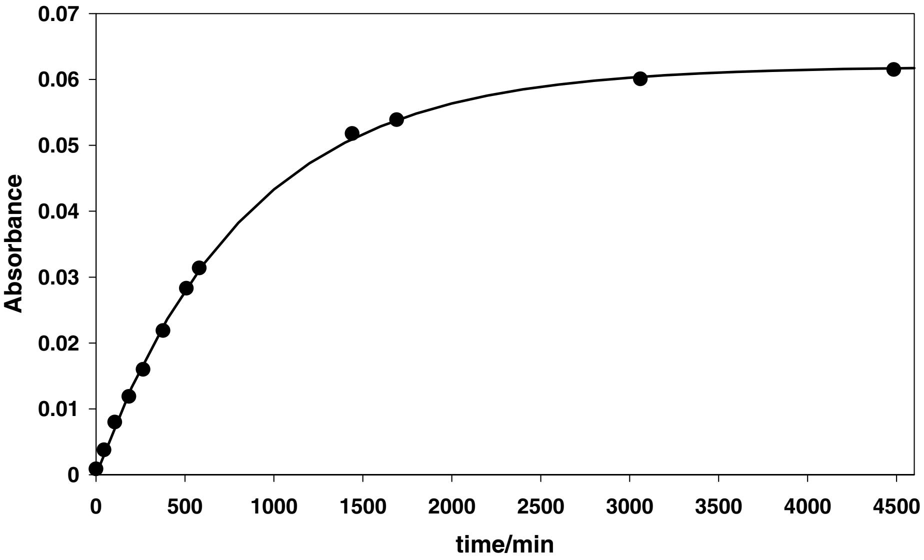


Fig. 2. Absorbance at 706 nm of the reaction mixture C_{60}–anthracene as a function of time, for a temperature of 49 °C. The solid line is the fit with Eq. (15) (for the fitted parameters, see Table 1).

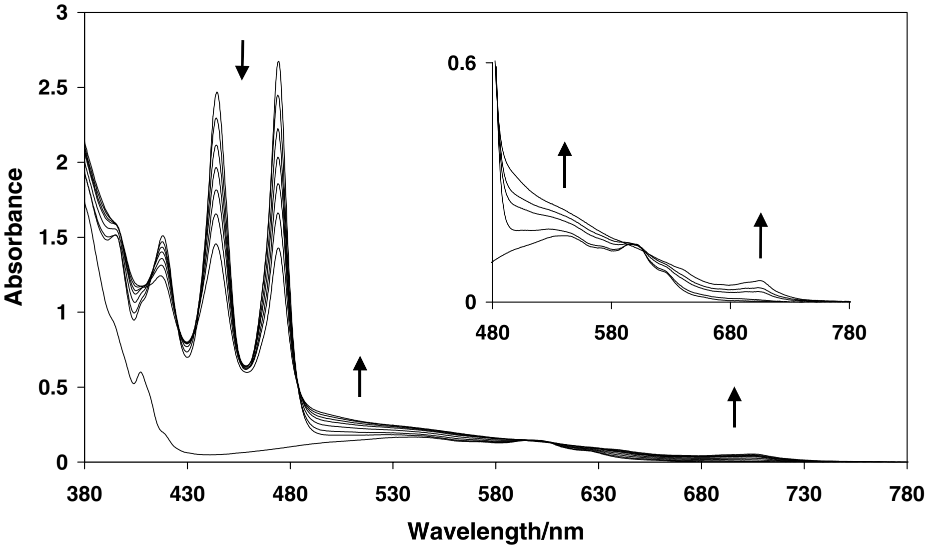
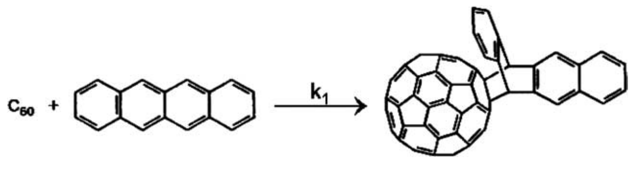


Fig. 3. Electronic absorption spectra of the reaction mixture C_{60}–tetracene as a function of time, for a temperature of 59 °C. The absorption spectrum with the lowest 436 nm absorption corresponds to the pure C_{60} solution. The other spectra correspond to the reaction mixture for reaction times of 0, 36, 84, 139, 191, 267 and 408 min. Inset: pure C_{60} solution and reaction mixture for 0, 84, 139 and 408 min.

the 640 and 706 nm absorption bands suffice to identify the reaction product as the mono-adduct of C_{60} and tetracene, formed upon [4 + 2] cycloaddition, Scheme 2.



Scheme 2.

The addition occurs at one of the 30 equivalent 6–6 bonds of C_{60}, and the reaction is regioselective from the point of view of tetracene, taking place at one of the inner rings. It is expected that, in the long wavelength range, this compound should display an absorption spectrum identical to that of the anthracene monoadduct. The existence of isosbestic points (as observed for the anthracene mixture) at 409, 436, 586 and 612 nm, Fig. 3, confirms that multiple addition is negligible for the experimental conditions used. Identical results were obtained for all the other temperatures.

Table 2
Fitted parameter and calculated rate constant for the reaction between C_{60} and tetracene

T (°C)	Γ (10^{-6} s^{-1})	k_1 (10^{-2} M^{-1} s^{-1})
25	2.0	3.1
33	3.9	9.6
40	6.9	16
46	11	26
54	14	32
59	30	47

Unlike the situation with anthracene, it is observed that the long time limit of the absorbance, A_∞, is essentially temperature independent and coincident with the value expected for complete conversion of the fullerene (0.058). The reaction is therefore irreversible at all temperatures. In such a case the parameter β in Eq. (8) becomes

$$\beta = \frac{[F]_0}{[A]_0} \tag{16}$$

and is no longer a fitting parameter, since its value is known. The data were fitted with Eq. (9) (with β fixed at the value given by Eq. (16)). The values of Γ for several temperatures are given in Table 2 (see also Fig. 4). Values of k_1 were computed from Γ, and are also presented in Table 2.

5. Discussion and conclusions

The activation parameters of the reactions studied, obtained from the Arrhenius plots of the rate constants, are given in Table 3. In the experimental temperature range the reaction of C_{60} with anthracene is reversible, while the reaction of C_{60} with tetracene is essentially irreversible. This results at least in part from the fact that the activation energy of the anthracene reaction is ca. 10 kJ mol^{-1} higher than that of tetracene. Mainly for this reason, the second order rate constant for the direct reaction at room temperature is two orders of magnitude higher for tetracene, 6.5×10^{-2} vs. 2.9×10^{-4} M^{-1} s^{-1} for anthracene. The observed activation energy difference of 10 kJ mol^{-1} is in close agreement with the results of quantum-chemical calculations for two Diels–Alder reactions involving these acenes: The computed differences are 10 and 11 kJ mol^{-1} with ethene [8], and acetylene [7] as the dienophile, respectively. Theoretical calculations also predict a more negative reaction enthalpy for the tetracene reaction [7,8], which may also correlate with a higher activation energy for the reverse reaction.

The available activation and thermodynamic parameters for the reactions of C_{60} with dienes are collected in Table 4. With respect to the direct reaction, it is seen that the activation enthalpy is smallest for the cyclopentadiene reaction, where no aromaticity reduction occurs.

Table 3
Arrhenius parameters for the reactions of C_{60} with anthracene and tetracene

	Diels–Alder		Reverse Diels–Alder	
	log(A/M^{-1} s^{-1})	E_a (kJ mol^{-1})	log(A/s^{-1})	E_a (kJ mol^{-1})
Anthracene	6.8	59	16.9	140
Tetracene	7.4	49	–	–

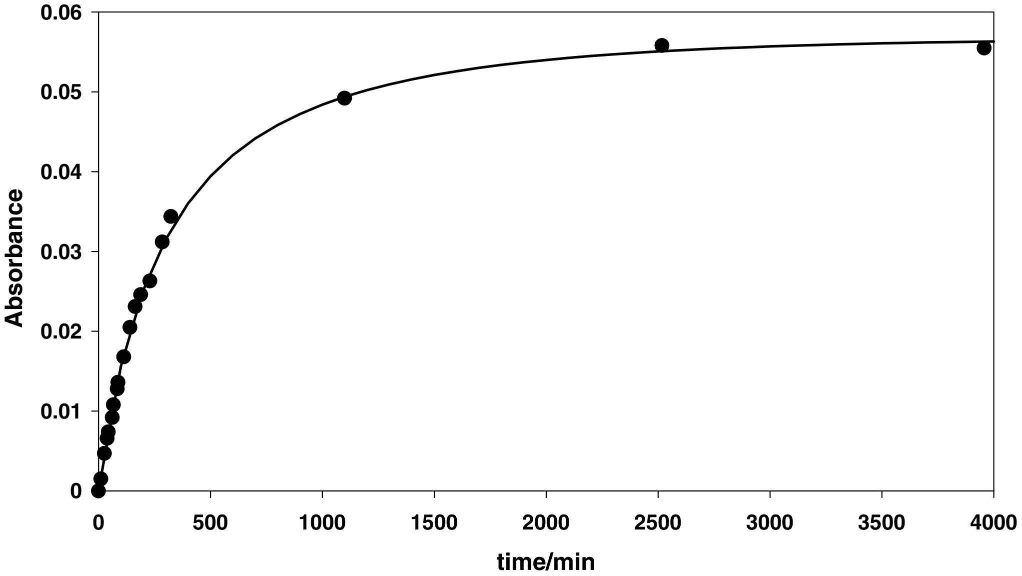


Fig. 4. Absorbance at 706 nm of the reaction mixture C_{60}–tetracene as a function of time, for a temperature of 54 °C. The solid line is the fit with Eq. (9) (for the fitted parameter, see Table 2).

Table 4
Activation and thermodynamic parameters (1 M, 298 K) for the Diels–Alder reaction of C_{60} with several dienes

Diene	Direct Diels–Alder		Reverse Diels–Alder		Reaction		Reference
	$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	$\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1})	
Anthracene	57	−123	138	71	−81	−195	This work
9,10-Dimethylanthracene	–	–	–	–	−96	−256	[16]
Tetracene	47	−111	–	–	–	–	This work
Cyclopentadiene	27	−161	109	−12	−82	−149	[4,5]

This aromaticity reduction is larger for anthracene than for tetracene, and consequently the reaction with this last compound has the lowest enthalpy of activation of the two. It is expected that the activation enthalpy will decrease smoothly along the acene series, being highest for benzene and approaching the cyclohexadiene and cyclopentadiene values when the number of rings is very large. The activation entropy is always negative and large, as expected for a Diels–Alder reaction [17], and does not vary significantly with the diene. With respect to the reverse reaction, the activation enthalpies for the only two reactions available are high, and surprisingly the highest value is that of anthracene. The two activation entropies work however in the opposite direction, and the $t_{1/2}$ at 90 °C are 39 and 20 min (calculated), for cyclopentadiene and anthracene adducts, respectively. The origin of the relatively large positive value of the activation entropy for the anthracene reaction remains to be understood. The reaction enthalpies (Table 4) are large and negative, as expected for Diels–Alder reactions [17]. The reaction entropies are also large and negative. The highest value, observed for 9,10-dimethylanthracene, may be directly related with a particularly facile retro-Diels–Alder reaction for this compound [16]. Further studies are nevertheless necessary to better understand all these aspects.

In this work, it is observed that tetracene reacts much more readily with C_{60} than does anthracene, the different reactivities of anthracene and tetracene towards C_{60} correlating with the respective aromaticity loss upon cycloaddition, as previously predicted theoretically [6–8]. The two monoadducts display different behavior as regards the dissociation back to the reagents. In the studied temperature range, tetracene monoadduct decomposition by retro-Diels–Alder reaction is negligible, while the anthracene monoadduct is unstable above room temperature.

Acknowledgements

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