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Experimental survey of the kinetics of acene Diels–Alder reactions

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Second-order rate constants were gathered for solution Diels–Alder reactions of substituted and unsubstituted acenes, with the intention of ascertaining ideal diene–dienophile combinations. Particular focus was placed on the larger ring systems namely tetracene, pentacene, and rubrene. The rate constants between the acenes ranged roughly six orders of magnitude, from the slowest reacting diene, rubrene, to the fastest diene, pentacene. The utilized dienophiles covered a large range of reactivity from 2,3-dichloromaleic anhydride to tetracyanoethylene. To aid in the interpretation of acene reactivity, constants were compared to the extensive body of Diels–Alder literature with well-studied dienes such as anthracene and *trans*-1-methoxy-1,3-butadiene serving as points of reference. Complex reaction kinetics for the addition of MeTAD and rubrene was found: initial fast consumption generated an intermediate, followed by dramatically slower product formation. The kinetic data creates a foundation for the analysis of prior and future reactions between organic semiconductor acene materials with volatized dienophiles, a surface functionalization technique for enhancing these electronic materials.

Keywords: rubrene; 4-methyl-1,2,4-triazoline-3,5-dione; UV–vis; stopped flow; steric hindrance; rate constants; stereoisomers

INTRODUCTION

For 85 years the Diels–Alder reaction has provided chemists with the ability to form C—C bonds and has continuously evolved to match modern scientists' needs and interests. These interests include a remarkably regio-selective reaction within aqueous molecular hosts exhibiting enzymatic behavior,[1] a versatile means for linking functionalizable organic molecules directly to semiconductor surfaces like silicon,[2,3] or acting as the model reaction in deciphering RNA catalyzed C—C bond formation *in vitro*,[4] with each example providing a new facet for this classic reaction. One additional example is our recent communication, where the reaction is applied to the *surface* of tetracene and rubrene single crystals via vapor dosing of the dienophiles.[5] When these organic semiconductors have their *surface* composition modified, it alters many of the properties, including device performance.[6] From a mechanistic standpoint, this system demonstrated unusual steric effects; the reaction of one face of the tetracene crystal is virtually inert, while another face is facile. The dienophiles' steric bulk is also expected to play a critical role for these confined systems. However, analysis of surface data has been hindered by the relative lack of corresponding solution kinetic data.

While the rate of anthracene's reaction has been studied extensively with a range of dienophiles[7–10] and tetracene/pentacene has been studied theoretically[11,12] (with limited experimental reports),[13] we seek to generate an expansive report to aid in future interpretations of acene systems. Herein, we report the kinetic data for rubrene, tetracene, and pentacene with common dienophiles (*N*-methylmaleimide, fumarodinitrile, 4-methyl-1,2,4-triazoline-3,5-dione, tetracyanoethylene, and maleic anhydride) and specialized molecules used in surface reactions (2,3-dichloromaleic anhydride, *p*-benzoquinone, and tetrafluoro-1,4-benzoquinone) (Fig. 1). The molecules selected for these experiments were chosen to encompass a range of reactivity and expand the data library of acene/dienophile pairs, but an even greater priority was placed on the applicability of these molecules to later use for vapor/solid reaction on organic semiconductor surfaces. For example, several of the halogenated dienophiles were picked as they provide ideal diagnostic signals for surface analysis, like XPS, ToF-SIMS, or mass spectrometry. We compare these systems with the well-studied *trans*-1-methoxy-1,3-butadiene and anthracene, which serves as a point of reference for systems of interest.

EXPERIMENTAL

NMR kinetic measurements

General kinetic experiments were performed at 85 °C in toluene-d_8 and monitored directly via ^{1}H NMR. Dienes were prepared as a stock solution of deuterated toluene at a concentration of approximately 2 mM with the internal standard, 1,2,4,5-tetramethylbenzene, added at 10 times the concentration of the diene. Neat dienophile was added directly to the NMR tube (already at 85 °C), with the concentration at a 10-fold excess relative to the diene, and outside of initial hand agitation, no stirring was used, and reactions were kept in the dark. Consumption of the diene was monitored as a function of time to determine the pseudo-first order rate constant, k_{obs}, and these values were periodically checked with the values for product formation to ensure that starting material was not being oxidized, degraded, precipitated, etc.

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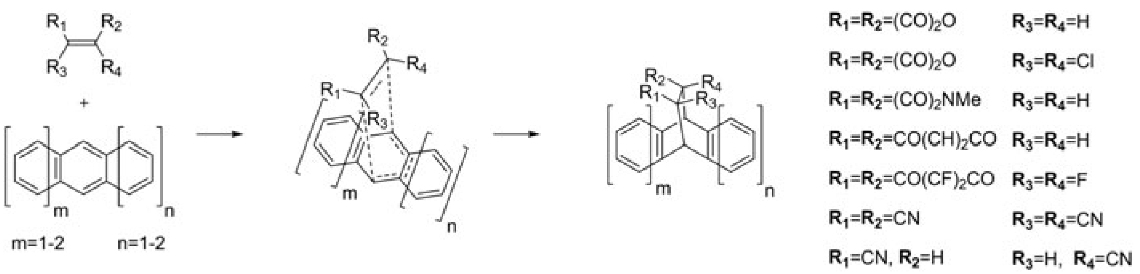

Figure 1. The reaction pathway of an acene type diene with generic R_{1-4} substituted dienophiles. Acene systems for these experiments consist of three or more linearly fused benzene rings: anthracene, tetracene, pentacene, and rubrene. Dienophiles spanned a range of reactivity and consisted of substituted anhydrides, MeTAD, a substituted maleimide, quinones, and cyano substituted olefins. Structures of acenes and dienophiles are also listed in Fig. 3

From these general procedures, several nuances must be reported. The long reaction time for rubrene required that air free techniques be utilized (glove box and schlenk flask) with aliquots removed periodically. Similarly, the sensitivity of *trans*-1-methoxy-1,3-butadiene meant that samples were prepared in the glove box. Additionally, rubrene's characteristic signals could not be used to monitor the rate of reaction. As a result, production formation was used to determine kinetics rather than starting material consumption.

The extent of reaction was monitored over time for a period of anywhere from 20 min to >35 days. In the case of reactions completing in less than 30 min, measurements were initially taken every 30 s, then every minute after t = 5 min and then every 2 min after t = 10 min. Transient acquisition took approximately 16 s (two transients), and triplicate measurements of starting materials gave integrations within ±3%. For reactions reaching completion in more than an hour but less than a day, measurements were taken every 5 min until t = 30 min, then every 10–60 min thereafter (~60 s acquisition time, eight transients). For slower reactions, taking 24 to 72 h, the initial data point was acquired within the first hour of the reaction initiation and was acquired thereafter every 4 to 16 h (~103 s acquisition time, 16 transients). The rubrene kinetic run was taken approximately every 7 days and displayed nearly equimolar formation of oxidized rubrene and adduct. In every other instance no discernible side products were seen in the final spectra, and when examined, consumed starting material directly correlated to product formation. Raw NMR data files (FID) are contained as a separate data file in the Supporting Information.

UV–vis kinetic measurements

The final class of reactions is those demonstrating rapid kinetics. Because of their rate, reactions were performed at room temperature, at 10 to 100-fold lower concentrations, and with a UV–vis. These reactions extended anywhere from 1 s to 24 h. For the fast reactions between tetracene and tetracyanoethylene or 4-methyl-1,2,4-triazoline-3,5-dione, a stopped-flow UV–vis was used to acquire the data at a rapid rate. Additionally, for these reactions, chloroform was used as the solvent because of a charge transfer complex between tetracyanoethylene and toluene.[14] As pentacene has been reported to readily oxidize, reaction solutions were degassed before analysis.[15,16] As a manner of consistency, all other UV–vis samples were prepared in a similar manner. Diene concentration was monitored by using absorbance of the lowest energy band, and analysis was performed in a manner analogous to the NMR experiments. To facilitate comparison of the kinetics at elevated and room temperature, the reaction between tetracene and *N*-methylmaleimide was performed at both temperatures utilizing the respective instrumentation. Data plots for UV–vis experiments can be found in the Supporting Information.

RESULTS AND DISCUSSION

Determination of second-order rate constants

All reactions, except for the reaction between *trans*-1-methoxy-1,3-butadiene with maleic anhydride and rubrene with 4-methyl-1.2.4-triazoline-3,5-dione, took place cleanly and gave linear ln[acene] vs. time plots. Reactions were treated as pseudo-first-order, and known dienophile concentrations allowed determination of the second-order rate constant, k_S ($M^{-1}s^{-1}$). Rate constants from data collected at 85 °C and room temperature are listed in Tables 1 and 2, respectively (as $1000 \times k_S$). To associate the rate constant obtained at 85 °C to the room temperature measurement, data on tetracene's reaction with *N*-methylmaleimide was collected at both temperatures. This produced one second-order constant at 85 °C ($1.2 \times 10^{-1}\ M^{-1}s^{-1}$) and another at room temperature ($1.5 \times 10^{-2}\ M^{-1}s^{-1}$). Furthermore, the rate constant for the tetracene/maleic anhydride reaction was measured three times, producing rate constant values within a 17% agreement of one

Table 1. Rate constants for all elevated temperature reactions (85 °C)

Diene	Dienophile	$k_S \times 1000$ ($M^{-1}s^{-1}$)
Rubrene	*N*-Methylmaleimide	0.004
trans-1-Methoxy-1,3-butadiene	*N*-Methylmaleimide	1.4
trans-1-Methoxy-1,3-butadiene	Maleic anhydride	6.4
Anthracene	*N*-Methylmaleimide	1.7
Anthracene	Maleic anhydride	0.21
Tetracene	*N*-Methylmaleimide	120
Tetracene	Maleic anhydride	19
Tetracene	Tetrafluoro-1,4-benzoquinone	5.6
Tetracene	*p*-Benzoquinone	0.91
Tetracene	Fumarodinitrile	0.35
Tetracene	2,3-Dichloromaleic anhydride	0.29

Table 2. Rate constants for all room temperature reactions (20–25 °C)

Diene	Dienophile	$k_S \times 1000$ ($M^{-1}s^{-1}$)
Tetracene	Tetracyanoethylene	5 000 000
Tetracene	4-Methyl-1,2, 4-triazoline-3,5-dione	690 000
Tetracene	*N*-Methylmaleimide	15
Pentacene	*N*-Methylmaleimide	110
Rubrene	Tetracyanoethylene	—
Rubrene	4-Methyl-1,2, 4-triazoline-3,5-dione	k_1 ($M^{-1}s^{-1}$) = 22 $k_2 \times 1000$ ($M\,s^{-1}$) = 0.019

another (standard deviation), and the errors were assumed to be of similar magnitude for the other reactions. Tetracene, pentacene, and rubrene generate more than one diastereoisomer, termed *endo* and *exo*,[17] for each reaction ring because of the asymmetry produced in the adducts. However these isomers are relatively consistent between acenes (generally about 1:2) and do not display unusual kinetics, so the two are combined here.

Established theory of Diels–Alder reactivity

In this section we aim to introduce much of the experimental or theoretical precedence of the Diels–Alder on acenes and highlight how our data contributes to this area. Each subsequent paragraph within this section first describes consensus in literature and concludes with our data and analysis. To begin, unsubstituted acenes are reasonably facile partners in the Diels–Alder reaction as the fused aromatic core provides several electron rich dienes, all of which are a viable site for the reaction. Of these dienes, the centermost ring is primarily attacked during reaction (Fig. 2); here the loss of aromaticity in the product is less substantial than for reaction at outlying rings.[18] Theoretical calculations, of reaction between acenes and acetylene, predict 100% reactivity on the B rings for anthracene and the B rings of tetracene. When examined experimentally using ^{1}H NMR spectra, these systems contain splitting patterns which would allow us to distinguish these structural isomers. In all instances, the data supports the adduct formation exclusively on the inner most ring of anthracene and tetracene.

In contrast to tetracene and anthracene, pentacene should be the exception, with a mere 6.7 kJ per mole difference between the activation energies on the C and B rings which corresponds to a roughly 6:1 ratio of products (when one considers the duplicity of reaction sites for the B ring).[18] In our experiments, multiple products were present in the reaction mixture having chemical shifts commensurate of bridgehead protons (4.92–4.68 ppm) suggesting both B and C ring reaction. These components were separated via HPLC, and UV detection was used to distinguish the anthracene moiety of the B ring isomer from the naphthalene moieties of the major C ring isomer. According to ^{1}H NMR, the ratio of C to B isomers was nearly equivalent to the proposed 6:1 ratio (when a 1:1 pentacene:*N*-methylmaleimide mixture was heated to 110 °C for several minutes, an 8.5:1 ratio occurred). Additional experimental details and results are contained in the supporting information, including HPLC chromatograms, NMR integrations, and a UV spectrum of the two separated components from the reaction mixture.

The data above also allows us to briefly comment on the applicability of aromaticity surrogates, such as NICS (nucleus-independent chemical shifts). NICS is one of the most widely employed indicators of aromaticity and was proposed by Schleyer *et al.* to be used as an assessment of reactivity based on the magnetic properties of a structure.[19] As a qualitative means of examining ring reactivity in polyacene systems, more negative NICS values are used to predict the location of reaction (i.e. reaction will occur on the given ring where a more negative NICS value exists). When examining our structural isomer data, NICS values (more precisely the NICS(0)π values given by Schleyer)[18] having a difference of 3 or more generated only the central ring isomer. For example, anthracene and tetracene differ in NICS values between their B and A rings by 3.1. In the case of pentacene, the difference between C and A is 4.5 (no detectable amount of A ring isomers were generated in our experiments). Additionally, small differences in NICS(0)π values (the difference between the C and B ring in pentacene is only 0.9) generated the aforementioned mixture of structural isomers. It would be interesting to study a more extended system in the future, such as hexacene, where the NICS(0)π difference is 1.5.

Theory also predicts[18] that each successive linear addition of a benzene ring to an acene system causes an increase in reactivity, a result borne out in previous experiments.[13] If the observed trend is described using the aromaticity of the central ring, opposite rates of reaction would be expected; however, such assessment neglects the nature of the formed product and its substantial contribution to the reaction pathway and rate.[18] In our data the trend along the acenes is similar (Fig. 3): when *N*-methylmaleimide reacts with tetracene as opposed to anthracene, the observed rate constant increased by 68 times (Table 1). This is consistent with theoretical calculations which predict rate differences of 38 times from anthracene to tetracene with acetylene,[18] and is comparable to experimental results on similar systems.[13] This trend continued with pentacene as the reaction with *N*-methylmaleimide was seven times faster compared to the same reaction with tetracene (Table 2).

Literature precedence also provides a predicted trend in dienophile reactivity, one expected to carry over to our acene systems. The reactants commonly utilized in Diels–Alder reactions (tetracyanoethylene, 4-methyl-1,2,4-triazoline-3,5-dione, *N*-methylmaleimide, maleic anhydride, and fumarodinitrile; listed in order of reactivity) thus provide a

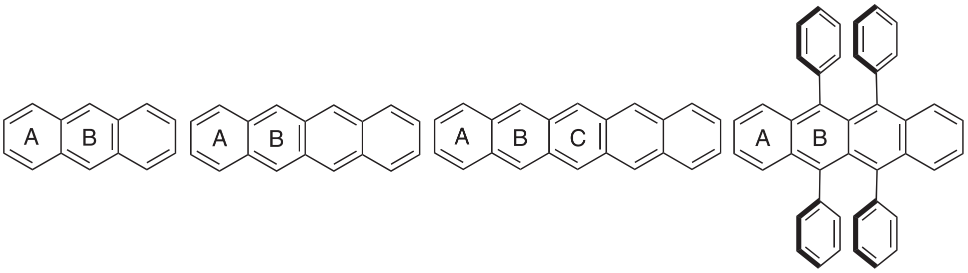

Figure 2. The labeling of the rings in the acenes studied in this work. Acene systems consisted of anthracene, tetracene, pentacene, and rubrene, respectively, shown above. Substantial difference in reactivity exists between rings in the same acene: electronically, A is the least reactive and C is the most

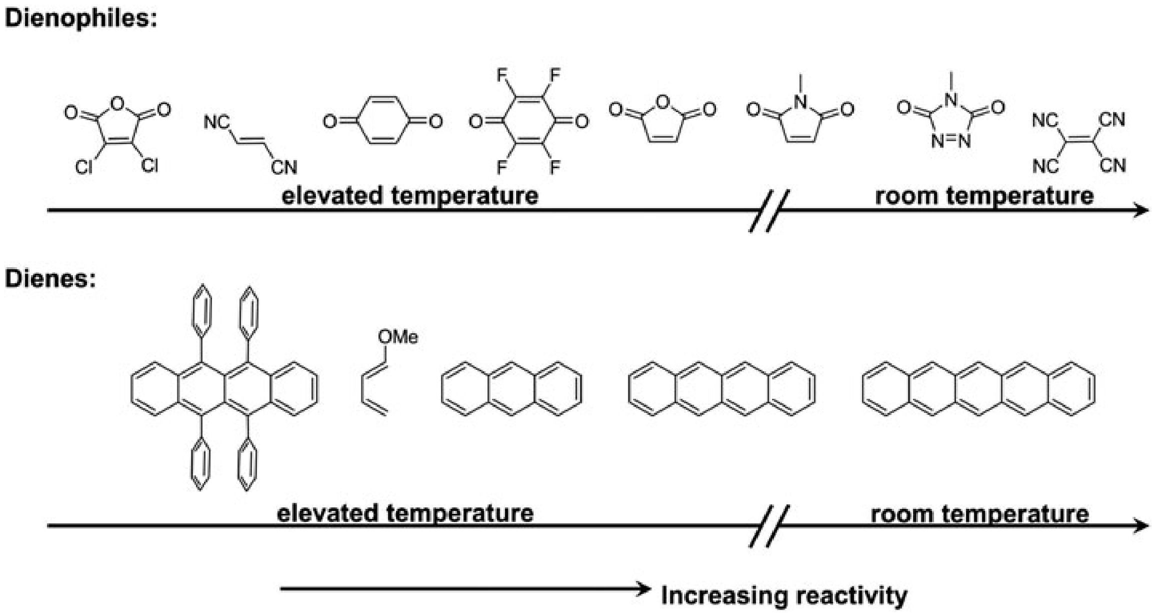

Figure 3. Dienophiles and dienes used to test the reactivity of acene class materials in the Diels–Alder reaction and trends in reactivity

reference point which will allow the relative kinetics of the second, surface specific, group to be referenced to a greater body of literature. For the established group, the trend in our data matched that which was anticipated, e.g. tetracyanoethylene displayed the fastest reaction time, 4-methyl-1,2,4-triazoline-3,5-dione was more facile than the anhydride, while lower reactivity was observed with fumarodinitrile.[20] Experimental rate constant data reported by Biermann and Schmidt, for reaction between tetracene and maleic anhydride (trichlorobenzene, 91.5 °C), differs by just a factor of five which is easily attributed to the slight difference in solvent and temperature.

Of further interest was the impressive similarity in literature rate constants of *N*-methylmaleimide and maleic anhydride with dienes spanning reactivity of over a million fold.[21] It was because of this trend that comparable reactivity between these dienophiles with the acenes was anticipated. Our results do deviate from this slightly. When the two are reacted with *trans*-1-methoxy-1,3-butadiene, maleic anhydride occurred 4.5 times faster than with *N*-methylmaleimide, notably outside the 0.5–2 range reported.[21] This ordering is inverted for the acenes, where the reaction of maleic anhydride occurred at a rate 0.1 and 0.17 times that of *N*-methylmaleimide for both anthracene and tetracene. Although slightly different from reported results, this trend was not investigated further with our other diene–dienophile pairings.

Incorporation of halogens for XPS measurements: electronic and steric effects

The primary motivation for this work is to provide reference data for reactions we wish to study on surfaces. Measurement at surfaces often needs tagged molecules, whereby the addition of halide(s) is convenient. Typically halogens are not found as contaminants either inherently in the organic acenes or within common atmospheric adsorbates, making them an appropriate group for proving definite reactivity. Furthermore, many halogen substituted dienophiles are readily available for purchase, and give us the potential to tag many of the other compounds listed in Fig. 3. Molecules like 2,3-dichloromaleic anhydride, a doubly chlorinated maleic anhydride derivative, and tetrafluoro-1,4-benzoquinone, a perfluorinated benzoquinone, are expected to participate in the Diels–Alder reaction and have sufficient volatility, making the surface/vapor reaction viable.[5] We seek not to only understand their base reactivity in comparison to their unsubstituted versions, but to tease out information on electronic and steric effects using the slight variance in halogen electronegativity, halogen size, and ring size.

Chemical intuition suggests that, based purely on electronic effects, electron-withdrawing halogen substituents should higher reactivity in the Diels–Alder reaction. This is supported by theory which predicts that these substituents result in a stabilized $\text{LUMO}_{\text{dienophile}}$ allowing for a more overlap with the $\text{HOMO}_{\text{diene}}$.[22] Detailed analysis of almost one hundred diene/dienophile combinations allowed Kiselev and Konovalov[11] to develop an empirical model of the energy of the system based on three thermodynamic factors. The first two are extent of frontier orbital interaction: the HOMO/LUMO energy difference and the interatomic distance between the diene's reactive carbons (C_1, C_4) which have a strong influence on the overlap coefficients.[23] In addition they add a factor pertaining to the energy of bond cleavage/formation. Interestingly though, their discerned relationship (much like chemical intuition) predicts faster reactivity for halogenated dienophiles, but experimental evidence (including that same work) shows *reduced* reaction rates when the substitution is on the double bond in the dienophile.

In fact, virtually all instances of Diels–Alder reactions show inhibited reaction for chloro- or bromo-substituted dienophiles, signifying substantial effects brought on by size of the substituent which counters its ability to withdraw electron density.[10,24] In a report by Andrews and Keefer, a single chlorine substitution caused a decrease in rate of 2–8 times, and the decelerating effect was considered to be caused by more double bond character existing in the C—Cl bond of the dienophile, thereby reducing the C—C double bond character. The exception to this is fluorinated species, which have been reported to accelerate Diels–Alder reactions.[25] We too find analogous reactivity in the halogenated species: the addition of fluorine to benzoquinone *sped up* the reaction 6-fold, while the addition of chlorine to maleic anhydride caused a 65-fold *decrease* in the rate constant. It would be interesting to see if this effect is amplified at the surface where access to the diene is dramatically more hindered than in solution. This will be reexamined once surface kinetic experiments are determined.

Encumbered rubrene substrates and surface viable reactions

Rubrene is one of the most attention-grabbing materials currently being tested for organic electronics because of its high carrier mobility and increased device performance when functionalized.[6] Interestingly, exhaustive literature searches for Diels–Alder reactions of rubrene show only one report of an adduct (formed with *N*-methylmaleimide)[26] and no reports of the kinetic aspect of this reaction. This is most likely because of the fact that the promising device behavior is rather recent.[27]

Overall, our results for rubrene were quite interesting. Tetracyanoethylene (TCNE), one of the fastest dienophiles in literature,[11] showed no reactivity towards rubrene at room temperature (24 h). In fact even when heating the reaction to 125 °C for 13 days, no appreciable signal was found in the region from 6.5 to 3.5 ppm, which is normally associated with these adducts.[5] For these measurements, the smallest resolvable signal in this region corresponded to 0.5% of the starting material, and this signal cannot be conclusively assigned this to product. This is in contrast with the reaction of *N*-methylmaleimide (a dramatically slower dienophile) which was 4% complete at this time, even at lower temperatures.

The TCNE rubrene reaction contrasts nicely with our other fast dienophile, 4-methyl-1,2,4-triazoline-3,5-dione (MeTAD), which although generally slower than tetracyanoethylene in the acene Diels–Alder reactions (Table 2),[28] reacted completely with rubrene in ~1-h time. This result is not entirely surprising; the large phenyl substituents on the central rubrene ring are expected to make this substrate particularly sensitive to the sterics of the dienophile. TCNE's substitution on both ends of the olefin makes it particularly slow in this regard, while the 1,2 positions of MeTAD are unsubstituted rendering the reaction more facile.

It was also interesting that in the case of rubrene with MeTAD, the reaction occurred but did not follow pseudo-first-order reactivity. Within 40 s of reacting, the rubrene concentration appeared to decrease by half (from 0.2 mM to ~0.1 mM) followed by dramatically slower kinetics. To confirm the influence of two distinct rates, the reaction was monitored via stopped flow UV–vis. Figure 4 shows an absorbance vs. time plot over the course of 1000 s, where rubrene was monitored at 432 nm. Visibly different rates of reaction occur, neither of which follow pseudo-first-order reactivity. Many mechanisms common to Diels–Alder reaction of TADs could provide justification for a non-pseudo-first-order rate (zwitterion −,+ or aziridinium ion, AI, or precomplex formation),[29,30] and all mechanisms imply that the starting material is consumed *rapidly* to form intermediates before slowing, as equilibrium becomes important. Such kinetics should follow Eqn 1.

$$\text{RUB} + \text{MeTAD} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{I} \xrightarrow{k_2} \text{Diels-Alder Adduct} \quad (1)$$

To confirm the presence of an intermediate in this reaction ^{1}H NMR spectroscopy was utilized. Proton spectra indicated that within the first 15–20 min of reaction, rubrene was consumed (~50% consumption), but no product was present. Specifically, the adduct protons at 2.9 ppm (corresponding to the *N*-methyl protons) and 5.4 ppm (corresponding to the bridgehead protons) were absent. Formation of an intermediate could be suggested by the transient peak at 2.6 ppm, which after 40 h no longer persists in the ^{1}H NMR spectrum but is replaced by the presence of peaks from the isolated adduct. We report two rates for this reaction, k_1 and k_2. The first, k_1 equal to 22 $M^{-1}s^{-1}$, was calculated assuming pseudo-first-order reactivity in the initial rate (1.2 s of data, Fig. 4 inset) before k_{-1} becomes significant. The rapid kinetics leads to a standard deviation of 22% for this value. It was also interesting that the data for k_2 appeared to correspond to zero order reactivity (Fig. 4), and its value was equal to 1.9×10^{-5} M s^{-1}.

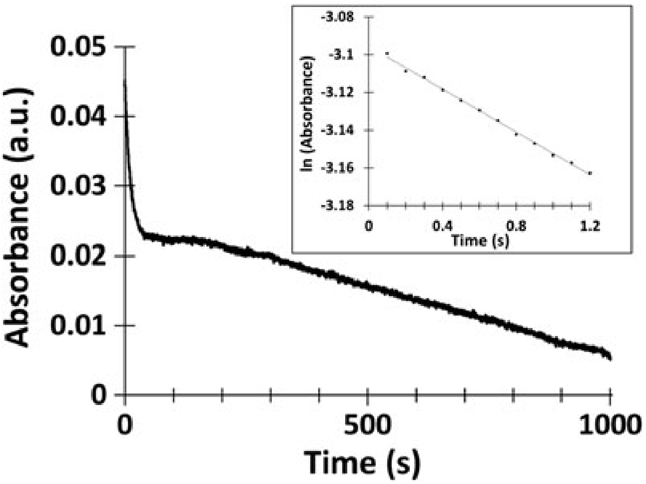

Figure 4. UV–vis stopped flow was used to monitor the reaction between Rubrene and MeTAD at 432 nm for nearly 17 min. The inset displays the natural log of the data points in the first 1.2 s of reaction versus time, with a linear fit used to calculate the pseudo-first-order rate constant

In addition to displaying interesting kinetics, rubrene also allows us to comment on the relative reactivity of each ring in tetracene. From a reactivity standpoint, rubrene should behave as a substituted version of tetracene with phenyl groups on the reactive B rings (Fig. 2). Based off of assignments of products in our kinetic run, any reactivity of the B rings in rubrene is well below the detection limit of the experiment, leaving only the A rings to participate in cycloaddition. Unsurprisingly, the rate of rubrene was very slow, taking 5 weeks to generate 10% product adduct (exclusively one diastereomer). As previously mentioned, this reduced rate constant for the A ring is because of a decrease in the enthalpy of reaction and increase in activation barrier, in comparison to the B ring. More importantly, the gathered rate constant data for the reaction between *N*-methylmaleimide and rubrene gave us the ability to comment on reactivity of the hindered diene relative to the reactivity of its unhindered counterpart, tetracene.

Similar electron distribution between the A rings of tetracene and rubrene allows for predictions on the reactivity of rubrene. Based on this assumption, we can infer that the A ring of rubrene should have the similar reactivity to the A ring of tetracene. Theoretical calculations examining approximate differences in reaction rate between the A and B rings of tetracene with acetylene (at 85 °C), predict a 9060-fold difference, in favor of reactivity at the B ring (calculations are without consideration of the prefactor).[18] We would then naively expect the reactivity of rubrene to be slower than tetracene by roughly this amount, as it is electronically similar to tetracene but is sterically forced to react at the A ring as opposed to the B ring. If substantial differences in the calculated and theoretical rate constants between tetracene and rubrene exist, it would suggest substantial steric effects induced by the presence of phenyl rings on the reactivity *of the A ring*. Rate constant data supports slight steric influence by the introduction of phenyl substituents to tetracene, as rubrene was approximately 30 000 times slower.

These same discussions also play a heavy role in reanalyzing surface data for tetracene (as well as rubrene). Our surface experiments[5] showed incomplete reaction at 24 h between maleic anhydride and tetracene, a result that seems at odds with the observation of adduct for the dramatically slower rubrene. The fact that tetracene and rubrene crystals reacted in such similar amounts of time would make more sense if the reaction was occurring on same deactivated A ring in both cases. Indeed the crowded environment of a crystal surface could lead to sterically demanding reactions, possibly allowing primarily the exposure of the A rings. This would not be without precedence; confinement effects have limited the reactivity in a similar system. Kwon reported that moving a monolayer immobilized dienophile from the surface to subsurface reduced reactivity by a factor of 8 and when recessed by an additional ~ 2 Å the rate declined by an additional factor of 3.5.[31] Thus this explanation seems plausible, but obtaining experimental proof is challenging as this would require assignment of the crystallographic faces of the single crystal surfaces.[32] These challenging experiments, along with rate data on the various faces, would allow for definitive comment.

CONCLUSIONS

In closing, these data provide an expansive set of Diels–Alder acene–dienophile pairs and allows for comparison of reactivity between acene type dienes with surface-relevant dienophiles. Observed kinetics are consistent with general notions of the Diels–Alder; both the size and electronic nature of the dienophiles influenced rate of reaction. It was also observed that the central ring was primarily attacked for reaction in each system, that the reactivity of the acenes was influenced by the number of linearly fused benzene rings (larger being faster), and the kinetics for rubrene were reported for the first time. Of most importance to us, the data has given an ability to loosely predict crystal substrate reactivity for in progress solid state kinetic experiments. Faster reacting dienophiles, like tetracyanoethylene or tetrafluoro-1,4-benzoquinone, are good targets for studying crystal reactivity, and in addition to their speed they have the potential to provide spectroscopically interesting signals. Other molecules like *N*-methylmaleimide and *p*-benzoquinone are nominally biologically interesting surface addendums, producing films with the ability for further functionalization. Overall this work provides precedence for a range of surface specific studies.

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