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Role of Surface Phenomena on the Reaction of Molecular Solids: the Diels-Alder Reaction on Pentacene

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Abstract

Reactivity trends for molecular solids cannot be explained exclusively through topochemical phenomenon (i.e. diffusivity, reaction cavities) or electronic structure of the molecules. As an example of this class, Diels-Alder reactions of small molecules with pentacene thin films are examined to elucidate the importance of surface phenomena on reactivity. Polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) has observed that vapors from the small molecules condense on the surface, in a non-covalent manner, to form a coating 2-3 molecules thick. The phase of this layer can provide increased surface diffusion (both reactant and product) which rapidly accelerates the reaction rate. Kinetic studies of pentacene thin-film reactions demonstrate the importance of this condensed state to trends in reactivity, with layers in a quasi-liquid state showing rate acceleration of 13-30 times compared to those in a quasi-solid state. Scanning electron microscopy provides further evidence of this phase behavior, while solid-state UV-vis confirms kinetic results.

Introduction

When organic synthesis migrates to the solid phase, remarkable chemistry abounds. Embodied by ship-in-bottle synthesis,[1] encapsulated cycloadditions,[2,3] or crystallographic channel driven reactivity,[4] these reactions display remarkable stereoselectivity,[5,6] a previously unknown light mediated decarbonylation,[7] or mediate other reactions which cannot occur in solution.[8] These reactions are also intriguing because the precedence of the solution phase is lost and collision theory is but a minor contributing factor to modeling kinetics. Without these foundations of classical chemistry, one must reassess what underpins reactivity. Topochemical consideration are understood to dictate reactivity.[9]

The classical gas-solid reaction of Paul and Curtin demonstrate the uniqueness of organic solid-phase chemistry.[10] Here, ammonia gas diffuses into crystals of *p*-bromobenzoic anhydride, and reacts with a vastly accelerated rate at a single crystal face. Three new processes modulate reactivity (Figure 1a). First, the vapor phase reactant must diffuse into the solid material.[11,12] Next, the reactant must explore a small reaction cavity for a viable transition state with the substrate.[9] Finally, the new products often generate significant reorganization of any crystalline order.[13] Over the years, the mechanistic understanding has been refined and gas-solid reactivity has been shown to be dependent on substrate packing and lattice vibrations, sterics, and of course, reactant diffusivity in the crystal.[11,12] To support this burgeoning field, modest theoretical models have been developed, and empirical relationships have been established.[14,15]

Yet in studying the current state of gas-solid organic reactions (or solid phase reactions broadly), it is apparent that these findings reflect only half of the mechanism. Yes, the materials must diffuse to the solid, and will often intercalate within it, but transitions between these two events requires significant surface phenomena. For one, any gas-solid reaction is initiated via the adsorption of the vapor phase material onto the surface (Figure 1b). Large swaths of literature are devoted to modeling this adsorption behavior (i.e. Langmuir or BET isotherms), but exclusively for classical inorganic surfaces.[16] These same inorganic surface studies demonstrate that reactions typically follow a Langmuir-Hinshelwood mechanism whereby the vapor phase reactant must first adsorb on the surface, followed by diffusion on the surface until encountering another reactive species (Figure 1c).[17] In both processes, factors like sticking probability, coverage, diffusion, and residence time on the surface must now be considered (Figure 1b, d).[18] Finally, it is often assumed that the substrate is static, but once it has reacted, the lattice mismatch between the product and substrate mean that the product is driven to self-aggregate on the surface of solid.[19,20] In all these instances, the primary precedence is almost exclusively from inorganic surfaces; only a handful of studies have scratched the surface how surface effects apply to organic substrates.[21,22] This limits the advancement of organic solid phase chemistry in the context of waste free reaction,[23,24] asymmetric synthesis,[5,6] atmospheric/aerosol chemistry,[25] crystal modification,[26,27] and polymer generation (to name but a few).[28]

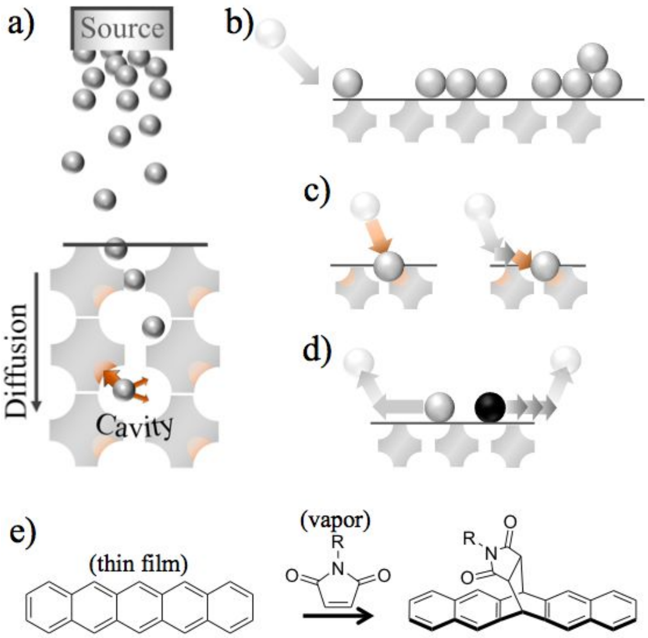

Figure 1. *a) Schematic of standard model of gas solid reaction with molecular substrate. Vapors transport from the source into the molecular crystal, often through preferred channels. The size and orientation of a reaction cavity dictates the accessibility of the reactive sites on the molecule, affecting the rate and regio/stereoselectivity. b) Molecular adsorption via Henry's Law, Langmuir, or BET isotherms (left to right). Henry's Law and Langmuir assume minimal interaction of incoming vapors with molecules adsorbed on the surface, while for BET, multilayers form preferentially. c) Eley-Rideal reactions occur via direct collision of gas phase reagent with surface site (left), while Langmuir-Hinshelwood reactions require surface diffusion (right). d) Adsorbates' surface diffusion varies significantly, as does the residence time on the surface and sticking probability. e) Diels-Alder reaction of thin-film pentacene with vapors of maleimides.*

Herein, we begin to uncover how surface phenomena drive solid phase reactivity (Figure 1e). Using the Diels-Alder reaction of pentacene thin-films with vapor phase adsorbates as our model system, we study a series of molecules originally intended to probe the role of vapor concentration on reactivity, but which contrarily demonstrates the limited applicability of basic collision theory to these surface-based molecules. As alternatives, adsorbate phase, sterics, and other surface considerations are examined to explain reactivity. The combination of these measured surface phenomena serve to bridge the gap in the knowledge that exists for solid phase organic reactions.

Experimental Section

Materials. All metals used are of 99.9% purity or higher. Pentacene (sublimed grade) was commercially obtained along with the small molecule reactants (*N*-methylmaleimide, *N*-ethylmaleimide, and *N*-propylmaleimide, *N*-*tert*-butylmaleimide, *N*-methylsuccinimide, maleic anhydride, all 97% purity or higher).

Thin-Film Pentacene Preparation. Metal backed substrates were prepared using a Kurt J. Lesker NANO38 thermal evaporator to deposit 5 nm of Cr, 50 nm of Ag, and 50 nm of Au sequentially onto a piranha cleaned (3:1 H_2SO_4: H_2O_2) microscope slides that had been cut to a size of 11 × 25 mm. Metal evaporation occurred at a base pressure below 1.0×10^{-6} Torr at deposition rate of 1 Å/s. Immediately after metal deposition, the substrates were placed in a home built high-vacuum sublimation chamber with a source to sample distance of 16-17.5 cm, and 60 nm of pentacene was thermally sublimed onto the surface at a base pressure below 5.5×10^{-6} Torr at a rate of 1 Å/s.

General Reaction Conditions. Pentacene thin films were placed in a 100 mL Schlenk tube at the end opposite of a vial that contained 8 mg of the small molecule reactant. The Schlenk tube was evacuated and refilled with nitrogen three times before the tube was placed in an oven at 50 ºC. After 18 h, residual vapors in the Schlenk tube were condensed away from the samples using dry ice. Trace amounts of residual reactant were removed from the surface by evacuating the samples to pressures $< 10^{-5}$ Torr for 1 h.

Infrared Analysis. The samples' surfaces were analyzed before and after reaction using polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) using a Bruker Optics Tensor 37 FTIR with PMA 50 accessory and MCT detector. Thin-films were analyzed at resolution of 8 cm^{-1}.

In Situ Infrared Analysis. A subset of samples were monitored during the reaction progression by performing the reaction within a Harrick Refractor Reactor which was integrated into the Tensor 37/PMA 50 setup. Both the thin-film and small molecule were loaded into the reactor in a manner similar to the general reaction conditions. Sample amounts were also consistent with Schlenk tube conditions (2-20 mg). An inert environment was generated by extensive (>10 min) purging of the Refractor Reactor with nitrogen.

UV-vis Analysis. Samples were prepared in a similar manner to the standard thin-film pentacene preparation with the exception of the metal backing which was comprised of only 3 nm of Cr and 10 nm of Au. Sample analysis was performed using a Shimadzu UV-2550 UV-vis using transmission mode. Compensation for scattering (Mie) was applied at lower wavelengths.

Theoretical Methods. Harmonic vibrational frequencies and IR intensities of isolated molecules of *N*-methylmaleimide, *N*-ethylmaleimide, *N*-propylmaleimide, and *N*-tert-butylmaleimide pentacene adducts were computed using the B3LYP/6-31G* level of theory, as implemented in the NWChem 6.5 suite of electronic structure programs.[30]

Scanning Electron Microscopy. Surface morphology of the thin-film pentacene was examined both before and after reaction using a Hitachi SU-3500 scanning electron microscope. Images were acquired at an acceleration voltage of 5 keV and at an angle of either 0 or 45.

Thin-Film Tetracene Preparation and Reaction. Tetracene thin films were prepared in a manner identical to pentacene thin films. After deposition, the films were annealed at 40 ºC for 24 h under nitrogen. These samples were then reacted in a similar manner to the pentacene substrates with the exception of the reaction temperature, which was 40 ºC.

Quartz Crystal Microbalance Measurements. The thickness and adsorption kinetics of physisorbed molecules was determined via Inficon single front load quartz crystal microbalance (SL-A0E48) with SQM160 high resolution monitor. For these experiments, tetracene was deposited onto the microbalance sensor in the home built high-vacuum sublimation chamber, the QCM was isolated from the vacuum pumps, then the small molecule reactants were dosed directly into the chamber, and the thickness monitored. The density for the tetracene thin films was set to 1.3,[31] and any physisorbed small molecules were assumed to be at similar density. High vacuum was later introduced to remove any non-chemically bonded species.

Results and Discussion

To study the impact of surface phenomenon on solid phase reactions, an appropriate model system is needed. The Diels-Alder reaction of small molecules with pentacene thin-films is suitable in this regard because the substrate has a well-defined crystal structure,[32] minimal intramolecular motion, and the reaction itself has been well-studied in the solution phase,[33,34] so as to provide context regarding crystal's effects on reactivity. There are two other arguments for its use. First, the reaction generates no side products which could contaminate the surface (or whose desorption from the surface would introduce additional complexities to the studies). Second, it is one of the handful of systems where a classical organic reaction has already been demonstrated between a vaporous small molecules and an organic substrate.[19,26] These experiments provide a primer on expected reactivity, specifically that the overall trend was similar to that found in solution phase.[34] Here, the small molecules' rate of reaction with pentacene thin-films had the following trend: *N*-methylmaleimide reacted significantly faster than maleimide or tetrafluorobenzoquinone, the two of which had similar kinetics.[19]

These initial results present a quandary. On one hand, a massive store of surface literature indicates surface based reactions are multistep processes and rarely parallel solution based kinetics.[17] On the other hand, the initial results suggest a solution-like behavior and that simple gas phase activation barriers[34,36] were, in fact, a good first approximation of reactivity.[19] Clearly, the two must be reconciled, and thus these experiments set out to differentiate the two phenomena. The simplest means to do so is to examine a series of small molecule reactants that had similar sterics and solution kinetics thereby isolating the role of any surface based phenomena.

This experiment was put to practice when the vapors of about 8 mg of three small molecules were allowed to diffuse through a Schlenk tube to the pentacene substrate for 18 h at 50 ºC. Here, *N*-methylmaleimide, *N*-ethylmaleimide, and *N*-propylmaleimide (k_{soln}=0.69, 0.26, and 0.27 M^{-1} s^{-1} respectively, Figure S1) were the kinetically comparable series. Reaction progress was observed via polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS): product generation was quantified using the carbonyl stretches at 1703-1705 cm^{-1}, while starting material consumption was monitored via the loss of intensity of the pentacene out-of-plane vibration at 910 cm^{-1}.[36]

When monitoring starting material consumption, *N*-propylmaleimide reacted significantly faster than *N*-methylmaleimide (Figure 2a). As observed via the 910 cm^{-1} vibration mode, pentacene is nearly completely consumed after 18 hours, while *N*-methylmaleimide shows a small amount of reaction, despite k_{soln} for propylmaleimide being 2.6 times *slower*. This is even more striking when one considers that *N*-propylmaleimide has a lower vapor pressure and thus concentration above the pentacene surface. The same is true for the rate of reaction with *N*-ethylmaleimide, again despite its slower solution kinetics. The 1700 cm^{-1} stretches (Figure 2b) are more challenging to interpret as the data is complicated by difference in absorption coefficient for the carbonyls (we have calculated a variance of 15%, Figure S2), and by the potential for the products to adopt different orientations relative to the surface normal, thereby diminishing or amplifying their absorption.[37] Despite this, the trend observed for both product generation (1700 cm^{-1}) and starting material consumption (910 cm^{-1}) is unambiguous: reactivity at the surface does not mirror that of solution. Consumption trends for thin films across the maleimides show 10 ± 7%, 45 ± 21%, 64 ± 28%, and 74 ± 10% consumption for *N*-methylmaleimide, *N*-*tert*-butylmaleimide (a related small molecule), *N*-ethylmaleimide, and *N*-propylmaleimide respectively. Reaction with *N*-methylmaleimide shows a 20-30 fold reduction in rate, relative to the other maleimides, when moving from solution phase reaction to the thin film.

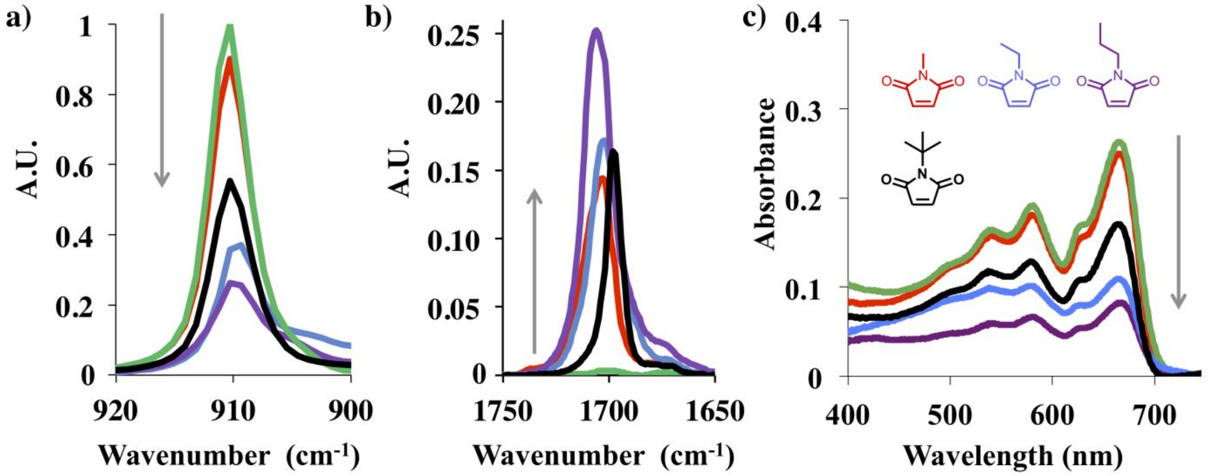

Figure 2. *Reactions of thin-film pentacene (green) with N-methylmaleimide (red), N-tert-*butylmaleimide *(black) N-ethylmaleimide (blue), N-propylmaleimide (purple). a) pentacene consumption monitored via PM-IRRAS spectra, averages over three trials and normalized to an initial out of plane vibration value of 1. b) product formation monitored via PM-IRRAS spectra,*

averaged over three trials and normalized to an initial out of plane vibration value of 1 c) pentacene consumption monitored via UV-vis in transmission mode.

As the data was rather unexpected, we sought to confirm reactivity trends via UV-vis, which has several advantages that are complementary to the IRRAS technique. First, the anisotropy associated with the absorption of visible light is much smaller, and thus measurements become less dependent on orientation of products or any reorientation of the pentacene thin film. This is in notable contrast to IRRAS were absorptions can be completely absent if the dipole is oriented parallel to the surface.[37] Second, the Davydov splitting from S_0-S_1 absorption band occurs in a region free of interference from other signals, and thus provides excellent quantification of pentacene consumption.[38] Finally, the UV-vis data, combined with the PM-IRRAS data, can allow us to differentiate annealing of the pentacene from reaction: annealing (reorientation) would alter the 910 cm^{-1} stretch but leave the visible spectrum unchanged, coincidental decreases in both correspond to reaction.

When reacting thin-films of pentacene on optically transparent gold, the trend is confirmed via UV-vis (Figure 2c). In fact, both the ethyl *and* propyl substituted maleimides are now clearly more reactive than the methyl counterpart, and dramatically so. While reactions with *N*-methylmaleimide have consumed only 5% of substrate, *N*-propylmaleimide and *N*-ethylmaleimide are mostly consumed (59 and 69% respectively). We can thus conclude that, here, solution kinetics are not an effective predictor of reactivity. The data also confirms that the difference in signal is due to reaction, and not an artifact from orientation changes or differences in absorption coefficient.

Results of the reactions between *N*-methylmaleimide, *N*-ethylmaleimide, and *N*-propylmaleimide and thin-film pentacene show that a mechanism based solely on collision theory could not have been less appropriate. If molecular collisions were to drive reactivity, solution and solid phase reactivity trends should have been similar; or at the most, the solid phase reactivity of *N*-ethylmaleimide and *N*-propylmaleimide would be further dampened by lower vapor pressure and slight steric effects.[39] The reaction of thin-film pentacene with the vapor of the three maleimides indicate that *neither solution kinetics, sterics, nor vapor pressure* were an appropriate predictor of reactivity. In fact, sterics are such a minor factor that even *N*-*tert*-butylmaleimide (k_{soln}=0.051 M^{-1} s^{-1}) reacts with the surface at a significantly faster rate than *N*-methylmaleimide (Figure 2, S3).

The above data require a new explanation. We posit that the trends may make sense if phase is taken into account. At standard reaction conditions (50 ºC), *N*-ethylmaleimide, *N*-propylmaleimide, and *N*-*tert*-butylmaleimide are liquids, while *N*-methylmaleimide is a solid. If the materials first adsorb onto the surface, with a significant residence time before reacting, then adsorbate phase may play a very large role.

The proposed mechanism is founded upon BET theory which postulates that, for some molecules, adsorption is a combination of two events. In BET adsorption, the first event is the physisorption, or non-covalent binding of adsorbates to the pentacene surface (Figure 1b). For the second, the intermolecular interactions for the small molecules are so strong that incident molecules can form multilayers on-top of those already physisorbed on the surface.[40] These multilayers (commonly 5-6 adsorbates thick),[41] can adopt two-dimension-like phase behavior.[42,43] The small molecules utilized here have significant interaction with each other (~65-75 kJ/mol), and similar molecules have been reported to adsorb onto traditional inorganic surfaces in this manner.[16] If the surface reaction first begins by forming multilayers of physisorbed material, a collection of molecules in a quasi-liquid phase would have dramatically higher rates of diffusion across the surface, and thus would be more likely to find a reactive site. In contrast, the mobility of a molecule in the quasi-solid phase (such as *N*-methylmaleimide) would be significantly limited. Thus, by utilizing BET adsorption as part of our mechanism, phase can play a prominent role in the kinetics of the reaction, and this would explain the trends in maleimide reactivity.

The results above have been combined in Table 1 with data for maleic anhydride and previously published data on maleimide and tetrafluorobenzoquinone.[19] Indeed, it appears that phase plays the dominant role in reactions. Of the seven reported values, the relative rates of surface reaction appear perfectly sorted according to adsorbate phase, with the liquids being faster. This includes the aforementioned maleimide and tetrafluorobenzoquinone, which are solids are reaction temperature. The most extraordinary, though, was *N*-*tert*-butylmaleimide. The bulky compound, which is a liquid at the reaction temperature, reacted faster than any of the high melting point materials, in contrast to its sluggish solution kinetics. Taken together, one finds that all liquid small molecules have at least 13× faster rates of reaction in the thin-film than would have been predicted based on solution kinetics (Table 1). Finally, it is worth noting that the surface reaction of *N*-*tert*-butylmaleimide is indeed slower than that of *N*-ethyl and *N*-propylmaleimide. This implies that, at least for compounds of the same phase, steric effects still impact reactivity. Overall though, sterics play a very muted role.

Table 1
Reaction with Pentacene

Reactant	Thin-film Relative consumption (IR)	Solution Relative Rate (k)	Phase at reaction conditions
N-propylmaleimide	**>7.4**	0.40	liquid
N-ethylmaleimide	**6.5**	0.38	
N-*tert*-butylmaleimide	**4.5**	0.077	
Maleic anhydride	**2.4**[19]	0.19[19]	
N-methylmaleimide	**1**	1	solid
Maleimide	**0.56**[19]	0.21[19]	
Tetrafluorobenzoquinone	**0.39**[19]	0.14[19]	

We have found these results to be consistent on an analogous thin film substrate, tetracene. Here, reactions with *N*-methyl, ethyl, and propylmaleimide were run in a manner similar to pentacene thin-films. Again, *N*-ethyl and propylmaleimide reacted more than an order of magnitude faster than *N*-methyl maleimide (Figure S4), despite the change in substrate and the reduction in temperature (from 50 ºC to 40 ºC). At this juncture the source of this acceleration was sought.

As a physisorbed state is central to our mechanism, significant effort was devoted to observing these condensed materials. Indirect evidence was first observed in pentacene thin films that had been reacted with maleic anhydride. Here scanning electron microscope (SEM) images of the surface demonstrate the topography of the pentacene surface has been changed compared to the original thin film. Near-textureless surface features abound the sample (Figure 3a) and contain virtually no roughness. This is in strong contrast to the pristine tetracene and pentacene surfaces (Figure 3b, typical RMS roughness of 10-20 nm).[19] Even more stark contrast is seen compared to small molecule reactions which generate quasi-solid phase: these result in a *roughening* of the surface[26] and/or formation of surface asperities.[19,20] The smoothing process is not limited to the prominent circle features; the remaining areas are also changed. As can be seen in Figure 3c, a slight "sheen" appears across the entire reacted surface, again reducing surface topography. The sample shown in Figure 3c also contains a crack (between the red arrows) which reveals the original texture which can be used for comparison. It is inferred that the crystallites which dominate the surface topography[21,44] reorganize due to the adsorbed material, a finding in line with other reports.[20]

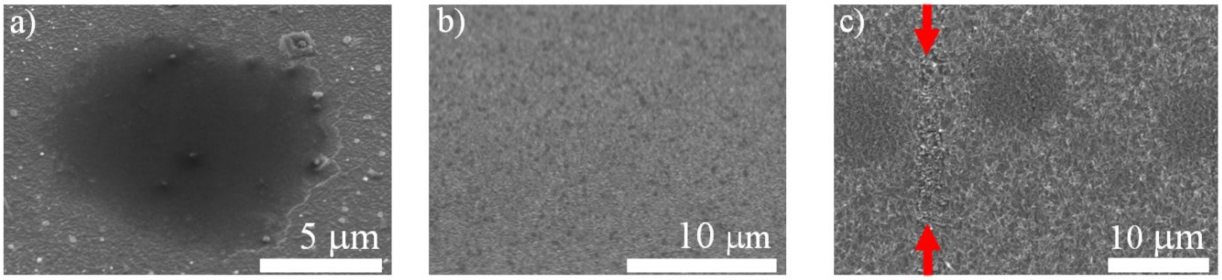

Figure 3. *a) Pentacene thin film that has been reacted with maleic anhydride. b) Unreacted pentacene thin film c) Pentacene thin film reacted with maleic anhydride. Crack between red arrow lacks the surface coating and is similar of the topography of an unreacted surface*

This physisorbed state was also detected by quartz crystal microbalance (QCM) and spectroscopic signatures of this state were identified via IR. In the former, acene films were deposited on a QCM which is capable of resolving small changes in mass caused by the adsorption onto the surface (with data typically denoted as the thickness added by deposited layer). As can be seen in Figure 4a, the coating of the surface rapidly increases over the timescale of hours, this same layer is then quickly removed by exposing the acene to high vacuum. In the latter, in situ IR analysis of reactions were performed by integrating the reaction chamber into the IR setup. We are able to observe the presence of physisorbed material for the reaction of *N*-ethylmaleimide with the pentacene surface. Unsurprisingly, a large majority of the *N*-ethylmaleimide has undergone reaction (Figure S5). However, Figure 4b contains the difference in carbonyl stretch intensity between the final measurement at reaction conditions versus after it had been purged with nitrogen for 30 min. The decrease in intensity around 1715 cm^{-1} is small but corresponds to approximately 2-3 monolayers worth of material.[19,20] It is important to note that only a gentle purge is required to remove this material, and that subsequent exposure to high vacuum conditions lead to no further desorption. As discussed below, both are suggestive of a weakly physisorbed state.

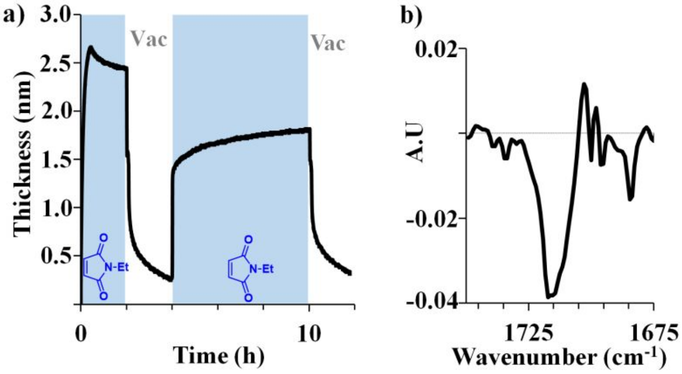

Figure 4. *a) Change in the thickness of a tetracene thin film that is exposed to* N-*ethylmaleimide at room temperature. Blue regions show the increasing thickness due to exposure to the small molecule reactant, while white regions are time intervals when the molecular source is closed off and high vacuum is applied to the film. b) PM-IRRAS subtraction spectra of N-ethylmaleimide reacted with a pentacene thin film. The spectra taken after 6 hours of reaction at 50 ºC was subtracted by the spectra taken after 30 minutes of exposure to a N_2 purge.*

Throughout this analysis, there has been an alternative explanation for the presence of non-covalently bonded material. It is also possible that the small molecules are absorbed into the subsurface rather than physisorbed on top; molecular absorption into organic materials is a well-established phenomenon.[12] It is important to differentiate whether absorption or physisorption is the primary means for small molecules to interact with the pentacene thin films, as the two have different implications for their induced kinetic effects. The series of results below suggest that for these reactants and conditions, absorption likely plays a minor role.

Differentiation between physisorption and absorption was first examined via the different types of desorption profiles seen for surface versus subsurface material. Multilayer-adsorption (BET) of vaporous materials are generally weakly interacting with the surface or themselves, and can be removed under mild conditions (Figure 1b, far right).[16] In contrast, absorption/desorption into a non-porous material, such as pentacene requires significant activation. Removing absorbed molecules the size of the maleimides may require very low pressures or heating. Typical desorption profiles for adsorbed (BET) molecules were measured by using *N*-methylsuccinimide on a pure gold surface (prepared using a sublimation chamber). Samples were coated to a level that was perceptible to the eye, even in the short time moving the sample from the chamber to the IR, a visible loss of material occurs. IR data confirms the presence of a small amount of material in the surface (Figure 5a), while the metallic lattice of the gold surface means no absorption is possible. After a brief (5 min) purge of IR chamber with nitrogen, no measureable signal remains, indicating that physisorbed *N*-methylsuccinimide is easily removed. This is consistent with reports for similar molecules.[26] Next, the desorption profile for absorbed material was established. Again, *N*-methylsuccinimide was used as this molecule lacks the necessary functional groups for a Diels-Alder reaction. *N*-methylsuccinimide was allowed to diffuse into a pentacene thin-film again, in the in situ setup where the reaction chamber is integrated into the IR bench. At our standard reaction conditions (50 ºC), an appreciable amount of *N*-methylsuccinimide is observed, despite the fact that no reaction occurs (Figure 5b). Upon purging with nitrogen (5 min), it appears that roughly 5% of this is weakly bound to the surface, and desorbs under conditions identical to the physisorbed material on gold. The remainder of the material persists after extensive purging (> 15 min, no change in intensity) and can be concluded to be absorbed. In fact, extended periods of time under high vacuum conditions well below the vapor pressure for this material ($<10^{-5}$ Torr, 18 h, Figure 5b) are necessary for its removal. Over this time period 30% of the absorbed material can be removed. The remaining material, which has presumably diffused far into the film, would require extended evacuation, possibly at elevated temperatures. This can be used to support the earlier hypothesis that during the reaction of *N*-ethylmaleimide on the small amount of weakly bound material is multilayer-adsorption. Figure 4b shows that this layer can be easily removed with a gentle stream of nitrogen, similar to the multilayer-adsorption of *N*-methylsuccinimide on gold.

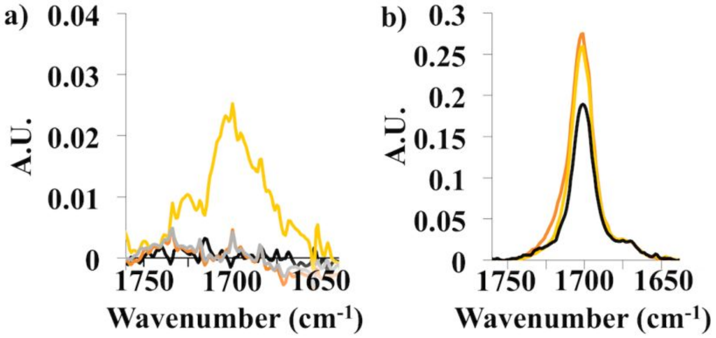

Figure 5. *a) IR spectra of* N-methylsuccinimide *deposited onto a bare gold surface (yellow) and subjected to a N_2 purge for 5 min (orange) and then 10 min (gray). The black line is a spectra of the gold slide taken before deposition. b) PM-IRRAS spectra of N-methylsuccinimide as deposited a pentacene thin film (orange) after being subjected to a N_2 purge for 5 min (yellow), and high vacuum for 18 h (black).*

Our findings on *N*-ethylmaleimide appear consistent with other data reported elsewhere. Earlier thin firm data[26] has shown extended high vacuum exposure to have a negligible change on reacted surfaces. Additionally, the use of a thermal probe (whereby the sample temperature is slowly increased) coupled with mass spectrometry, only show fragments of the small molecules in the presence of the molecule ion (i.e. it is only found in its reacted form).[27] Out of a series of molecules spanning a massive range of reactivity and sterics, only the relatively inert fumarodinitrile showed any sign of the absorption.[27] In light of the unreactive *N*-methylsuccinimide data showing absorption, we believe that for most of the small molecules, the rate of reaction far exceeds diffusion into the subsurface, and only in the case of relatively inert reactants is absorption an appreciable process.

It is the presence of this physisorbed (and infrequently absorbed) material which allows us to explain the data in Table 1. Unreacted material is present at 2-3 monolayers coverage allowing for a quasi-liquid or quasi-solid phase to be generated at the surface. The phase difference could accelerate reactions via three mechanisms, none of which are mutually exclusive. In the first, the change from quasi-solid to quasi-liquid simply allows for greater surface diffusion of the adsorbed molecules (Figure 1d) increasing successful collisions. This mechanism is central to classical surface science.[17,45] In the second, the quasi-liquid results in greater molecular freedom of pentacene molecules in the thin films, and possibly even solvation. Here adsorbed/absorbed molecules relax the surface structure of pentacene; normally the confined arrangement of the solid lattice inhibits reaction.[8,9] In the final, the adsorbed material is responsible for solvating the generated products; as a result the products are unable to passivate the surface. It has already been shown that the products can self-aggregate into asperities on the surface under extended conditions, and that it cannot do so without the presence of residual vapor.[19,20] Our findings here provide direct measurement of this physisorbed state which must underpin product reorganization. While other factors contribute to reaction kinetics (bulk diffusion, inherent reactivity of the molecules, etc.), we have provided a clear evidence that surface phenomena can play a critical role in solid phase reactivity.

Conclusions

In summary, we have demonstrated that the reactivity of thin-film pentacene is highly predicated on the adsorbate phase and only weakly correlated to traditional chemical considerations. PM-IRRAS measurements demonstrated that *N*-propylmaleimide and *N*-ethylmaleimide reacted faster with pentacene thin films than *N*-methylmaleimide despite having lower vapor pressures and greater steric hindrance. In contrast, adsorbate phase at the reaction temperature was found to be strongly correlated with reaction rates. We have proposed a mechanism based on the BET model of adsorption, whereby adsorbates in the liquid phase experience far greater diffusion than their counterparts in the solid phase. The results suggest new insights into surface phenomena are necessary to better understand gas-solid reactions.

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