THE JOURNAL OF PHYSICAL CHEMISTRY C

A Window on Surface Explosions: Tartaric Acid on Cu(110)

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Supporting Information

ABSTRACT: Autocatalytic reaction mechanisms are observed in a range of important chemical processes including catalysis, radical-mediated explosions, and biosynthesis. Because of their complexity, the microscopic details of autocatalytic reaction mechanisms have been difficult to study on surfaces and heterogeneous catalysts. Autocatalytic decomposition reactions of *S*,*S*- and *R*,*R*-tartaric acid (TA) adsorbed on Cu(110) offer molecular-level insight into aspects of these processes, which until now, were largely a matter of speculation. The



decomposition of TA/Cu(110) is initiated by a slow, irreversible process that forms vacancies in the adsorbed TA layer, followed by a vacancy-mediated, explosive decomposition process that yields CO_2 and small hydrocarbon products. Initiation of the explosive decomposition of TA/Cu(110) has been studied by measurement of the reaction kinetics, time-resolved low energy electron diffraction (LEED), and time-resolved scanning tunneling microscopy (STM). Initiation results in a decrease in the local coverage of TA and a concomitant increase in the areal vacancy concentration. Observations of explosive TA decomposition on the $Cu(651)^S$ surface suggest that initiation does not occur at structural defects in the surface, as has been suggested in the past. Once the vacancy concentration reaches a critical value, the explosive, autocatalytic decomposition step dominates the TA decomposition rate. The onset of the explosive decomposition of TA on Cu(110) is accompanied by the extraction of Cu atoms from the surface to form a ($\pm 6,7; \mp 2,1$) overlayer that is readily observable using LEED and STM. The explosive decomposition step is second-order in vacancy concentration and accelerates with increasing extent of reaction.

1. INTRODUCTION

Over the past forty years, studies of surface reaction kinetics have revealed a small but growing number of surface reactions that proceed by mechanisms that are autocatalytic and in many instances referred to as surface explosions.¹⁻¹¹ The signature phenomenology of any such process is that, under isothermal conditions, the rate of reaction accelerates with the extent of reaction. For example, in a classical radical chain explosion mechanism, there is a chain branching step in which the reaction of one radical species produces two radicals, $\bullet \rightarrow 2 \bullet$. In the absence of radical quenching reactions, the chain branching step results in an exponential increase in the radical concentration with time. On a surface, a similar condition can arise for adsorbate decomposition reactions that require the presence of an empty site or vacancy. For example, consider the dissociation of adsorbed A₂ followed by rapid desorption of A into the gas phase:

$$A_2^* + * \to 2A^* \to 2A_g + 2^*$$
 (Scheme 1)

where * represents an adsorption site. From a mechanistic perspective, the vacant sites fulfill the same role as gas-phase radicals in the sense that the resulting kinetics yield an exponential growth in vacancy concentration and hence lead to a surface explosion. It is important to note that this is not the only mechanism that can lead to surface explosion behavior, but it is the one deemed to be operative in the explosive decomposition of tartaric acid (TA) on Cu(110), the focus of this work.^{11–15}

Surface explosions were first reported in the work of Madix et al. studying the decomposition of formic acid on Ni(110) surfaces.^{1–4} Since then, explosive or autocatalytic decomposition has been observed in the decomposition of formic and acetic acid on many metal surfaces.^{9,16–23} It is important to note that, while the majority of these studies have been performed on low Miller index single-crystal metal surfaces under ultrahigh vacuum conditions, surface explosions have also been observed for acetate decomposition on nanoparticulate Rh catalysts operating at atmospheric pressures.^{9,24,25} Another class of explosive surface processes is the reaction in mixed overlayers of NO and CO^{5,6,26–29} or NO and H₂.^{30,31} The final example is dissociative adsorption that is autocatalyzed by the presence of the adsorbed species.^{7,32–34}

Explosive adsorbate decomposition reactions have for the most part been studied through use of temperature-

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Received:December 4, 2012Revised:February 3, 2013Published:February 4, 2013
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programmed reaction spectroscopy (TPRS) in which reactants are first adsorbed on the surface of interest at low temperature and then heated, either isothermally or at constant rate, to induce reaction. The reaction rate is monitored as a product desorption rate using a mass spectrometer. There are two key signatures of explosive surface reaction kinetics. One is the observation of product desorption peaks that occur over very narrow temperature ranges ($\Delta T_{p} = 1-5$ K) during heating, temperature ranges that cannot be accounted for by standard zero-, first-, or second-order reaction kinetics. The second signature is the observation of reaction rates that increase with time or extent of reaction during isothermal heating. Ultimately, of course, all surface reaction rates decline as the adsorbed reactant becomes depleted from the surface. These two signature phenomena of surface explosions, narrow product desorption peaks during heating and accelerating reaction rates at constant temperature, can only be understood in terms of rate laws that describe autocatalytic processes.

The most common model for understanding explosive decomposition of adsorbates invokes the participation of a vacant site in the rate-limiting elementary step. As a result, their kinetics are described by rate laws of the form

$$r = k \cdot \theta (1 - \theta) \tag{1}$$

where θ represents a fractional coverage of the adsorbate relative to its saturation coverage on the surface.^{8,9,11,35,36} The fractional areal vacancy concentration is represented by the $(1 - \theta)$ term. Obviously, at a fractional coverage of $\theta > 0.5$, the rate increases as the coverage decreases. The unrealistic feature of this model is that, when $\theta = 1$, the adsorbate is stable indefinitely and to infinite temperatures. However, once decomposition has been initiated and $\theta = 1 - \varepsilon$, the rate becomes finite and will increase with decreasing coverage. Some models of this process use a mean field approach such as eq 1 in which the adsorbates (and vacancies) are assumed to be diffusing rapidly on the surface.⁸ Others assume that the vacancies form islands (empty patches) and that decomposition only occurs at the edges of the growing vacancy islands. This leads to rate laws of the form

$$r = k \cdot \theta (1 - \theta)^{1/2} \tag{2}$$

where the 1/2-order of the vacancy concentration term arises from the relationship between the perimeter length and the area of the vacancy islands.^{17,18,37}

One of the most poorly understood aspects of surface explosions is the initiation process. When the initial adsorbate coverage is $\theta = 1$, how is the explosion initiated? Many of the attempts to model TPD spectra of explosion processes have invoked rate laws of the form

$$r = k \cdot \theta (1 - \theta + f) \tag{3}$$

where *f* represents the coverage of initiation sites.^{3,38,39} In a number of cases, these initiation sites are associated with the presence of defects on the surface, although there is no direct evidence that this is the case. Vacancies in adsorbate overlayers could also be formed by thermal fluctuations in local density or some irreversible process such as adsorbate desorption. These are difficult processes to probe, and very little light has been shed on the initiation of surface explosions; however, the chemistry of *S*,*S*- and *R*,*R*-tartaric acid (TA, HO₂CCH(OH)-CH(OH)CO₂H) on the Cu(110) surface, studied in this work, offers a window into the explosion initiation process.

The surface chemistry of S,S- and R,R-TA on Cu(110) has been documented by Raval et al. $^{12,40-43}$ and by Ernst et al.^{11,15,44,45} over the past decade. At low coverages and temperatures <400 K, adsorbed TA forms a bitartrate species that is deprotonated at both ends, $-O_2CCH(OH)CH(OH)$ -CO₂-. The adsorbed S,S- and R,R-bitartrate form ordered overlayers denoted (9,0; -1,2) and (9,0; 1,2), respectively. These are enantiomorphous overlayers that have been observed using both low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The (9,0; ±1,2) overlayer lattices have a nominal absolute coverage of [TA] = $\frac{1}{6}$ ML (monolayer) relative to the areal density of Cu atoms in the Cu(110) surface. At absolute coverages of $[TA] > \frac{1}{6} ML$, the $(9,0; \pm 1,2)$ overlayer coexists with a (4,0; 2,1) overlayer with a nominal absolute coverage of $[TA] = \frac{1}{4}$ ML. This overlayer lattice can also be referred to as a $c(2\times 4)$ overlayer and is formed by a monotartrate species that is deprotonated only at one end, -O₂CCH(OH)CH(OH)CO₂H.⁴³ Åt absolute coverages of [TA] > $^{1}/_{4}$ ML, TA forms a densely packed overlayer that has been denoted $(\pm 4,1; \pm 2,5)$ and has a nominal absolute coverage of $[TA] = \frac{5}{18}$ ML. This (±4,1; $\pm 2,5$) overlayer has the saturation absolute coverage of TA on Cu(110) and for the purposes of this work will be assigned a fractional coverage of θ_{TA} = 1. Within this definition of fractional coverage, the (4,0; 2,1) overlayer has $\theta_{TA} = 0.90$, and the (9,0; $\pm 1,2$) overlayer has $\theta_{TA} = 0.60$. We have observed all of the previously reported overlayers; however, to be consistent with the general overlayer notation rules recently proposed by Ernst,⁴⁶ we will denote the $(\pm 4,1; \pm 2,5)$ overlayer as $(\pm 4,1;$ ∓2,4).

More important than the ordered overlayers are the kinetics of TA/Cu(110) decomposition to yield CO₂ desorption. Both Raval and Ernst have observed decomposition reaction kinetics that are consistent with an explosive mechanism.^{11,12,15} The CO₂ peak desorption temperature shifted from 450 K at low coverage to 520 K at $\theta_{TA} = 1$, and the desorption peak width dropped to $\Delta T_p \approx 2$ K. These are signatures of a vacancy-mediated, explosive decomposition mechanism.

This paper provides the first molecular-level insight into the processes that initiate explosive decomposition on surfaces. Kinetic data are presented for the surface explosion of TA/ Cu(110) obtained under a range of conditions including variable initial coverages and isothermal heating over a range of temperatures. By comparing the explosive TA decomposition kinetics on Cu(110) and the stepped kinked Cu(651) surface, we provide evidence that defects in the surface are not the initiation sites. By conducting annealing and quenching experiments during isothermal decomposition, we demonstrate that the initiation process is irreversible. Finally, STM imaging and LEED of the surface during isothermal initiation demonstrate that the initiation process results in the slow, irreversible loss of TA and the formation of patches of surface with a local coverage of θ_{TA} = 0.90. STM imaging and LEED show that the onset of the explosion is accompanied by a process in which Cu atoms extracted from the Cu(110) surface layer form Cu adatom rows that are ordered into a previously unreported ($\pm 6,7$; $\mp 2,1$) overlayer. Finally, on the basis of these observations, we suggest and fit to the kinetic data a rate law that explicitly accounts for the kinetics of the irreversible initiation process.

The use of the chiral S,S- and R,R- forms of TA leads to the formation of chiral overlayers. S,S-TA forms the (9,0;-1,2), (4,0;2,1), (-4,1;2,4), and (-6,7;2,1) overlayers. R,R-TA forms

the (9,0;1,2), (4,0;2,1), (4,1;-2,4), and (6,7;-2,1) overlayers. While the (4,0;2,1) overlayer is not chiral, the others are. Because the Cu(110) is not chiral, the chirality of the TA and the structures that it forms do not impact the surface reaction kinetics described in this paper. When referring generically to the chiral overlayer structures formed by *S*,*S*- and *R*,*R*- TA we will use the notation (9,0; \pm 1,2), (\pm 4,1; \mp 2,4), and (\pm 6,7; \mp 2,1).

2. EXPERIMENTAL SECTION

The TPRS and LEED studies of TA adsorption and decomposition on Cu(110) and $Cu(651)^{S}$ surfaces were conducted in two ultrahigh vacuum (UHV) surface science chambers at Carnegie Mellon University. The STM experiments were conducted in a UHV chamber at Tufts University.

The Cu(110) and Cu(651) single crystals were purchased from a commercial source (Monocrystals Inc.). Each single crystal disk was ~ 10 mm in diameter and ~ 2 mm thick and was polished as received. The crystals used for LEED and TPRS experiments were spot-welded between two Ta wires at the end of a UHV manipulator. Each could be heated or cooled over the temperature range 80-1000 K with the temperature measurement being made by a chromel-alumel thermocouple spot-welded to the edge of the crystal. An identical Cu(110)crystal was used for STM studies. The crystal was mounted to a Ta sample plate with Ta strips that did not cover any part of the crystal face. Isothermal STM experiments were carried out in the STM stage using a pyrolitic boron nitride heating element embedded behind the sample. The sample temperature was monitored via a chromel-alumel thermocouple mounted in the STM stage. This setup allowed heating to temperatures in the range 300-500 K and stabilization of the temperature within ± 1 K of the desired set point for a period of hours.

The single-crystal sample surfaces used for TPRS and LEED studies were cleaned by cycles of Ar^+ sputtering followed by annealing at temperatures of 900–1000 K. The crystallographic orientations of the single-crystal surfaces used for the TPRS experiments were verified using LEED.

The crystalline powders of S,S-TA (Sigma-Aldrich, >99.5% enantiopurity) and R,R-TA (Fluka, > 99.7% enantiopurity) were used as received. The chirality of TA does not influence its surface chemistry on the achiral Cu(110) surface. Note, however, that the surface chemistries of racemic TA and *meso*-TA differ from that of its enantiomerically pure forms.^{11,14,15,44,45} TA was deposited on the surfaces of the single crystals by exposing them to TA vapor emanating from sublimation sources mounted in each of the UHV chambers. These sublimation sources were constructed from glass vials heated by passing electrical current through resistive metal (nickel-chromium or tungsten) wire coiled tightly around the vials. The temperatures of the sources were monitored by chromel-alumel thermocouples placed in direct contact with the vial walls. The TA fluxes incident on the Cu surfaces from the sublimation sources depended on the source temperature (338–358 K) and on the distance between the source and the sample surface. In general, exposure of TA to the surfaces was controlled by the time of exposure to TA vapor emanating from the source, while the source temperature and the distance to the Cu(110) surface were fixed.

TPRS measurements were performed by first adsorbing TA on the Cu(110) or Cu(651)^S surfaces at 405 K. This temperature allowed saturation of the monotartrate monolayer in the (\pm 4,1; \mp 2,4) phase on Cu(110) without allowing the

formation of TA multilayers.^{42,43} Lower exposure times were used to generate subsaturation coverages. The sample was then positioned within 1–2 mm of the aperture to the mass spectrometer and heated while monitoring the signals at one or more m/q ratios. The temperature of the sample was controlled to generate a constant heating rate for normal TPRS or constant temperature for isothermal TPRS. Unless otherwise indicated, the heating rate was 1 K/s, and the mass spectrometer monitored the signal at m/q = 44 to measure the rate of CO₂ evolution from the surface.

LEED patterns were obtained from the clean and TAmodified Cu(110) surfaces held at 90–110 K using an OCI Vacuum Microengineering optics with 77° solid angle view and a 75 mm diameter dual microchannel plate for image intensification. This allowed LEED patterns to be obtained with an electron beam current of a few nanoamps, thereby minimizing damage to the TA overlayer. Because the microchannel plates and the phosphorus screen are flat, the reciprocal space image of the LEED pattern is slightly distorted from the true reciprocal lattice as obtained with a spherical screen. This has not complicated the assignment of the LEED patterns.

The TA/Cu(110) surface was imaged with molecular resolution using an Omicron Nanotechnology variable-temperature, ultrahigh vacuum, scanning tunneling microscope (VT-UHV-STM). The base pressure in the STM chamber was $<1 \times$ 10^{-10} mbar. The Cu(110) surface was cleaned in a sample preparation chamber by cycles of Ar⁺ ion bombardment using a current of 20 μ A at 1500 eV. The final cleaning cycle before depositing TA was a 20 min sputter followed by a 10 min anneal to 700 K. TA was deposited onto the Cu(110) surface inside the preparation chamber using a sublimation source similar to ones used for the TPRS and LEED measurements. After TA deposition, the sample was transferred under vacuum into the STM chamber. The sample was then annealed at 405 K for 60 s to generate the $(\pm 4,1; \pm 2,4)$ overlayer with $\theta_{TA} = 1$. STM images were acquired with either Omicron or Veeco etched W tips.

3. RESULTS

In the following sections we will refer to the absolute coverage of TA on the Cu(110) surfaces using the notation [TA] and in units of molecules per Cu where the Cu atoms are those in the topmost rows of the Cu(110) surface. We will refer to the fractional coverage as $\theta_{TA} = [TA]/[TA]_{sat}$ where $[TA]_{sat} = 0.278$ molecules/Cu is the saturation coverage of TA in the (±4,1; \mp 2,4) overlayer generated by adsorption at 405 K and containing 5 TA molecules per 18 Cu atoms in the unit cell. The initial fractional coverage of TA adsorbed prior to a TPRS experiment will be referred to as θ_{TA}^0 .

3.1. Explosive Decomposition Kinetics for TA/Cu(110). The decomposition of TA on the Cu(110) surface during TPRS exhibits the two signature phenomena of an explosive reaction mechanism: occurrence of the reaction over a very narrow temperature range and a peak reaction rate that shifts to higher temperature with increasing initial TA coverage. Figure 1 shows a series of TPR spectra for *S*,*S*-TA decomposition during heating at 1.0 K/s and using a range of initial TA coverages, $\theta_{TA}^0 = 0.18-1$. These were obtained by monitoring the desorption rate of CO₂, which because CO₂ desorbs very rapidly from Cu(110), serves as a measure of the rate of TA decomposition. These data are consistent with those reported by Ernst et al.¹¹ The first observation is that the peaks shift from 432 to 499 K



Figure 1. TPRS of CO₂ produced by decomposition of *S*,*S*-TA on Cu(110) following increasing exposures to *S*,*S*-TA vapor. The exposure times are labeled with each TPRS spectrum. The left-hand inset shows the lowest coverage decomposition spectra with T_p at 435 K. The right-hand inset shows the highest coverage TPRS spectrum with a peak width at half-maximum of <1 K. The heating rate in all cases was 1 K/s.

as the initial TA coverage is increased from $\theta_{TA}^0 = 0.18-1$. This shift in T_p of ~70 K is similar to those observed for surface explosion reactions of molecules such as succinic acid $(HO_2CCH_2CH_2CO_2H)^{13,47}$ and malic acid $(HO_2CCH(OH)-CH_2CO_2H)^{48,49}$ that are structurally related to TA and have also been studied on Cu(110). At low values of θ_{TA}^0 , the leading edges of the peaks overlap one another as shown in the lefthand inset of Figure 1; however, once the initial coverage reaches $\theta_{TA}^0 > 0.5$, the leading edges begin to undercut those at lower initial coverages. This is a clear indication that, at a given temperature, the initial rate is decreasing with increasing initial coverage. In other words, the adsorbate is being stabilized on the surface by increasing initial coverage, or equivalently, it is being stabilized by the decreasing initial vacancy concentration, $1 - \theta_{TA}^{0}$. Note that T_{p} becomes very sensitive to θ_{TA}^{0} as it approaches $\theta_{TA}^{0} = 1$ and that the peak width, ΔT_{p} , becomes extremely small. The sensitivity to coverage near $\theta_{TA}^{0} = 1$ is a consequence of the fact that a small fractional change in θ_{TA}^0 causes a large fractional change in the vacancy concentration, 1 $-\theta_{TA}^0$. The right-hand inset in Figure 1 shows that, at $\theta_{TA}^0 = 1$, the peak width has a value of $\Delta T_{\rm p}$ < 1 K. This is difficult to measure accurately as the temperature interval of the data collection scheme was 0.3 K. It is important to note that the extreme sensitivity of $T_{\rm p}$ to coverage in the region near $\theta_{\rm TA}^0 = 1$, means that the measured peak width is very sensitive to the uniformity of coverage across the surface. Variations of 1% in local coverage would have measurable impact on the peak width, and so, we have taken extreme care to ensure uniformity of coverage by positioning the sample as far as possible from the TA sublimation source during deposition. The peak width of ΔT_p < 1 K for TA decomposition on Cu(110) is lower than any previously recorded peak width for a surface explosion.

The use of the TPR spectra in Figure 1 for modeling of the TA/Cu(110) explosion kinetics requires some means of calibrating the initial TA coverage, θ_{TA}^0 . Because the kinetics are sensitive to vacancy concentration, this requires a robust means of estimating the coverage when $\theta_{TA}^0 \approx 1$. This has been accomplished by fitting the measured CO₂ peak area at each exposure time to a monotonically increasing function of time (Supporting Information, Figure S1). This provides a good



Figure 2. Experimental measurements (bottom row) and model simulations (top row) of the kinetics of *S*,*S*-TA decomposition on Cu(110) to yield CO₂ desorption. (Left column) TPRS using various initial coverages of *S*,*S*-TA in the range $\theta_{SS-TA}^0 = 0.18-1.0$, as labeled with experimental data in bottom graph. Heating rate was 1 K/s. (Middle column) TPRS using heating rates in the range 0.25–4 K/s as labeled in the bottom graph. Initial coverage of *S*,*S*-TA was $\theta_{SS-TA}^0 = 1$. (Right column) Isothermal decomposition of *S*,*S*-TA on Cu(110) at temperatures in the range 440–470 K, as labeled in the bottom graph. Initial coverage of *S*,*S*-TA was $\theta_{SS-TA}^0 = 1$.

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representation of the TA uptake versus exposure time, but it is clear that the measured CO₂ yields appear to decrease at very high exposures (>400 s). This is an artifact of the extremely narrow peak widths as the coverage approaches $\theta_{TA}^0 = 1$ and the fact that there are only 3–4 data points defining the peak. For the purposes of defining coverages, we have used the CO₂ yield after an exposure of 400 s to define the saturation coverage, $\theta_{TA}^0 = 1$.

In order to gain further insight into the explosive decomposition kinetics of TA/Cu(110), we have conducted TPRS experiments using heating rates in the range $\beta = 0.25 -$ 4.0 K/s and isothermal heating at temperatures in the range 440-470 K. Figure 2 shows six panels of TPRS data and simulations of the decomposition kinetics as measured using TPRS. The lower three panels illustrate the experimentally determined TPR spectra, and the upper three panels illustrate the predictions of a kinetic model that will be described later. The lower left-hand panel simply reproduces data from Figure 1 with the associated initial coverages, θ_{TA}^0 , in order to allow direct comparison with the predictions of the kinetic model. The lower middle panel of Figure 2 shows a set of TPR spectra obtained for the saturated TA overlayer using heating rates in the range $\beta = 0.25 - 4.0$ K/s. As expected, the value of $T_{\rm p}$ increases with heating rate.

For an explosive decomposition process, the isothermal rate must increase with the extent of reaction. In the case of TA decomposition on Cu(110), this phenomenology is somewhat implied by the increase in $T_{\rm p}$ with increasing $\theta_{\rm TA}^{\rm 0}$ as shown in Figure 1. However, the TPRS experiment is complicated by the fact that the temperature is increasing throughout the extent of reaction, also increasing the rate through the influence of temperature on the rate constant. Prior studies of surface explosions have used isothermal TPRS to reveal the increase in rate with extent of reaction.^{4,5,17} The lower right-hand panel of Figure 2 shows the isothermal TPRS of TA decomposition on Cu(110) at temperatures in the range 440-470 K. The isothermal condition was achieved by heating the Cu(110)sample to the desired temperature at 1 K/s under feedback control and then using a constant temperature set point. The temperature ramp is indicated in the inset to Figure 3 and reveals an overshoot of <1 K and a settling time of \sim 10 s. Figure 2 (lower right) shows that, at 440 K, there is an induction period or initiation time of >400 s during which there is no detectable CO₂ desorption. After 400 s at 440 K, the rate of TA decomposition to CO₂ starts to increase until it reaches a maximum at \sim 500 s and then drops to zero as the TA is consumed. Not surprisingly, the initiation time decreases with increasing temperature, obviously approaching zero as the temperature tends toward 499 K, the value of T_p observed during TPRS at a heating rate of $\beta = 1$ K/s. At 470 K, one can already observe CO₂ desorption at the point of reaching constant temperature, and so, we have not collected data for isothermal temperatures >470 K. These isothermal data are clear evidence of the autocatalytic or explosive decomposition of TA on Cu(110).

The isothermal TPRS experiment is well suited to identifying the products of TA decomposition on the Cu(110) surface. Isothermal TPR spectra have been used to monitor desorption signals at m/q = 2, 12–18, 25–33, 41–46, and 58. These reveal that the major products of decomposition are CO₂, H₂, and H₂O plus several small hydrocarbons consisting primarily of methanol, formaldehyde, ethanol, and acetaldehyde. All species desorb with the same time profiles except that there is some





Figure 3. Isothermal decomposition of *R*,*R*-TA on $Cu(651)^{S}$ at 450 K. The inset shows the temperature ramp during heating and the stabilization at 450 K. The upper trace (offset for clarity) is an experiment in which the temperature was held at 450 K for 600 s. The explosive decomposition is much like that observed on Cu(110). The lower trace shows six desorption spectra obtained by holding the surface at 450 K for 100 s and then cooling (at ~1 K/s) for 100 s before starting another temperature ramp. The spectra have been stitched together such that the time axis represents only the time at 450 K. Initial coverage of *R*,*R*-TA was $\theta_{R-TA}^{0} = 1$.

desorption of H₂ prior to desorption of the other products (Supporting Information, Figure S2). This suggests that the TA decomposition mechanism is one in which the adsorbed monotartrate is first deprotonated to form the bitartrate. Subsequent cleavage of a $C-CO_2$ bond to yield CO_2 may then be the rate-limiting step that leads to rapid fragmentation and product desorption.

3.2. Explosion Initiation: TPRS of R,R-TA/Cu(651)^S. In order to explore the characteristics of the explosion initiation process, we have studied the explosive decomposition of R,R-TA on $Cu(651)^{S}$. The ideal structure of the $Cu(651)^{S}$ surface is shown in Figure 3. It is vicinal to the (110) plane and thus has (110) terraces that are separated by kinked step edges. Note, that the $Cu(651)^{S}$ surface has a chiral structure, hence the denotation "S". $^{50-52}$ The initial objective of our study of R,R-TA decomposition kinetics on $Cu(651)^{S}$ is to determine whether or not the explosive decomposition of TA can occur on such a highly defected surface. As mentioned earlier, prior studies of surface explosions have suggested that defects on surfaces may be responsible for initiation of surface explosions; however, the nature of the defect has never been clearly defined.^{3,38,39} If the defect initiation sites are structural features such as steps or kinks, it is not obvious that a surface such as $Cu(651)^{S}$ with kinks and steps spaced by molecular dimensions would induce explosive decomposition of adsorbed TA. The area of the ideal unit cell on the $Cu(651)^{S}$ surface is ~5.5 times that of the Cu(110) unit cell, which means that, at a saturation absolute coverage of $[TA]_{sat} = 0.278$, there are ~1.5 TA molecules per kink site on the Cu(651)^S surface. In other words, there are almost as many kink defects for initiation as TA molecules to undergo explosion. Nonetheless, R,R-TA does exhibit explosive decomposition kinetics on the $Cu(651)^{s}$ surface that are quite similar to those observed on the Cu(110) surface. The upper trace of Figure 3 is an isothermal



Figure 4. LEED, real space representations of the unit cell and STM images of the (A) (4,1; -2,4), (B) (4,0; 2,1), and (C) (6,7; -2,1) overlayers formed by high coverages of *R*,*R*-TA on Cu(110). The two left-hand panels show the reciprocal space lattice and the corresponding LEED pattern. The middle panel shows the real space lattice superimposed on the ideal Cu(110) surface. The two right-hand panels show the STM image and its superposition on the real space lattice.

TPRS of *R*,*R*-TA/Cu(651)^S at 450 K and starting with $\theta_{TA}^0 = 1$. The insert is a plot of the temperature profile as the set point changes from a heating rate of 1 K/s to a constant T = 450 K. The upper TPRS trace shows an initiation period of ~300 s followed by explosive decomposition and the complete consumption of the *R*,*R*-TA by ~400 s. At 450 K, the induction periods are comparable on the Cu(651)^S and Cu(110) surfaces, although it should be pointed out that the measurements on Cu(651)^S were done in a different apparatus than those on the Cu(110) surface and the temperature measurements may not be reproduced exactly. Nonetheless, the explosive decomposition occurs on Cu(651)^S, and the implication is that defects in surface structure are not responsible for initiation of the explosion.

The explosion initiation process that is occurring during the isothermal induction period is not accompanied by detectable desorption of CO₂. At this point one can ask whether or not the initiation process is reversible? One could imagine, for example, that heating of the adsorbed layer causes diffusion that results in fluctuations in local density or local vacancy formation. If that process were reversible, then these fluctuations in local density would disappear during cooling, and the system would return to its initial state, unless the explosion process had begun. To address this question, we have conducted an experiment in which the $R_r - TA/Cu(651)^s$ surface was quenched intermittently during the anneal at 450 K. The lower trace of Figure 3 is an isothermal TPR spectrum of R,R-TA/Cu(651)^S obtained by using a sequential temperature profile in which the $Cu(651)^{S}$ surface was repeatedly heated to 450 at 1 K/s, held at 450 K for 100 s, and then, cooled to 300 K. The dashed lines indicate the temperature profiles but stitched together so that the beginning and end of the consecutive isothermal anneal periods are aligned. The TPRS trace shows the CO₂ desorption signals obtained only

while the sample was at 450 K. During the first three 100 s periods, there is no detectable CO_2 desorption until the very end of the third period. During the fourth heating cycle, there is clearly observable desorption of CO_2 that reaches a maximum and then decays. A residual amount of CO_2 desorbs during the fifth cycle and almost none during the sixth. The point clearly illustrated by the data in Figure 3 is that the initiation process is irreversible. In spite of the interrupted heating profile, the explosive decomposition of $R_{J}R$ -TA/Cu(651)^S still occurs between 300 and 400 s of annealing at 450 K.

3.3. Ordered Phases of TA on Cu(110). *S*,*S*- and *R*,*R*-TA form a number of well-ordered overlayers on the Cu(110) surface that have been observed in this work and by others with LEED and with STM.^{12-15,41-43,53} The lowest coverage phases formed by TA are denoted (9,0; \pm 1,2), occur across a wide range of coverages, and are formed by the adsorbed bitartrate species. Because our interest is predominantly in the explosion initiation, we describe our observations of the higher coverage (4,0; 2,1) and (\pm 4,1; \mp 2,4) phases. In addition, we document a previously unreported (\pm 6,7; \mp 2,1) phase that appears to be relevant to the explosion initiation process.

3.3.1. (4,1; -2,4) R,R-TA/Cu(110). At its saturation coverage, R,R-TA is adsorbed as a monotartrate species in a chiral (4,1; -2,4) unit cell with an absolute coverage of [TA] = 0.278molecules/Cu. This overlayer lattice is identical to one that has been indexed as (4,1; 2,5) in other work.^{11,12,40,43} The LEED pattern and reciprocal space lattice vectors for the (4,1; -2,4) overlayer formed by R,R-TA/Cu(110) are shown in the two left-hand panels of Figure 4A. The real space lattice shown in the middle panel of Figure 4A illustrates the rectangular lattice. The STM image, with and without an overlay of the real space lattice, is shown in the two right-hand panels of Figure 4A.

3.3.2. (4,0; 2,1) R,R-TA/Cu(110). At an absolute coverage of [TA] = 0.25 molecules/Cu, TA is adsorbed as a monotartrate



Figure 5. Isothermal TPRS of TA on Cu(110) at 440 K with accompanying STM images of the surface. Initial coverage of *R*,*R*-TA was $\theta_{R,R-TA}^0 = 1$. The STM images were obtained by stopping the heating at every after each 50 s interval and cooling to room temperature. The surface starts in the (4,1; -2,4) phase at saturation coverage. The (4,0; 2,1) phase begins to appear after 50 s and is readily apparent after 150 s; however, there is no detectable CO₂ desorption. The onset of detectable CO₂ desorption is accompanied by the formation of the (6,7; -2,1) phase that dominates during the explosive decomposition. Scale bars are 10 nm.

species on the Cu(110) surface and in an achiral (4,0; 2,1) lattice. This overlayer can also be described as having a c(2×4) periodicity with respect to the substrate. The LEED pattern and reciprocal space lattice vectors for this phase are shown in the two left-hand panels of Figure 4B. The real space lattice on the Cu(110) surface is shown in the middle panel of Figure 4B. The STM image, with and without an overlay of the real space lattice, of this overlayer is shown in the two right-hand panels. The STM image reveals a pseudohexagonal array of molecules on the surface, consistent with the periodicity of the real space overlayer lattice.

3.3.3. (6,7; -2,1) *R*,*R*-*TA*/*Cu*(110). A Cu(110) surface with the (4,0; 2,1) phase of *R*,*R*-TA was heated at 1 K/s to 483 K, just below the explosion temperature, and then quenched. This resulted in the formation of the chiral (6,7; -2,1) overlayer with the LEED pattern and reciprocal space lattice displayed in the two left-hand panels of Figure 4C and the real space lattice shown in the middle panel of Figure 4C. This overlayer has not been reported previously, but appears to be relevant to the

onset of the explosion reaction. X-ray photoelectron spectra taken before and after the annealing to 483 K indicate a \sim 5% reduction in the coverage of adsorbed *R*,*R*-TA. The two righthand panels of Figure 4C show an STM image of this overlayer, with and without an overlay of the real space lattice. It is clearly quite unlike any other STM image of this surface in that it reveals the presence of rows of Cu adatoms, presumably extracted from the Cu(110) plane to reside on the surface. Although the contrast in this image does not reveal them, there are features between the rows of Cu adatoms that can be observed under other imaging conditions and arise from TA molecules on the surface.

The $(\pm 6,7; \mp 2,1)$ unit cell has an area that is 20 times that of the (1×1) unit cell of the Cu(110) surface. Given that the (4,0; 2,1) unit cell has a nominal absolute coverage of [TA] = 0.25 molecules/Cu and that the $(\pm 6,7; \mp 2,1)$ unit cell occurs at a coverage that is similar to that of the (4,0; 2,1) phase, the nominal absolute coverage of the $(\pm 6,7; \mp 2,1)$ phase is postulated to be [TA] = 0.25 (if, the initial coverage was in fact



Figure 6. TPRS and LEED patterns obtained during isothermal annealing of the S,S-TA/Cu(110) surface at 440 K. The sample temperature was quenched every 100 s to obtain the LEED pattern. The TPR spectrum is only plotted for the time at which the Cu(110) surface is at 440 K. The LEED images evolve with time from (-4,1; 2,4) to (4,0; 2,1) to (-6,7; 2,1) and finally to the (1,0; 0,1) pattern.

slightly higher than the nominal value of [TA] = 0.25). However, the spacing between the Cu adatom rows observed in the STM images is not perfectly uniform, consistent with the streakiness of the diffraction spots in the close packed rows of the LEED pattern. Thus, it is neither meaningful nor necessary to try to ascribe a precise coverage to this overlayer.

3.4. Isothermal STM and LEED during Initiation and Explosion of TA/Cu(110). The unusual initiation-explosion behavior of TA/Cu(110) creates an unusual opportunity to monitor the slow changes occurring on the surface during isothermal heating and leading to the explosive decomposition reaction. The initiation period followed by explosive release of CO₂ illustrated in the lower right-hand panel of Figure 2 was also observed in the STM chamber by monitoring of the CO₂ signal using the mass spectrometer in its sample preparation chamber. Furthermore, the data illustrated in Figure 3 indicate that quenching the sample temperature during isothermal heating does not significantly perturb the initiation and explosion kinetics. As a consequence, it has been possible to study the initiation process with STM by annealing the TA/ Cu(110) at 445 K and quenching the temperature to 300 K after every 50 s of isothermal annealing. The temperature measurement on the STM is not as accurate as in the TPRS apparatus, but the reaction initiation time observed in the STM suggests that the temperature corresponds roughly to the TPRS spectrum observed at 440 K in the TPRS apparatus. Figure 5 shows an isothermal TPR spectrum obtained in the TPRS chamber with the TA/Cu(110) at 440 K. Also shown are a number of STM images of the TA/Cu(110) surface (heated to 445 K in the STM chamber) obtained by quenching at various

times throughout the initiation and explosive decomposition process.

To conduct these STM experiments, the R,R-TA/Cu(110) surface was saturated at 405 K with an initial coverage of θ_{TA}^0 = 1. The STM image at t = 0 s clearly shows the ordered (4,1; -2,4) phase. At t = 50 s (STM image not shown), there is some evidence of disordered regions in the (-4,1; 2,4) phase that appear to grow from the step edge running vertically through the image. At t = 100 s, there is further evidence of the disordered region, and it appears to grow predominantly from the top of the step edge onto the terrace. At t = 150 s, the surface is clearly covered with domains of both the (4,1; -2,4)and the (4,0; 2,1) phase. The (4,0; 2,1) domains grow across the terraces from the step edge. Note that the local coverage in the (4,0; 2,1) phase is θ_{TA} = 0.90 relative to the local coverage of $\theta_{TA} = 1$ in the saturated (4,1; -2,4) phase. This means that there has been a global decrease in the coverage of adsorbed *R*,*R*-TA but with no detectable CO_2 desorption. At t = 300 s, with the onset of measurable CO_2 desorption, one observes the appearance of the rows of Cu adatoms that have been extracted from the Cu(110) surface. At t = 400 s, the rows of Cu atoms are ordered into the (6,7; -2,1) structure. The explosive decomposition then accelerates, and by t = 550 s, the surface is clean and free of adsorbed R,R-TA.

In addition to STM, LEED can be used to monitor the changes on the surface occurring during isothermal annealing of TA/Cu(110). Figure 6 shows a set of LEED patterns and an isothermal TPR spectrum obtained from a saturated layer of S,S-TA/Cu(110) annealed at 440 K but with periodic interruption of the annealing every 100 s to cool the sample

and obtain a LEED pattern. The interrupted TPR spectrum is analogous to that obtained from $Cu(651)^{S}$ (Figure 3) and reveals the irreversibility of the explosion initiation process on Cu(110). Although the isothermal TPR spectrum taken in the LEED chamber has much lower signal-to-noise than those obtained in the TPRS chamber (Figures 2 and 5), it is more than sufficient to observe the explosion reaction. The key point about the data in Figure 6 is that there is a direct link between the time scale for the evolution of the LEED patterns and the TPR spectrum because they were obtained from the same TA/ Cu(110) sample during one experiment. Before annealing at 440 K, the surface exhibits the (-4,1; 2,4) LEED pattern associated with the saturated layer of S,S-TA/Cu(110). After heating at 440 K for 100 and 200 s, the surface exhibits the LEED pattern of the (4,0; 2,1) overlayer. After annealing for 300 s, just prior to the onset of the explosion reaction, the appearance of the (-6,7; 2,1) pattern is observed. The (-6,7;2,1) pattern is well developed after 400 s at the peak of the reaction rate. After 500 s and the completion of the reaction, the (1,0; 0,1) pattern of the clean Cu(110) surface is observed. This temporal evolution of the LEED patterns in Figure 6 is consistent with the evolution of the STM images shown in Figure 5 and reveals the nature of the irreversible changes to the surface occurring prior to the onset of observable CO_2 desorption.

The slow nature of the initiation process and the fact that it is irreversible have enabled this STM/LEED study of the initiation process, allowing us to capture snap shots of the TA/Cu(110) surface evolving at ~445 K but with periodic quenching to 300 K as shown in Figures 5 and 6. In fact, we have also been able to obtain STM images of the surface undergoing initiation while the temperature is held at 445 K. These illustrate with much higher time resolution the process documented by the select images shown in Figure 5. Clearly, the initiation process is one in which there is a net decrease in the coverage of adsorbed TA and an increase in the areal vacancy concentration, as revealed by the conversion from the $(\pm 4,1; \pm 2,4)$ phase to the (4,0; 2,1) phase. Whether this is due to the decomposition of adsorbed TA, molecular desorption, or some other irreversible process is not clear. While we cannot detect desorption of CO₂ during the early parts of the initiation period, it may simply be that the rate of decomposition over the long time period of the initiation process is simply too low to be detected. The onset of the detectable CO₂ desorption is accompanied by the appearance of the $(\pm 6,7; \pm 2,1)$ phase, although the cause-effect relationship is unclear.

4. DISCUSSION

The decomposition of TA/Cu(110) has opened a window that sheds light on the initiation events that lead to the onset of autocatalytic surface explosions. Until now, these were largely a matter of speculation. Although the data presented in this report are derived from TA decomposition on Cu(110) and Cu(651)^S surfaces, they probably shed light on a number of the previously observed surface explosion reactions. Our discussion of the surface explosion process revolves around two steps. To put it into the terminology of classical radical explosion mechanisms, these are the initiation step and the branching step.

There are several mechanisms that have been postulated for the chain branching steps. The most commonly considered is the vacancy formation model described by the steps in Scheme 1 above. This leads to rate equations such as eqs 1-3 that depend on the vacancy concentrations as represented by the $(1 - \theta)$ terms.^{3,8,9,11,17,18,35–39} A related mechanism postulates the existence of a catalytic intermediate:

$$A^* + B^* \to 2B^* \qquad (Scheme 2)$$

This mechanism is probably relevant to the recent observations of autocatalytic adsorption processes.^{7,32–34} In this scenario, the catalytic intermediate, B*, is an adsorbed molecular species, but in general terms, one could think of a vacancy as a catalytic intermediate. A third explosion mechanism invokes the existence of adsorbate or surface phase transitions that occur over very narrow temperature ranges and lead to the formation of kinetically destabilized adsorbates.^{5,28,29,54} Finally, one can always imagine or postulate coverage dependent activation barriers that could yield the kinetic phenomena associated with surface explosions.^{5,19,55,56}

4.1. Explosion Initiation. Within the framework of the model for vacancy-mediated, surface explosion reactions, the nature of the initiation step has always been a matter of speculation. In other words, when the coverage of adsorbed species is $\theta = 1$, how is the first vacancy formed? Often, it has been assumed that the reaction is initiated at defects in the surface whose nature is not explicitly discussed. In kinetic modeling studies, these are represented by the quantity *f* in eq 3, which explicitly prevents the vacancy term from ever reaching $(1 - \theta + f) = 0.^{3,38,39}$

The role of surface defects as explosion initiation sites has been probed in this work by comparison of the explosion kinetics on the Cu(110) and the $Cu(651)^{S}$ surfaces. Given the vastly different surface structures, the fact that $Cu(651)^{s}$ has an extremely high step and kink density, and the fact that both surfaces exhibit explosive TA decomposition on similar time scales during isothermal heating, it seems unlikely that the initiation step involves structural defects in the surface. As mentioned earlier, the density of kinks on the $Cu(651)^{S}$ surface is roughly equal to the saturation TA coverage. In other words, there is a kink defect for every one or two adsorbed TA molecules. It should be pointed out that the conclusion that surface structural effects are not initiation sites for explosive surface decomposition was probably already evident based on the fact that surface explosion kinetics have been observed in the decomposition of acetic acid on nanoparticulate Rh supported on Al_2O_3 .^{9,57} The surfaces of those nanoparticles must expose fairly high concentrations of defects and edges.

Assuming that the initiation is not the result of defects but rather some activated process on the surface, one can ask whether this process is reversible or not. This is addressed by the isothermal STM imaging and LEED experiments (Figure 5 and 6, respectively) and the interrupted isothermal TPRS experiments on Cu(651)^S and Cu(110) illustrated in Figures 3 and 6, respectively. The fact that the induction period is dependent only on the time at the anneal temperature (~450 K) and not influenced by the periodic quenching demonstrates that the initiation step is irreversible. The temperature dependence of the initiation periods observed in the isothermal heating experiments of Figure 2, suggests that one can think of the initiation step in terms of an irreversible activated process. The STM images indicate that the initiation process is accompanied by a loss of TA from the surface resulting in the conversion of the $(\pm 4,1; \pm 2,4)$ saturation coverage phase to the (4,0; 2,1) phase.

One point to be emphasized on the basis of our observations is that the reduction in local adsorbate coverage does not mean

the reduction to zero as is implied in some discussions of the surface explosion process that invoke the formation of vacancy islands or extended holes in the adsorbate overlayer.^{17,18,37,38} Lateral diffusion is sufficiently rapid that vacancies formed during the induction period do not form large "holes" in the overlayer that then expand during the explosion phase of the reaction. Even during the formation of the ($\pm 6,7; \pm 2,1$) phase, which is clearly occurring during the explosion phase, there is no evidence from STM of the presence of bare patches of the surface surrounded by regions of high local coverage.

4.2. Surface Explosion Kinetics. Most previous efforts to model the kinetics of vacancy mediated surface explosion reactions have used rate laws such as eqs 1-3 to model the results of TPRS experiments.^{3,8,9,17,18,35,37-39} A few have analyzed more sophisticated, multistep microkinetic models of the mechanism, and some have used kinetic Monte Carlo methods.^{26,30,31} As mentioned, the initiation process has not been well defined in many of these models, largely, because there has been little firm basis for choosing between postulated initiation processes. In the course of this work, we have obtained a fairly comprehensive set of kinetic data for TA decomposition on Cu(110) and gained some insight into the nature of the initiation process. On the basis of this insight, we have chosen to model our TPR spectra using a rate expression that explicitly represents the initiation process as a reaction step that creates vacancies via consumption of adsorbed TA:

$$r = k_{i}\theta + k_{e}\theta(1-\theta)^{n}$$
⁽⁴⁾

where k_i is a rate constant for the initiation process, k_e is the rate constant for the explosion, and *n* defines the order of the explosion reaction with respect to the vacancy concentration. By using this expression to simulate the CO₂ TPR spectra, we are explicitly assuming that the initiation process generates CO₂ in addition to creating vacancies. The use of the rate law expressed in eq 4 explicitly accounts for the irreversible initiation process by introducing a new parameter, k_i , that must be estimated from the kinetic data but at the same time eliminates any assumption about initiation site density, denoted by the parameter *f* in previous models.^{3,38,39} However, the model does assume that the reaction kinetics do not differ between the different phases of adsorbed TA and are well described by a mean field description.

The TPR spectra illustrated in Figure 2 have been simulated using the rate expression of eq 4 and used to estimate the activation energies and pre-exponential factors that determine the two rates constants: A_i , E_i , $A_{e'}$, and E_e . The predicted spectra are shown in the top row of Figure 2 for comparison with the measurements illustrated in the bottom row. The values of the parameters derived from this process are listed in Table 1. The parameter estimation approach has searched for the values of $\ln(A_i)$, E_i , $\ln(A_e)$, and E_e that minimize the differences between

Table 1. Kinetic Parameters Estimated^{*a*} for the Explosive Decomposition of TA/Cu(110) Using eq 4 with n = 2

	A (1/s)	E (kJ/mol)
initiation, k _i	3.7×10^{3}	63
explosion, k_{e}	6.1× 10 ¹³	125

^{*a*}Parameter estimation by minimization of $\sum (x_{expt} - x_{model})^2 / x_{expt}^2$ where *x* are the peak temperatures and the peak times for the variable coverage, variable heating rate, and isothermal heating rate TPRS data in Figure 2. the predicted and measured values of T_p for the TPR spectra and the predicted and measured values of the peak times, $t_{\rm p}$, for the isothermal decomposition reactions. Note first that the parameter estimation process restricted the values of the reaction order in vacancy concentration to $n = \frac{1}{2}$, 1, or 2 and identified the optimal reaction order of n = 2. This suggests that two vacancies are needed for TA dissociation. It is worth noting that reaction orders of $n = \frac{1}{2}$ or 1 cannot come close to predicting the wide range of temperatures spanned by the coverage-dependent TPR spectra shown in Figures 1 and 2. This range of peak temperatures is an explicit consequence of the rate law, the slow production of vacancies by the initiation process, and the fact that two adjacent vacancies are needed for explosive decomposition. The initiation process has been chosen to be first order in coverage, but in reality, it would be hard to discern this from the data because $\theta \approx 1$ during the initiation process, and thus, the order of the initiation term does not have much influence on its magnitude.

In radical chain and radical explosion processes, there are termination or quenching processes that determine the number of radicals generated by each initiation event. In a surface explosion reaction, one can ask the question, how many TA molecules decompose autocatalytically for each vacancy created by an initiation step? Because the rate law is separated into an initiation term and an explosion term, one can identify the contribution to the total rate from each of these processes throughout the course of the reaction. As a consequence, one can find a time during the isothermal reactions or a temperature in the TPR spectra at which the initiation rate is equal to the explosion rate:

$$k_i \theta = k_e \theta (1 - \theta)^2 \tag{5}$$

This then defines a critical TA coverage, θ_{c} and therefore a critical vacancy concentration, θ_{vc} above which the explosion process dominates the overall reaction rate:

$$\theta_{\rm vc} = 1 - \theta_{\rm c} = \sqrt{k_{\rm i}/k_{\rm e}} \tag{6}$$

Using the kinetic parameters listed in Table 1 and derived from the TPRS data in Figure 2, the critical vacancy coverage can be calculated at any temperature and is found to vary from $\theta_{vc} =$ 0.03 at 450 K to $\theta_{vc} =$ 0.01 at 500 K. This means that, at 500 K, the peak temperature in the TPR spectrum obtained for $\theta_{TA}^0 = 1$ heated at 1 K/s, the creation of one vacancy leads to the subsequent autocatalytic decomposition of ~100 TA molecules. Note that this is far higher than the ratio of TA to kinks on the Cu(651)^S surface (~1.5) and thus suggests that kinks or steps are not the sites of initiation on the Cu(110) surface.

4.3. TA/Cu(110) Overlayer Transitions during Initiation. The ability to image the changes in the TA overlayer during isothermal decomposition has provided significant insight into the surface explosion process. The STM images shown in Figure 5 revealed the slow decrease in TA coverage that occurs during isothermal heating but could not be observed as CO_2 desorption. Furthermore, they have revealed that, rather than visible vacancy islands or holes in the overlayer, TA diffusion is sufficiently fast that the vacancy creation results in the formation of regions with local TA coverage that is lower than saturation. Although the low density regions observed in the STM images certainly seem to be associated with step edges, it is not necessarily the case that steps are the sites of vacancy formation. It is quite possible that vacancies diffuse to the step edges because they are better able

to accommodate the (4,0; 2,1) phase than the higher density $(\pm 4,1; \pm 2,4)$ phase.

Perhaps the most interesting of the structures formed is the $(\pm 6,7; \pm 2,1)$ phase that has been observed for the first time in this work using both LEED and STM. As one can see from comparison of Figures 5 and 6, this phase is observed at about the critical vacancy coverage at which the explosion reaction starts to dominate the overall TA decomposition rate. The STM images suggest that this is a phase in which the Cu atoms from the Cu(110) surface have been extracted from the top layer to reside in the adsorbate layer. Perhaps vacancies formed in the overlayer are being occupied by these Cu adatoms. The explosive decomposition of formic acid and acetic acid on Ni(110) has been studied with STM, and it has been shown that Ni atoms are extracted from the surface during formation of the adsorbed species.⁵⁸ During heating, the extracted Ni atoms are then released by the subsequent explosive decomposition process. The extraction of Cu atoms from the surface happens at some point during the adsorption and decomposition of TA on Cu(110). It is possible that they are present in the high coverage phases of TA on Cu(110) and then released during TA decomposition to form the $(\pm 6,7)$; $\mp 2,1$) phase. However, it is not possible to determine the cause and effect relationship between the formation of these adatoms and the onset of the surface explosion process.

The TA/Cu(110) system has opened a window on the processes that initiate surface explosion. However, this is a complex system in which three structural phases of the TA overlayer are present throughout the course of the explosion initiation process. Given the presence of multiple phases, changing coverages, and multiple parallel processes, it is not surprising that rate expression of eq 4 is incapable of reproducing all of the kinetic data exactly. In some respects it is remarkable that it does as well as it does. One question is whether these multiple phases are critical to the overall process. The fact that one can observe the same type of initiation and explosion kinetics on the Cu(651)^S surface suggests that the exact nature of the different phases of adsorbed TA on Cu(110)are not significant to the overall process or its kinetics. What is critical is the initial decrease in coverage cause by an initiation step, followed by the onset of the autocatalytic explosion. The $(\pm 4,1; \pm 2,4)$, (4,0; 2,1), and $(\pm 6,7; \pm 2,1)$ phases merely provide a convenient way to monitor the time-dependent changes occurring on the surface during initiation.

5. CONCLUSIONS

The explosive decomposition of TA on Cu(110) is initiated by an irreversible process that leads to a slow decrease in the coverage of TA on the surface and the concomitant formation of vacancies in the adsorbed overlayer. The initiation process is not associated with structural defects on the surface; instead, it can be described simply as an irreversible initiation step in the reaction mechanism that is then followed by the explosive autocatalytic decomposition of TA. The onset of the explosive decomposition is accompanied by the appearance of Cu adatoms on the Cu(110) surface, observed in LEED and by STM as a ($\pm 6,7$; $\mp 2,1$) phase.

ASSOCIATED CONTENT

S Supporting Information

(Figure S1) TA uptake versus exposure time to Cu(110) as measured using the areas of the CO_2 TPD spectra, illustrating the function fit to these data and then used to estimate the coverage versus exposure time; (Figure S2) the multimass TPD spectrum obtained during isothermal heating of TA/Cu(110) at 440 K, revealing the desorption of H₂ prior to the explosive decomposition of the remaining TA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the NSF through a collaborative grant CHE-1012358 (B.M., V.P., B.H., A.J.G.) and CHE-1012307 (T.J.L., E.C.H.S.). A.J.G. gratefully acknowledges the hospitality of the Fritz-Haber Institute during the writing of this manuscript.

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