Thermal and Low-Energy Electron-Driven Chemistry of Biacetyl on Ag(111)

E. D. Pylant, M. J. Hubbard, and J. M. White*

Department of Chemistry and Biochemistry, Center for Materials Chemistry, University of Texas, Austin, Texas 78712

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The thermal and electron-induced chemistry of biacetyl (CH₃COCOCH₃) on Ag(111) has been studied using temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. No thermal decomposition of biacetyl occurs, confirming that Ag(111) is inert with respect to the breaking of C–C, C=O, and C–H bonds. There are five molecular biacetyl desorption peaks in TPD–180, 178, 174, 188, and 215 K. The peak at 180 K is attributed to monolayer adsorption, and its saturation peak area is used to scale other TPD biacetyl peaks. The peak at 188 K is assigned to multilayers and that at 215 K to desorption from defect sites. The peaks at 174 and 188 K are discussed in terms of coverage dependent reorientation and bilayers. Nonthermal excitation pathways by which the surface chemistry of biacetyl may be directed were explored by irradiating 1 ML of biacetyl with 50 eV electrons. During irradiation, CO, CH₃, ketene (H₂C=C=O), and C₂H₆ desorb. After irradiation, five new post-irradiation TPD peaks appear. These are identified as H₂ at 210 K, CH₄ at 235 and 315 K, H₂C=C=O at 240 K, and reaction-limited CH₃COCOCH₃ at 440 K. XPS shows C_(a) and O_(a) remain on the surface after heating to 700 K.

1. Introduction

Surface chemical reactions, initiated by thermal and nonthermal means, are of great scientific and technological interest. Thermal activation of surface reactions is by far the most widely studied and, in applications, the most widely used. Excited electronic states generally do not play a significant role in thermal excitation; as the system is heated, other processes, e.g., bond rearrangement through vibrational activation of the ground electronic state, generally intervene before significant electronic excitation takes place.

Exploration of electronically altered states is interesting and challenging and motivates the work described here. Photon and electron activation are initiated quite differently than thermally activated processes. For example, when visible and ultraviolet photon excitation of a molecule occurs, the light couples to the electronic coordinates of the molecular system and in the Franck-Condon description leaves the nuclear coordinates initially unaltered. Subsequently energy typically flows into these coordinates and drives bond rearrangements. Similar considerations apply to activation using electrons. By systematically varying the energy of the electrons or photons, the newly formed excited state configuration can be changed, and in principle, specific chemistry, not governed by thermal distributions, can be realized. Simply put, specific electronic states can be populated which are not significantly populated by heating. Beyond intrinsically interesting issues of excitation and energy flow, we have used electron excitation to prepare, selectively, spectroscopically significant concentrations of adsorbed species derived from molecular adsorbates, e.g., vinyl and phenyl.¹

As one component of extending to oxygenates previous work in our laboratory that involves nonthermal excitation of hydrocarbons and organic halides,² we have undertaken a series of experiments involving biacetyl, CH₃COCOCH₃, adsorbed on single-crystal silver, Ag(111). Other oxygenates under study include methanol,³ methyl formate,⁴ and acetone.⁵ Unless O_(a) is present, the low-temperature, ca. 100 K, adsorption and

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desorption of oxygenates typically occur with little or no dissociation on Ag(110) and Ag(111).^{3–8} In such cases, nonthermal excitation and subsequent reaction chemistry become obvious through the appearance of reaction products. For instance, acetone, CH₃COCH₃, on Ag(111) shows no thermal activation and, below 5 eV, no photon activation, but when irradiated with 50 eV electrons, adsorbed acetyl, CH₃C_(a)O,⁹ and methyl, C_(a)H₃, fragments form.⁵ Similarly, electron activation of methyl formate, CH₃OCHO, on Ag(111) leads to the formation of C_(a)H₃ and formate, O_(a)CHO.⁴ In this context, biacetyl is of interest because it offers the possibility of selectively forming adsorbed acetyl groups through nonthermal excitation.

Studied over many years in the gas phase and in solution, biacetyl exhibits rich, wavelength dependent photochemistry, breaking and making bonds, and photophysics, intersystem crossing from singlet to triplet states, and light emission from singlet and triplet states.^{10–19} To our knowledge, there have been no investigations of adsorbed biacetyl at the monolayer level on any substrate. There are two studies involving adsorbed multilayers. In the first, quenching of light emission from photoexcited adsorbed biacetyl was studied as a function of its distance from Ag(111), using an NH₃ spacer layer and 440 nm photons.²⁰ In the second study, multilayers of biacetyl on quartz and on silver films were irradiated with 266 nm photons; CH₃ and CH₃CO radicals were produced.²¹

This paper describes the results of two kinds of activation—thermal and electron. Thermal activation is chemically simple; low-temperature adsorption and subsequent thermal desorption occurs without dissociation. This is evidenced by ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS), work function change ($\Delta \Phi$), and temperature-programmed desorption (TPD). These results provide valuable benchmarks for electron-induced chemistry, reported here, and photon-induced chemistry to be reported elsewhere.²² Setting aside possible coverage variations, we focus on a single coverage, motivated by the observation that photon irradiation of this coverage causes decomposition and prompt ejection, but no retention at the surface, of fragments. As demonstrated here, there is retention and ejection of products

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under 50 eV electron excitation. Previously, we have identified impact ionization as the activation process leading to these products.²³

2. Experimental Section

All experiments were carried out in an ultrahigh-vacuum chamber described elsewhere.²⁴ Briefly, the chamber is equipped with a quadrupole mass spectrometer (UTI 100C) for temperature-programmed desorption and residual gas analysis (RGA) and a double-pass cylindrical mirror analyzer (PHI 15-255GAR) for Auger electron spectroscopy (AES) and photoelectron measurements. Excitation sources include a VG Instruments X-ray source for X-ray photoelectron spectroscopy and a differentially pumped helium discharge He I and He II source for ultraviolet photoelectron spectroscopy and work function changes. The chamber is pumped with an ion pump, an auxiliary titanium sublimation pump, and a 170 L/s turbo-molecular pump.

The typical base pressure during experiments was 1×10^{-10} Torr. Substrate temperatures were measured using a chromel– alumel thermocouple welded to a tantalum loop inserted into a hole drilled in the edge of the crystal. By attachment to a liquid nitrogen reservoir, the sample could be cooled to 110 K and heated resistively to 1000 K. The crystal was cleaned by cycles of Ar⁺ ion sputtering and annealing to 675 K until no impurities were detected by AES.

Since electrons from the mass spectrometer filament influenced the results and since our instrumentation did not allow biasing the sample during TPD, during thermal desorption the sample was rotated about 90° away from line-of-sight with respect to the mass spectrometer. XPS made use of Mg K α radiation at 1253.6 eV and an analyzer pass energy of 50 or 100 eV. XPS scan windows were 15 eV wide, and data collection time was typically 15 min. Core level binding energies were referenced to the Ag (3d_{5/2}) photoelectron peak centered at 367.9 eV (peak width at half-maximum, $\Delta E_{1/2}$, is 1.7 eV). Binding energy uncertainties are ≈ 0.3 eV. XPS curves were fit using a least-squares algorithm.²⁵

The purity of biacetyl (Aldrich Chemical Corporation, 97% pure) was verified by mass spectrometry after several freezepump-thaw cycles. It was dosed through a directed microcapillary array placed 0.5 cm from the sample. To dose, the biacetyl partial pressure was first increased, indicated $\Delta P = 4$ \times 10⁻¹⁰ Torr at the system ion gauge, with the sample turned away from the doser. After the pressure stabilized, the dose was initiated by rotating the sample in front of the doser for a measured time. To terminate the dose, the sample was turned away from the doser and the leak valve promptly closed. The exposures, as monitored by TPD, although very reproducible, are not known in langmuirs because there is a molecular flux enhancement of approximately 100 (with respect to background biacetyl partial pressure rise) when the surface is positioned in front of the doser. Dosing times are used as a reliable, but relative, measure of exposure. Biacetyl coverages are defined, as described in section 3, in terms of the saturation of a characteristic TPD peak.

For electron activation, we used the mass spectrometer filament. As measured by the CMA, the energy distribution peaked at 50 ± 1 eV, and the current from the sample to ground was $\approx 16 \,\mu\text{A} (1.0 \times 10^{14} \text{ electrons s}^{-1})$. Since the sample area is 1 cm², the electron flux becomes 1.0×10^{14} electrons cm⁻² s⁻¹. Lower energy electrons were generated by adjusting the filament voltage of the mass spectrometer. As the energy was lowered, the current tended downward; constant fluences were maintained by increasing the irradiation time. During electron



Figure 1. Temperature-programmed desorption of biacetyl, CH_3 -COCOCH₃, as a function of coverage, after dosing at 110 K on Ag(111). The 43 amu signal, the most intense cracking fragment of biacetyl, was followed. The curve marked 1 ML is, as described in the text, defined as 1 ML and based on XPS amounts to 4.3×10^{14} molecules cm⁻². The inset replots the 7.5 ML curve and, overlain with it, TPD for 20 ML.

irradiation, the sample was placed in line-of-sight with the mass spectrometer. The flux uniformity over the crystal was investigated by measuring the sample-to-ground current as a function of the angular position of the sample away from its line-ofsight position. The angle was varied using the rotary motion capability of the manipulator which moves the sample on a 2 in. radius circle with respect to the manipulator's axis of rotation. The electron flux varied by no more than 10% over an angular range three times larger than that subtended by the sample with respect to the axis of rotation. Reaction rates are discussed in terms of cross sections (section 3). The latter are upper limits, since primary electrons reflected from the sample or secondary electrons generated within the substrate are not properly counted.

Using 70 eV electrons, the fragmentation of gas-phase biacetyl in the ionizer of our mass spectrometer is dominated by three species: (1) 86 amu $(CH_3CO)_2^+$, the parent ion, (2) 43 amu (CH_3CO^+) , the result of breaking the central C–C bond, and (3) 15 amu (CH_3^+) , from breaking a terminal C–C bond. At the detector, these give the following fragmentation pattern–86 amu:43 amu:15 amu:22:100:42, in reasonable agreement with 15:100:35 reported for 70 eV electrons.²⁶ Typically, parent TPD spectra are characterized by following the 43 amu signal, since it is the most intense.

3. Thermal Chemistry

3.1. Biacetyl Adsorption and Desorption. During both adsorption at 110 K and subsequent TPD, there is no evidence for thermal decomposition of biacetyl; desorption mass spectra are fully accounted as parent biacetyl, and the substrate is clean, as judged by XPS, after heating to 300 K. This confirms conditions for which Ag(111) is inactive with respect to dissociation of biacetyl. For coverages ranging from submonolayer to multilayer, TPD spectra, Figure 1, were taken following the most intense ion fragment at 43 amu, CH_3CO^+ . The spectra have been corrected systematically for background and system pumping speed.²⁷ The coverages, marked on each curve, are based on defining the low-coverage saturated 180 K peak as 1

ML. The reasonableness of this assignment is established below on the basis of XPS results. Above 1 ML, the peaks are not readily resolvable into monolayer and multilayer contributions. As the biacetyl coverage increases, bottom to top in Figure 1, four desorption peaks are identifiable—(1) one peak up to 1 ML, 179-180 K, (2) a split pair, 178 and 185 K, at and above 1.5 ML, (3) a shoulder, 174 K, at 2 ML, and (4) an unsaturable peak setting in at about 183 K (>4.5 ML) and moving to 188 K at 20 ML. Focusing on the 7.5 ML case, the shoulder is at position (c), the multilayer at position (d), and the split pair at positions (a) and (b). Below (Figure 8) for a somewhat higher pumping speed, we also resolve a small peak at 215 K which is attributed to adsorption at defect sites, on the basis of adsorption after sputtering with no annealing (not shown) which gave a much more intense peak at 215 K. With the ML definition in mind and the thick multilayer established, we are left with two further assignments. At 1.5 ML there are two peaks; the lower temperature peak is assigned, as outlined below, to desorption from local regions where the number density is equivalent to that of the monolayer case, while the higher temperature peak is assigned to desorption from local regions where the number density is higher. Whether these two peaks involve reorientations of first-layer-adsorbed CH3COCOCH3 or bilayers of CH3COCOCH3 or some composite involving both cannot be fully resolved.

The inset shows the 20 ML data and a replot of the 7.5 ML case. It is of interest that the shoulder at 174 K disappears as the coverage increases suggesting restructuring of the whole adsorbate layer. The two curves are superimposable, except in the shoulder region. This is taken to indicate zero-order desorption kinetics away from the shoulder region. Assuming zero-order kinetics, analysis of the 20 ML curve from 177 to 185 K gives an activation energy of 75.6 ± 5 kJ mol⁻¹. There is one other multilayer system for comparison; biacetyl on Si(100) exhibits, for 5 ML, a peak at 190 K²⁸ which is in acceptable agreement with Figure 1.

With these thick multilayer results in hand, we turn to the low-coverage cases. When the difference between the 1 and 1.5 ML spectra is taken, the low-temperature peak at 180 K is preserved and the additional 0.5 ML coverage appears at higher temperatures. Compared to desorption of an initial coverage of 0.3 ML, the lowest curve in Figure 1, the desorption of the last 0.3 ML from an initial coverage of 1.5 ML occurs at measurably higher temperatures, ca. 6 K (179 vs 185 K). This strongly suggests that the 0.3 ML coverages have different structures in the two cases and, in turn, that passing from 1 to 1.5 ML at 110 K leads to restructuring of the entire adsorbate layer.

As for the inset data of Figure 1, these changes are subtle, have very little effect on the desorption activation energy, and are not analyzable further with TPD alone. As indicated below, XPS and UPS, while helpful, do not address these subtle changes. In all likelihood, changes of molecular orientation are involved. Characterizing them using coverage dependent intensity variations of infrared vibrational bands is planned.

The lowest coverages, 0.3 and 1 ML, are consistent with firstorder desorption with a slight amount of attractive adsorbate adsorbate interaction. The latter is evidenced in a very detailed analysis of the peak position, which increases ~ 2 K between 0.3 and 1 ML, and the peak shape which broadens on the hightemperature side. In passing from 0.3 to 1 ML, a model based on first-order kinetics with a coverage dependent activation energy gives no more than 11 kJ mol⁻¹ ML⁻¹ for the attractive interaction parameter. Thus, it is reasonable to use a first-order desorption model for analysis of the 1 ML TPD peak. On the



Figure 2. Biacetyl TPD peak area (mass 43) as a function of dose time. Biacetyl was dosed at 110 K after raising the background CH₃COCOCH₃ pressure to 4×10^{-10} Torr.

basis of the Chan–Aris–Weinberg method,²⁹ the calculated activation energy for desorption of 1 ML was 47 ± 5 kJ mol⁻¹.

To ascertain how the uptake varied with dosing time, we calculated the desorption peak areas in ML units and correlated them with the dosing time, Figure 2. The linear correlation over the full range of doses and TPD profiles shown in Figure 1 indicates a constant sticking coefficient, probably unity.

The multilayer peak is at a slightly higher temperature than the monolayer peak, perhaps indicating that biacetyl interacts more strongly with itself than with the silver surface. However, since the peak temperatures are separated by no more than 5 K, interaction energy differences are, at most, small. In fact, the small peak temperature difference may be due to changes in the preexponential factor. Several studies have observed similar behavior for molecular desorption peaks in such systems as SO₂/metals, C₆H₆/metals, and SF₆ on Ni(111).^{30–34}

In the monolayer regime, we suggest biacetyl adsorbs with both oxygen atoms toward the Ag(111) in an eclipsed conformation, thereby maximizing the oxygen lone-pair interactions with unfilled metal orbitals and minimizing the repulsion of the methyl groups with the surface. Gas-phase biacetyl exists in two conformers, eclipsed and trans, with a small barrier (20 kJ mol⁻¹) separating them.³⁵ At 300 K, the trans form is favored. The eclipsed geometry is intuitively favored for adsorption on Ag since it allows occupied lone pairs on both oxygen atoms to interact with unfilled orbitals on Ag.

3.2. X-ray Photoelectron Spectroscopy. XPS results are consistent with nondissociative adsorption and desorption of biacetyl. Only one O(1s) chemical state is observed—532.7 eV with a fwhm of 2.0 eV (Figure 3). This peak is typical of molecular carbonyl groups (Table 1). In passing from 1 to 24 ML, this peak width remains at 2.0 eV while the peak position shifts 0.4 eV higher, 533.1 eV, a typical shift for reduced core hole screening in thick multilayers. Similarly, the C(1s) spectra, Figure 4, shift higher by 0.3 eV. As expected, there are two distinct C(1s) peaks at all coverages, 285.2 and 288.1 eV, typical of molecular alkyl and carbonyl groups, respectively. These have equal intensities and widths, 2.0 eV, at all coverages, consistent with molecular adsorption. Using sensitivity factors for C(1s) and O(1s), the C-to-O ratio is 2.0 ± 0.1 over the range

 TABLE 1: Binding Energy Assignments for 1 ML

 Biacetyl/Ag(111)

C(1s)	0(1s)	ref
288.1	532.7	this work
285.2		this work
287.9		36
	532.7	37
284.7		36
	C(1s) 288.1 285.2 287.9 284.7	C(1s) 0(1s) 288.1 532.7 285.2 287.9 532.7 284.7

^{*a*} Atoms of interest denoted with boldface type. ^{*b*} Ph = phenyl.



Figure 3. O(1s) XPS for three coverages of biacetyl on Ag(111) at 110 K.



Figure 4. C(1s) XPS for three coverages of biacetyl on Ag(111) at 110 K; the O(1s) spectra in Figure 3 were taken at the same time.

of coverages shown in Figures 3 and 4. Importantly, when the adsorbate-substrate system was heated, all the C(1s) and O(1s) intensity disappeared by 300 K (not shown).

XPS peak areas, corresponding to the 1 ML assignment of Figure 1, were used to calculate the absolute coverage of biacetyl in molecules per square centimeter. XPS coverages are based on atomic iodine. CF₃I, which dissociates with ejection of CF₃, was dosed at 600 K to saturate the surface with iodine. A



Figure 5. He(II) UPS of 1 and 21.5 ML of biacetyl on Ag(111). The Ag substrate contribution has been subtracted out of the 1 ML, but not the 21.5 ML, spectrum. Molecular orbital assignments are: (a) $10a_g$; (b) $9b_u$; (c) $2b_g$, $2a_u$, $9a_g$; (d) $8b_u$, $8a_g$, $1b_g$; (e) $7b_u$, $1a_u$, $7a_g$; (f) $6b_u$; (g) $6a_g$; (h) $5b_u$, $5a_g$. Binding energies are given in Table 2.

TABLE 2:	UPS (He II)	Binding	Energy	Assignments	for	1
ML Biacetyl	/Ag(111)					

assignments	1 ML biacetyl/ Ag (eV)	multilayer biacetyl/ Ag (eV)	gas-phase ref—4.4 eV ^a (eV)
$10a_{g}(n_{O+})$	4.5	4.3	5.2
$9b_{u}(n_{O-})$	6.5	6.4	7.1
$2b_{g} (\pi_{CO-})$	8.1	8.0	8.2-9.6
$2a_u(\pi_{CO+})$			
9ag			
$8b_u, 8a_g, 1b_g$	9.5	9.4	10.1 - 10.8
$7b_u, 1a_u, 7a_g$	10.6	11.0	11.6-12.1
6b _u	11.5	11.9	13.0
6a _g	15.1	15.2	16.2
$5b_u, 5a_g$	18.4	19.7	19.6

^{*a*} Gas-phase spectra adjusted to the Fermi level of the 1 ML/Ag(111) spectrum. Add 4.4 eV to obtain their gas-phase values referenced to the gas-phase vacuum level.

saturation coverage of iodine results in a ($\sqrt{3} \times \sqrt{3}$)-R30° packing arrangement on Ag(111) corresponding to a I/Ag ratio of ¹/₃ or a coverage of 4.6 × 10¹⁴ atoms cm⁻².³⁸ This calibration was used, in conjunction with known atomic sensitivity factors and the measured C(1s) and O(1s) peak areas of 1 ML CH₃-COCOCH₃, to calculate that 4.3 × 10¹⁴ molecules cm⁻² comprise monolayer biacetyl. This is a very reasonable result; if one uses biacetyl's liquid-phase density and approximates biacetyl molecules as cubes, a monolayer would contain 3.6 × 10¹⁴ molecules cm⁻².

3.3. Ultraviolet Photoelectron Spectroscopy. To probe the valence orbitals of adsorbed $CH_3COCOCH_3$, ultraviolet photoelectron He(II) spectra were taken for 1 and 21.5 ML (Figure 5). The Ag contribution to the 1 ML, but not the 21.5 ML, spectrum was subtracted, and Fermi level referencing was utilized. Adsorbate-derived signals are clearly evident in both cases, and on the basis of gas-phase biacetyl UPS data,³⁹ orbital assignments (Table 2) are indicated by lower case letters and vertical lines. The gas-phase orbital energies, measured with respect to the vacuum level, have been shifted by 4.4 eV to reference them to the Fermi level of the adsorbate system. Consistent with the TPD and XPS results, there is nothing in

either of these spectra that is not readily attributable to adsorbed CH₃COCOCH₃.

In passing from the multilayer to the monolayer, there is evidence of modest differential shifting in peaks (a), (e), and (h). Such differential shifts are generally attributed to coverage dependent variations of the coupling of the particular orbitals to the substrate, in either or both the initial and final states. That the shifts in the highest lying valence orbitals are, at most, small is taken as further evidence of very weak interactions between CH₃COCOCH₃ and Ag(111). Referring to Table 2, orbital (a) at 4.5 eV for 1 ML is derived from the $10a_{g}(n_{O+})$ orbital of CH₃COCOCH₃, commonly referred to as a lone-pair orbital strongly localized on a carbonyl oxygen. The 0.3 eV shift of orbital (a) to lower binding energy (BE) between 1 and 21.5 ML is opposite the expectations for final state relaxation variations and is, thus, attributed to a small initial state variation consistent with a low-coverage adsorption model in which the two oxygens of CH₃COCOCH₃ are both weakly linked to Ag(111), i.e., CH₃CO_(a)CO_(a)CH₃. The shifts in orbitals (e) and (h) to higher BE with coverage is consistent with final state relaxation effects.

3.4. Work Function Change. One monolayer of biacetyl lowers the work function of Ag(111) by 0.3 eV. The lowered work function is consistent with a shift of electron density from CH₃COCOCH₃ toward Ag(111) as anticipated for the adsorption model proposed above.

4. Electron-Induced Chemistry

4.1. Overview of Electron-Driven Processes. While no surface reactions of $CH_3COCOCH_3$ on Ag(111) occur thermally, electron irradiation leads to a number of products, some of which are ejected during irradiation and others which are retained and contribute to products that desorb during TPD. The results are not describable by a single pathway, and because of this complexity, we introduce this section with an overview of our proposed reaction path model. As noted already in the Introduction, the focus is on 1 ML coverage because, unlike photon-driven chemistry of 1 ML, products of electron irradiation are retained. Examination of coverage variations, below and above 1 ML, is postponed for future work.

In schematic form, Figure 6 accounts for the observed products and outlines the proposed paths leading to them. During electron irradiation, relatively large amounts of CH₃ and CO are ejected along with smaller amounts of ketene $(CH_2=C=O)$ and C_2H_6 . These products demand that electron activation leads to both C-C and C-H bond breaking. Since the cross section for loss of biacetyl is negligible for energies below its ionization potential (9.55 eV),⁴⁰ the dominant activation mechanism is the impact ionization of biacetyl.²³ In subsequent TPD, CH₄, H₂, CH₂CO, and CH₃COCOCH₃ are observed. To account for these products and their peak temperatures, our model includes the retention of CH_{3(a)}, H_(a), CH₃C_(a)=O, C_{x(a)}H_y, and CH₂C-O_(a)C=OCH₃. While there is evidence for rehybridization of carbonyls to form species with the O bound to Ag and a C-O single bond, there is no evidence for electron-induced complete fragmentation of the carbonyl to give adsorbed atomic O. Between 500 and 700 K, atomic forms of C and O remain (<8% of the initial amounts) according to XPS; this implies some C–O bond breaking during TPD.

4.2. Ejection during Electron Irradiation. Having summarized our model, we turn our focus to those species which desorb during irradiation. In a very interesting set of experiments, denoted isoscans, we adsorbed 1 ML of biacetyl, held the temperature at 110 K, and monitored desorbing products during electron irradiation. After dosing, the sample was biased -90 V to repel electrons and then rotated in front of the electron



Figure 6. Overview of the proposed chemical reaction paths beginning, at the top, with 50 eV electron irradiation of 1 ML biacetyl molecularly adsorbed on Ag(111) at 110 K. Products ejected into the gas phase are indicated to the upper right, and products retained as adsorbates at 110 K are indicated beneath, in the second Ag(111) depiction. Subsequent TPD results are depicted further down the figure. The temperature range is arbitrarily divided into two segments, below and above 300 K. There is no detectable desorption above 500 K, but C and O are retained, at least to 700 K. Biac and ac denote biacetyl and acetyl, respectively.



Figure 7. Desorption during isothermal 50 eV electron irradiation of 1 ML biacetyl at 110 K. Desorption products are CO, CH₃, CH₂=C=O, and C₂H₆. The sharp rises and falls in the data are due to switching the electron irradiation on and off by unbiasing and biasing the sample -90 volts, respectively.

source. After the background pressure in the chamber was allowed to stabilize, the isoscan was started (Figure 7). After 60 s, the bias was removed and the sample grounded, allowing 50 eV electrons to strike the sample. After another 60 s, the

bias was again applied to stop the electron-stimulated desorption. This cycle was repeated for 10 min. The isoscans have contributions at 12, 13, 14, 15, 16, 28, 30, and 42 amu, but importantly, there is no contribution at either 86 or 43 amu, i.e., no electron-stimulated parent desorption. A blank experiment repeated the 10 min measurement with the -90 V bias constantly applied. The resulting background signals were subtracted, and Figure 7 shows the results for 15, 28, 42, and 30 amu. The prompt on-off character and the fact that the second (third) exposure begins with the intensity measured at the end of the first (second) exposure indicate that no detectable reaction occurs when the electron beam is off. We conclude that thermal effects do not make a significant contribution; the thermocouple temperature increased by no more than 2 K. This data is satisfactorily described by first-order decay; the resulting cross sections are presented below.

We attribute the observed masses to four desorption products: CH₃, CO, ketene (CH₂=C=O), and C₂H₆. The CH₃ and CO signals dominate, and the CH₃ signal is 1/4 that of CO. Ketene, identified on the basis of a literature standard fragmentation pattern, is ≈ 50 times smaller than the CO signal. The 30 amu signal, barely discernible above the noise, is ≈ 100 times smaller than the CO signal and is attributed to C_2H_6 . Other ion signals, expected for C_2H_6 fragmentation (26–29 amu), are not discernible above background. After subtracting the contribution of ketene to mass 14, the remaining intensity for masses 12-15 is attributed mainly to CH3 desorption. But since the cracking pattern for CH₃ is not known for our system, we cannot rule out a minor contribution from CH₂. Ketene (mass 42) desorption gives rise to some of mass 14 and all of mass 42. CO desorption accounts for all of mass 28 and most, if not all, of mass 16, when the cracking pattern of CO is taken into account. Consequently, although a small amount of methane desorption cannot be ruled out during electron irradiation, it is, at most, a very minor product. That methane does not make a significant contribution is confirmed by the fact that the mass 15 intensity exceeded that for mass 16 by a factor of 4. Methane gives a cracking ratio for 15/16 amu of ≈ 0.85 .

CH₃ and CO ejection require electron-induced C–C bond breaking in adsorbed CH₃COCOCH₃. There are two possible pathways. First, the central C–C bond of biacetyl could be broken through irradiation, and the resulting acetyl group might decompose into CH₃ and CO. One might then, contrary to observation, expect to see acetyl fragments, 43 amu, desorb during electron irradiation. The second possibility, favored because 43 amu fragments are retained, is electron-induced cleavage of one of the terminal C–C bonds to promptly eject CH₃. CO ejection would then arise from prompt decomposition, just before or just after neutralization of the resulting adsorbed CH₃CO–CO⁺ fragment. This decomposition step forms CO, which will not adsorb to Ag(111) at 110 K,⁴¹ and adsorbed acetyl, CH₃C_(a)O.

The only other ejected products, small amounts of C_2H_6 and CH_2CO , are attributed to reaction of two CH_3 fragments and to electron-induced C-H bond breaking followed by cleavage of the central C-C bond in $CH_2CO_{(a)}COCH_3$. As depicted in Figure 6 and discussed below, there is evidence that both $C_{(a)}H_3$ and $CH_2CO_{(a)}COCH_3$ play important roles in the subsequent TPD.

From the time dependence of the decay of ion signals like those of Figure 7, cross sections were calculated. The data (not shown) was generated using the following procedure: (1) a monolayer of biacetyl was adsorbed at 110 K, (2) the sample was biased -90 V and rotated in front of the mass spectrometer, (3) after allowing the background to stabilize, a multiplexed



Figure 8. Post-irradiation TPDs of 1 ML biacetyl (43 amu signal) for increasing, top to bottom, exposures to 50 eV electrons.

isoscan was started with the bias applied, and (4) after 60 s, the bias was removed for the rest of the scan, 600 s. Assuming the electron stimulated desorption reactions are first order, the following equation can be used to obtain the cross section, σ

$$\ln\{\Delta P_{x(g)(t)} / \Delta P_{x(g)(0)}\} = -\sigma F_{e}$$
(1)

where $\Delta P_{x(g)(0)}$ is the intensity attributed to the initial pressure of species *x* and $\Delta P_{x(g)(t)}$ is the intensity attributed to the pressure of species *x* at time t.⁴² F_{e} is the fluence of electrons irradiating the sample. The calculated cross sections for CH₃ and CO desorption were both $(3.4 \pm 0.3) \times 10^{-17}$ cm², that for ketene was $(4.1 \pm 0.6) \times 10^{-17}$ cm², and that for ethane was $(3.0 \pm 0.6) \times 10^{-17}$ cm². The uncertainties for ketene and ethane are larger due to the small amount of product desorbing (see Figure 7).

4.3. Loss of Parent TPD Signal. Another view is obtained by examining, for a series of experiments, how the parent TPD peak area decays with electron exposure. From this decay, a cross section was calculated for the total loss of biacetyl by all active channels, i.e., desorption of species plus retention of decomposition products. Post-irradiation TPDs for the desorption of biacetyl (mass 43) are shown in Figure 8 for numerous electron fluences. Clearly, the 180 K peak decays rapidly. At large fluences, a tiny biacetyl peak appears at 440 K (not shown). It is not due to unreacted biacetyl molecules and, therefore, is not considered in the following discussion. The cross section for total loss of biacetyl was calculated from

$$\ln\{I(t)/I(0)\} = -n\sigma(E)t = -(i_e t/eA)\sigma(E) = -F_e\sigma(E) \quad (2)$$

where I(t)/I(0) is the ratio of the biacetyl TPD peak areas before and after irradiation time *t*, *i*_e is the current density (A/cm²), *A* is the sample surface area, *e* is the electron charge, and *F*_e is the electron fluence (electrons/cm²).⁴³

As shown in Figure 9, the resulting slope is not constant with respect to electron fluence; the cross section drops as the fluence increases. An adequate fit is realized with two lines, i.e., two cross sections— $(8.0 \pm 0.2) \times 10^{-17}$ cm² and $(4.0 \pm 0.2) \times 10^{-17}$ cm². The decline is attributed to the accumulation of products which begin to inhibit the electron-driven decomposition of the remaining biacetyl for fluences greater than 1 ×



Figure 9. Semilogarithmic plot of the fractional decrease in 1 ML biacetyl (mass 43) TPD peak area as a function of electron fluence. The indicated cross sections for removal of biacetyl were calculated from the slopes.

 10^{16} electrons cm⁻². Interestingly, the smaller cross section is comparable to those, as outlined above, that describe the electron-initiated ejection of products. However, the total initial cross section for destruction of biacetyl is twice as large. This implies the reactions leading to adsorbed fragments are inhibited as the surface becomes cluttered with decomposition products, but the ejection reactions continue on with the same cross section.

4.4. Thermal Reactions of Species Retained after Electron Irradiation. This section deals with desorption after 1 ML of biacetyl was irradiated with 50 eV electrons. Consistent with our model, there is evidence for electron-induced C-C, C-H, and possibly even minor amounts of C=O bond breaking. Several major desorption channels appear in the post-irradiation TPD spectra. These products are identified as: H₂ between 210 and 230 K, ketene (H₂C=C=O) at 240 K, methane at 235 and 315 K, and reaction-limited biacetyl desorption at 440 K, Figure 10. Figure 11 summarizes the desorption areas as a function of fluence.

In the biacetyl desorption plots, (Figure 8), interesting features include: (1) the parent desorption temperature decreases from 180 to 174 K with increasing electron fluence, (2) the defect-site peak temperature (215 K) increases to 230 K with increasing fluence, and (3) indicative of defects inhibiting biacetyl's reactions with electrons, the defect-site peak decays approximately four times slower than the decay of the 1 ML peak.

The mass 42 desorption state at 240 K was identified as ketene. No higher mass ions (>42 amu) were observed at 240 K, and all detected ion intensities are in accord with the cracking fragments of gas-phase ketene. Further support for assignment to ketene is found by subtracting from the mass 14 peak the expected contribution from methane. The remaining area for mass 14 is in a ratio with mass 42 that is consistent with ketene desorption at 240 K.

In the region where mass 42 peaks, masses 15 and 16 also peak, with maxima at 235 K, Figure 10. When the area for desorption of biacetyl from defect sites is taken into account, the 15 and 16 amu peak areas are in the correct ratio for methane desorption. The peak at 315 K is also attributed to methane



Figure 10. Post-irradiation experiment on 1 ML of biacetyl adsorbed at 110 K and irradiated with 6.4×10^{16} electrons cm⁻². Proposed reactions leading to desorption of each peak are listed to the side of the plot. Biac = biacetyl, and H_(ac) = a hydrogen from the dehydrogenation of an acetyl group.



Figure 11. Accumulation of post-irradiation TPD products as a function of increasing electron fluence. These plots are each normalized to unity at the maximum. The mass 16 (total) curve combines the peak areas for both the 235 and 315 K desorption states.

desorption on the basis of fragmentation ratios. No masses higher than 16 were observed in the 315 K region of the TPD spectra. Since methane does not adsorb on silver at 110 K, it must form through a rate-determining surface reaction for both peaks in Figure 10. Another interesting point is the peak at 315 K is larger than the 235 K peak. Since both peaks are attributed to the same desorption species, this indicates that the concentration of species leading to the 315 K desorption channel is higher than for the 235 K channel.

At 440 K, only peaks for masses 15, 43, and 86 were observable in the TPD spectra. The cracking ratios for each of these peaks follows what is expected for biacetyl. However, since adsorbed biacetyl desorbs below 300 K, the desorption state at 440 K is attributed to the reaction-limited desorption of biacetyl; i.e., surface fragments assemble to form biacetyl.

The H₂ desorption spectra at different electron fluences (Figure 12) is intriguing. At low electron fluences the peak maximum is at 210 K. With increasing fluence, 5.3×10^{16} electrons cm⁻², the peak shifts higher in temperature to 230 K. Finally, at a fluence of 6.8×10^{16} electrons cm⁻² the peak maximum is once again at 210 K. This indicates the chemistry of H₂ desorption is complex and possibly involves several desorption channels, as does our model (Figure 6).



Figure 12. Post-irradiation TPD of dihydrogen (mass 2) for several electron fluences.



Figure 13. C(1s) post-irradiation XPS anneal series of 1 ML biacetyl on Ag(111) at 110 K with 6.4×10^{16} electrons cm⁻². The "dose" spectrum was taken after dosing one monolayer. The "irrad." spectrum was taken after irradiation. For each subsequent spectrum, the sample was flashed to the indicated temperature on the plot and then taken after the sample cooled back to 110 K.

As shown in Figure 11, all the TPD peak areas, normalized to their maxima, rise smoothly with increasing electron fluence. Assuming first-order kinetics, the cross section for accumulation of these products is $(2 \pm 1) \times 10^{-17}$ cm².

Figure 10 shows proposed reactions leading to TPD products. These reactions involve the species produced by impact ionization, Figure 6; CH₃, H, CH₃C_(a)=O, and CH₂C $-O_{(a)}$ C=OCH₃ are the major products. Surface hydrogen made during irradiation was expected, as observed, to recombine and desorb below 210 K.⁴⁴

The desorption peak for methane (mass 16) at 235 K is attributed to two pathways, one of which is $CH_{3(a)}$ species combining with surface H formed during irradiation. Other proposed reactions include the dehydrogenation of acetyl groups



Figure 14. O(1s) post-irradiation XPS anneal series of 1 ML biacetyl on Ag(111) at 110K with 6.4×10^{16} electrons cm⁻². The "dose" spectrum was taken after dosing one monolayer. The "irrad." spectrum was taken after irradiation. For each subsequent spectrum, the sample was flashed to the indicated temperature on the plot and then taken after the sample cooled back to 110 K.

TABLE 3:Binding Energy Assignments for 1 MLBiacetyl/Ag(111)+Electrons

species ^a	C(1s) exptl (eV)	0(1s) exptl (eV)	C(1s) ref (eV)	0(1s) ref (eV)	ref
C=O (biacetyl)	288.1	532.7			this work
C=O (EID products) ^{b}	286.9	531.8	286.4	532.0	47
=C $-$ O $-$ Ag (EID products)	286.9	530.1	287.2	530.5	48, 49
-CH ₃	285.2		285.0		47
$-CH_2$			284.7		50
С-О-С		533.6		533.4	51
C _(graphitic)	284.3		284.3		52
carbide	283.2		280.8		50
			-282.8		

^{*a*} Atoms of interest denoted with boldface type. ^{*b*} EID = electroninduced decomposition.

to produce ketene and surface hydrogen. Indications for this part of our model include: (1) evidence for the production of ketene by the dehydrogenation of acetyl groups is also found in the 50 eV electron irradiation of acetone/Ag(111);⁵ (2) since all surface hydrogen produced by irradiation should have desorbed by 210 K,44 the peak area above 210 K and extending to 260 K in the H₂ desorption spectra is attributed to recombination of hydrogen atoms made by the loss of hydrogen from $C_r H_v O_z$ groups, e.g., acetyl; (3) because no surface hydrogen produced by irradiation should remain on the surface above 210 K, the desorption peak for methane (mass 16) at 235 K is attributed to CH3(a) species combining with H atoms formed by dehydrogenation of acetyl fragments to desorb as methane; (4) since 1 ML ketene desorbs at 120 K,⁴⁵ the ketene (mass 42) desorption at 240 K must be due to a reaction-limited step; (5) indicative of multiple reaction products having the same ratelimiting step, i.e., the dehydrogenation of acetyl groups, methane (mass 16), ketene (mass 42), and hydrogen (mass 2) desorption tails end at 260 K.

Above 260 K, no $CH_{3(a)}$ groups remain on the surface. If they did, recombination of methyl groups would lead to ethane desorption at 273 K.⁴⁶ As the sample is heated further, some of the remaining hydrocarbon species decompose to produce

 TABLE 4:
 XPS Peak Area Ratios of C and O Left on the Surface by Chemical State (Normalized to Initial Amount of C and O on the Surface)

original C remaining			original O remaining						
peak positions	283.2	284.3	285.2-285.0	286.9	288.1	530.1	531.8	532.7	533.6
dose at 110 K	0	0	0.51	0	0.49	0	0	1	0
irradiation at 110 K	0.13	0	0.39	0.13	0.14	0.17	0.33	0.27	0.05
200 K	0.13	0	0.32	0.16	0.08	0.17	0.35	0.12	0.06
275 K	0.08	0	0.33	0.15	0	0.26	0.27	0	0.02
350 K	0.06	0	0.27	0.14	0	0.25	0.24	0	0.06
700 K	0	0.05	0	0	0	0.04	0	0	0.04

 TABLE 5:
 XPS Peak Area Ratios of C and O Lost during Irradiation and Subsequent Anneals

C/O ratio of desorbing species
2
1.9
1.8
only C desorption
1.7

more methane at 315 K. Finally, at 440 K, $CH_2C-O_{(a)}C=OCH_3$ scavenges a hydrogen atom from other decomposition species remaining on the surface to desorb as biacetyl. After this occurs, heating to 700 K leaves, as shown by XPS, small amounts of atomic carbon and oxygen (<8% of the initial amounts).

Future studies are planned to examine the effects of the initial coverage of biacetyl on the post-irradiation TPD product distribution; in particular, the relative amounts of methane and ketene desorption at 240 K may provide insight into whether there is a situation in which the C–C bond between the carbonyl groups is preferentially cleaved. Since signal-to-noise is an issue when there are many decomposition pathways and very little starting material, submonolayer studies are postponed here.

4.5. Post-irradiation XPS. XPS supports the argument that the post-irradiation desorption products are ketene, methane, and reaction-limited biacetyl. After irradiation of 1 ML of biacetyl with $6.4 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$, an XPS anneal series, Figure 13 and 14, was undertaken. The sample was heated to a selected temperature and cooled to 110 K, and XPS was acquired. Except for the 700 K spectra acquired at 100 eV pass energy because of the low intensity, all spectra were acquired using 50 eV pass energy and were fit with features having a fwhm of 2.0 ± 0.1 eV using a curve-fitting routine with an 85% Gaussian/Lorentzian mixture. The 700 K spectra were fit with a fwhm of 3.8 eV in the oxygen region and 3.2 eV in the carbon region.

The spectra, immediately after irradiation, are adequately fit with four carbon (283.2, 285.1, 286.9, and 288.1 eV) and four oxygen chemical states (530.1, 531.8, 532.7, and 533.6 eV). The chemical assignments are summarized in Table 3. Surface carbide (283.2 eV) indicates some multiple-bond breaking initiated by electrons. Upon heating to 200 K, loss of biacetyl occurs in TPD, and in agreement, the C(1s) intensities at 285.2 and 288.1 eV and O(1s) at 532.7 eV decline. Quantitation of the peak areas is given in Table 4. Moreover, the intensity lost is consistent with removal of two carbons for each oxygen, as expected for biacetyl. Table 5 includes the average C/O ratios for the material removed in successive anneals. In the second anneal, 275 K, the 288.1 eV C(1s) and 532.7 eV O(1s) peaks become negligible, consistent with complete removal of molecular biacetyl. Accompanying this loss, the 531.8 eV O(1s) intensity, assigned to C=O in an acetyl group, decays, while the 530.1 eV signal, assigned to O singly bound to both C and Ag, increases. At the same time, there is as slight downward shift (0.2 eV) of the 285.2 eV C(1s) peak. To account for these XPS changes and the desorption of ketene, we propose a surface reaction in which acetyl groups react to form ketene, which

 TABLE 6:
 XPS Peak Area Ratios of C and O Left on the Surface

	C/O ratio of remaining species	original C remaining	original O remaining
dose at 110 K	1.9	1.0	1.0
irradiation at 110 K	1.8	0.81	0.82
200 K	1.8	0.69	0.71
275 K	1.8	0.56	0.56
350 K	1.6	0.48	0.55
700 K	1.1	0.05	0.08

desorbs, and $CH_2=C-O_{(a)}C=OCH_3$, which leads to the high-temperature biacetyl desorption.

Upon annealing to 350 K, O(1s) does not change but the C(1s) intensity drops, consistent with CH₄ desorption. At 350 K, remaining O(1s) and C(1s) signals are consistent with some CH₂=C-O_(a)C=OCH₃. After heating to 700 K, only small broad C(1s) and O(1s) signals remain consistent with desorption of reaction-limited biacetyl desorption at 430 K and retention of some atomic C and O. We propose that the CH₂=C- $O_{(a)}$ C=OCH₃ species in our model acquires a hydrogen atom from one of the hydrocarbon-containing species left behind on the surface and desorbs as biacetyl.

Table 6 lists the C/O ratios at the surface for various conditions. Columns 3 and 4 of Table 6 give the fraction of the initial amounts of C and O that remain after various treatments. According to the interpretation given in the previous paragraph, the biacetyl recombination channel contributes more than a third of the total retained reaction products. This is consistent with TPD.

Flashing the sample to 700 K leaves a small amount of carbon (5% of the initial amount) and a comparable amount of oxygen on the surface. Since atomic oxygen by itself would recombine and desorb between 490 and 550 K,^{53,54} it is interesting that a small amount of oxygen remains to 700 K. No O₂ desorption is observed in our TPDs as we annealed from 350 to 700 K. There appear to be two states in the O(1s) spectrum at 700 K, both involving oxygen bound to carbon. One is assigned to C-O-C bonding, and the other to C-O-Ag species. The carbon remaining is, on the basis of the measured BE, graphitic in nature.⁵²

To make sure the remaining carbon and oxygen signals in the XP spectra were not due to background adsorption during the anneal series and/or X-ray-induced decomposition of biacetyl over extended periods of time, the sample was sputtered clean and annealed. One monolayer of biacetyl was then dosed and held for the same time used in the electron irradiation experiments, but with the electrons off. The sample was then flashed immediately to 700 K. No C or O was detected; i.e., the spectra were not distinguishable from the clean spectra 13 and 14.

4.6. UPS and Work Function Changes. Following the same annealing procedure, UPS shows changes in intensity and energy distribution consistent with the above model. Because there are a number of adsorbed species contributing, these valence band spectra are not analyzable in terms of species present. After heating to 700 K, the UPS spectrum is dominated

by Ag-derived features, but the influence of impurities, i.e., C and O, is evident in the non-negligible alteration of the Ag d-band region. After annealing to 700 K, the work function was, however, indistinguishable from that of clean Ag(111).

5. Conclusions

One monolayer biacetyl adsorbs at 110 K and desorbs molecularly on Ag(111) at 180 K. Fifty-electronvolt electron irradiation of biacetyl leads to the breaking of C-C and C-H bonds with very little, if any, electron-induced formation of atomic oxygen. Consequently, our model includes CH₃, H, CH₃C=O, CH₂=C=O, CO, and CH₂C $-O_{(a)}$ C=OCH₃ as the major reaction products (shown more fully in Figure 6). Ejection of CO, CH₃, ketene (CH₂=C=O), and ethane into the gas phase occurs during irradiation. CO and CH₃ are the major desorption species. No parent desorption is observed during irradiation. We propose that impact ionization leads to the cleavage of the H₃C-CO bond and prompt desorption of CH₃, leaving an excited -COCOCH3 species which decomposes to form acetyl and CO fragments, the latter desorbing. After irradiation, there is evidence for the following adsorbed species: CH₃, H, CH₃C=O, and CH₂C-O_(a)C=OCH₃. We propose two reaction pathways for the methane desorption peak at 235 K: (1) the CH₃ group combines with H which was formed on the surface during irradiation by the breaking of a C-H bond in biacetyl, and (2) the methyl fragment recombines with a hydrogen atom from the dehydrogenation of an acetyl group and, consequently, results in desorption of ketene and CH₄. Ketene desorption at 240 K supports this claim. Methane desorption at 315 K is attributed to decomposition of $C_x H_y O_z$, a process that leaves $C_{(a)}$ and $O_{(a)}$; the O(1s) XPS intensity does not change when this CH₄ desorbs. Finally, some partially dehydrogenated biacetyl fragments rehydrogenate by scavenging H from the remaining hydrocarbon species and desorb at 440 K as biacetyl. This leaves only minor quantities, $\leq 8\%$ of original amounts, of adsorbed C and O up to 700 K.

Further investigations are underway to examine biacetyl adsorption geometries by FTIR, the variation, with initial biacetyl coverage, of the electron-induced products, and the photon-induced chemistry of adsorbed biacetyl.

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