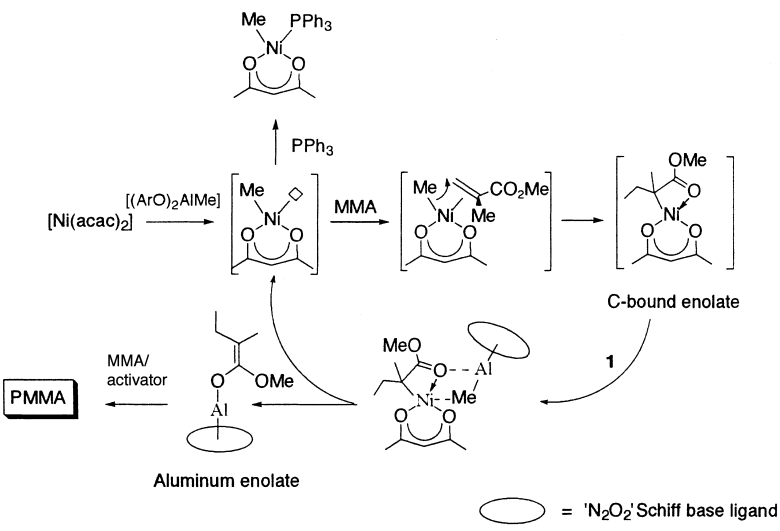

Scheme 1. Postulated mechanism for the role of nickel in the catalyzed formation of aluminum enolates.

additional equivalent of MMA binds to the nickel center, possibly in place of the carbonyl group (Scheme 1). To account for the catalytic dependence of the reaction on $[Ni(acac)_2]$ and the fact that the polymerization is centered at the $Al(\textit{t}Bu_4salen)$ component, transfer of the enolate from nickel to aluminum with concomitant transfer of the methyl group from aluminum to nickel is proposed (Scheme 1). This generates the active aluminum enolate species for polymerization and reforms the "[Ni(acac)Me]" catalyst. In a separate study we have successfully synthesized the aluminum enolate species, $[Al(\textit{t}Bu_4salen)\{OC(O\textit{t}Bu){=}CMe_2\}]$, and shown that this is an efficient initiator for MMA polymerization. These results will be reported in due course.

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# Reactive Intermediates on Metal Surfaces: A Ketene Monolayer on Single Crystal Platinum Generated by Photolysis of Pyridyl α-Diazoketones[**]

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Peter R. Norton, and Mark S. Workentin*

There is considerable current interest in understanding the chemistry of organic molecules as monolayers (saturated layer) on metal surfaces. Much of the effort in this regard has focused on long-chain alkyl thiols or disulfides on gold with

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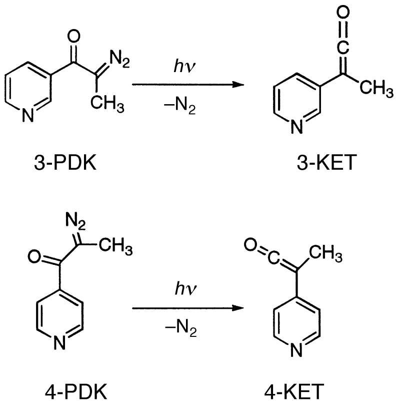
the ultimate goals of being able to control the interfacial properties for use in wide ranging material and device applications.[1] In contrast, examples of chemistry of smaller organic molecules as monolayers on metal and other electronic materials has not been as widely examined, although there is a large area of science which is directed at the adsorption of small molecules on metal surfaces. Our group's interest is in the study of photochemical reactions of molecules confined to metal surfaces and comparison of this reactivity to solution- and solid-phase transformations to try to gain a better understanding of the factors that control the reactions of organic molecules in these uniquely constrained environments. Considering the enormous amount of work in the area of self-assembled monolayers of long-chain alkyl thiols on gold, there are remarkably few studies reported on the photochemistry of these types of systems.[2–8] Examples of photochemical conversions of small organic molecule monolayers chemisorbed on metal surfaces remains virtually unexplored,[9–12] although photochemical conversions on semiconductor surfaces has led to many important discoveries.



Pyridine and substituted pyridines are a class of compounds that are known to form monolayers on platinum metal and their spectroscopic and electrochemical properties have been investigated in some detail.[13–18] Here we report the characterization of 3- and 4-substituted pyridyl $\alpha$-diazoketones (3-PDK and 4-PDK, respectively) as stable monolayers on single crystal platinum (Pt (110)) using ultra high vacuum (UHV) reflection absorption infrared spectroscopy (RAIRS). Furthermore, photolysis of these monolayers by irradiation at wavelengths of 300–400 nm releases molecular nitrogen to yield a pyridylketene functionality (3- and 4-KET) at the interface through a photo-Wolff rearrangement.[19] The IR spectroscopy of ketenes generated photochemically has been studied extensively in cryogenic matrices[20] and by laser flash photolysis with time-resolved-infrared detection.[21] To the best of our knowledge there is no example of the formation of a stable ketene generated photochemically on a metal surface, although small amounts of ketene itself have been observed by RAIRS on a metal surface through the thermal decomposition of acrolein.[22] Thus, this study represents the first direct spectroscopic evidence of a platinum surface modified with a photoreactive $\alpha$-diazocarbonyl monolayer and the subsequent selective formation of a stable ketene functionality in this type of environment. Diazocarbonyl and ketene functionalities have versatile reactivities and has very significant application in research and technology;[23, 24] we believe that knowledge of the interfacial reactivity in the present systems can be extended to provide a novel surface for template synthesis and modifications.

The diazoketones 3- and 4-PDK were synthesized by diazotization, using diazoethane, of the corresponding pyridoyl chlorides. Single crystal Pt (110) ($1 \times 2$ reconstructed) was prepared and cleaned in a manner previously described and mounted in a UHV system equipped with an FTIR spectrometer, a quadrupole mass spectrometer, an Auger spectrometer with 3-grid retarding field analyzer for low-energy electron diffraction (LEED), a focused UV/Vis Hg-Xe arc lamp light source, and appropriate dosers.[25] Monolayers of 3-PDK and 4-PDK were prepared by first dosing the clean Pt surface at 160 K to exposures corresponding to tens or even hundreds of monolayers. The resulting multilayer was then thermally desorbed by raising the temperature at 3 $\mathrm{K\,s^{-1}}$. The maximum rate of desorption occurred at 263 K as determined by temperature programmed desorption (TPD) studies of masses indicative of the pyridyl substrates, namely $m/z$: 161 ($M^+$), 105 ($C_7H_7N^+$), and 78 ($C_5H_4N^+$). No further desorption of these high mass ions was observed at higher temperatures following desorption of the multilayer at 263 K. We infer from this that the remaining monolayer (saturated layer) could not be desorbed thermally before its decomposition at approximately 370 K. Thermal decomposition of the monolayer was determined by monitoring the release of $N_2$ ($m/z$: 28) from the surface. Dosing at low temperatures was used to ensure a high coverage, which is known to favor binding of the pyridyl nitrogen atom to Pt over an orientation where the aromatic ring lies flat on the surface.[14–16] A second method for monolayer preparation consisted of dosing the clean Pt surface at 283 K, where multilayers do not form. This method yielded identical RAIR spectral features (see below) to that observed for monolayers produced by low temperature absorption followed by desorption of the multilayer. No CO signals are observed in the IR spectrum when the saturated layer was exposed to carbon monoxide, which indicates there are no available sites on the metal for its absorption.

Figure 1 shows the RAIR spectra of 3-PDK and 4-PDK on clean Pt (110) prepared using the second method and the corresponding transmission IR spectra for solutions of 3- and 4-PDK in $CCl_4$. The remarkable similarity of the diagnostic[26] antisymmetric (out-of-phase) C=N=N and the C=O absorptions between the solution-phase spectra of 3-PDK and 4-PDK and those obtained on the monolayer suggest that this functional group is stable on the Pt surface. The C=N=N stretches in the monolayer occur at 2081 and 2085 $\mathrm{cm^{-1}}$ for 3- and 4-PDK, respectively, a slightly higher wavenumber than in solution (2071 and 2072 $\mathrm{cm^{-1}}$). Slight shifts are expected when the pyridyl ring becomes more electron withdrawing as a result of the bonding of the nitrogen atom to Pt. The broadened C=O region of the monolayer spectrum (maximum absorption 1605 and 1615 $\mathrm{cm^{-1}}$) may indicate some interaction of the C=O group with the surface, or may simply be a result of intermolecular interactions on the monolayer, as is observed generally on metal surfaces.[27] Other absorptions arising from C–C and C–H stretches of

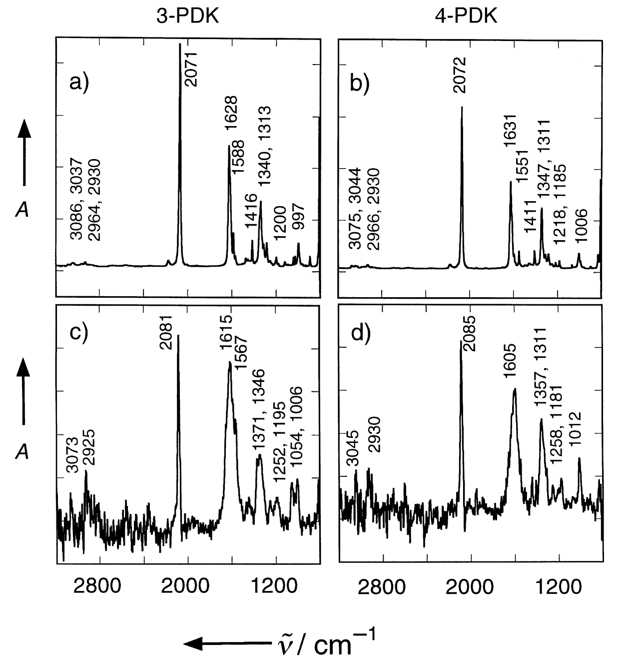


Figure 1. Comparison of the transmission IR spectra of solutions of a) 3-PDK and b) 4-PDK, measured in $CCl_4$ at 298 K (32 scans, 4 $cm^{-1}$ resolution) with the corresponding RAIR spectra of c) 3-PDK and d) 4-PDK as monolayers on Pt (110) dosed and measured at 283 K (500 scans, 4 $cm^{-1}$ resolution).

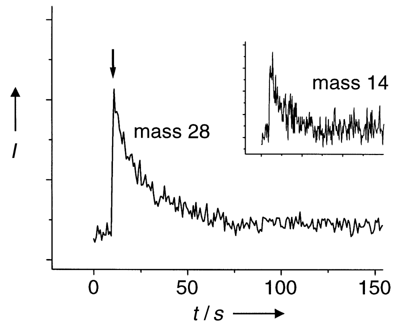


Figure 2. Mass spectrometer response monitoring the release of nitrogen gas (*m*/*z*: 28 and 14) from the diazoketone during the photolysis of 3-PDK monolayer on Pt (110). The arrow indicates when the surface was exposed to light.

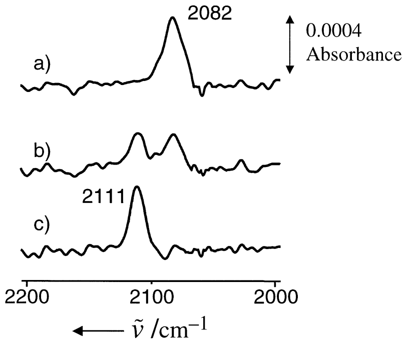


Figure 3. Partial RAIR spectra showing the changes in the 2000–2200 $cm^{-1}$ region of the spectrum on photolysis of Pt-3-PDK: a) prior to photolysis, b) at intermediate photolysis time, and c) after complete photolysis.

the pyridyl ring and ring breathing modes, as well as $CH_3$ umbrella modes are also observed in both the solution state and on the monolayer spectra. Key IR absorptions of both the transmission and RAIRS of 3-PDK and 4-PDK are included in Figure 1. Other researchers have shown that pyridine itself reorganizes at 300 K to form a $\alpha$-pyridyl species, which is formed by the cleavage of an $\alpha$-C–H bond.[14] While we see no evidence for this type of species by a perturbation of the frequencies of the pyridyl ring absorptions relative to those measured at low temperature, we can not rule it out. This is because the region of the spectrum that is diagnostic is dominated by other absorptions in the diazoketone or is outside our available spectral window. Clearly there is no significant change in the diagnostic C=N=N (2081 $cm^{-1}$) absorption or other main modes compared to the spectra at lower temperatures.

Compounds 3-PDK and 4-PDK form the respective ketene intermediates by the well known photo-Wolff rearrangement on photolysis with light of wavelength 300–400 nm.[28] The ketene is not long lived in solution and reacts with a variety of nucleophilic substrates. The loss of molecular nitrogen upon photolysis of the Pt-3-PDK and Pt-4-PDK monolayers is monitored by mass spectroscopy (*m*/*z*: 14 and 28; Figure 2). These masses are only detected when the surface is being irradiated. Importantly, no peak at *m*/*z* 78 or 105, which correspond to pyridyl fragments, are observed and indicate that photolysis does not cause desorption of the pyridyl moiety. Partial RAIR spectra measured at various times upon irradiation of the Pt-3-PDK monolayer at 300–400 nm are shown in Figure 3. Particularly diagnostic of the photolysis is the decay of the C=N=N antisymmetric absorption at 2081 $cm^{-1}$ and the concomitant formation of an equally intense absorption at 2111 $cm^{-1}$. The latter absorption continues to increase in magnitude during the photolysis and reaches a maximum when no further molecular nitrogen is liberated from the surface. This absorption is characteristic of a ketene C=C=O antisymmetric (out-of-phase) stretch.[19] Identical spectral features are observed in the photolysis of Pt-4-PDK. On the basis of the similarity, we assign the spectra obtained upon photolysis of Pt-3-PDK and Pt-4-PDK to Pt-3-KET and Pt-4-KET, respectively. Furthermore, conversion of the diazoketone to the ketene is high, based on the relative intensities of the C=N=N and the C=C=O absorptions before and after photolysis respectively.

Remarkably, the absorption at 2111 $cm^{-1}$ is stable and showed no appreciable loss in intensity for 30 minutes after irradiation (measurements after this time are hindered by poorer baseline corrections). The spectrum is also stable to continued irradiation at wavelengths of 300–400 nm. However, when this surface is exposed in a separate step to an overlayer of methanol dosed at 140 K, the antisymmetric C=C=O absorption disappears and changes in the intensity and shape in the C=O portion of the RAIR spectrum are observed. This loss of the absorption at 2111 $cm^{-1}$ with addition of a potential nucleophile provides further support for our assignment to the pyridylketene intermediate being generated on the metal surface.[19] This aspect of the reactivity, which can be exploited for functional derivatization of the surface, is currently being investigated.

In conclusion, we report the first spectroscopic evidence of a Pt surface modified with a pyridyl diazoketone monolayer.

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The stability of the pyridyl diazoketone on a Pt surface opens up the possibility of its use as a template for subsequent surface modifications using the rich chemistry of these functional groups. Furthermore, the diazoketone moiety of this monolayer can be selectively transformed to the remarkably stable pyridylketene functionality upon ultraviolet irradiation and loss of molecular nitrogen, presumably by a photo-Wolff reaction, analogous to the solution-phase chemistry. The spectroscopic evidence for the formation of the ketene suggests that its chemistry can also be used for subsequent surface modifications.

## *Experimental Section*

3-PDK and 4-PDK: The 3- and 4-pyridyl diazoketones were synthesized by reaction of their respective 3- and 4- pyridoyl chlorides with diazoethane, in an analogous way to the synthesis of other aryldiazoketones.[28] The substrates were purified by repeated chromatography on flash silica gel (80 g silica per 1 gram of diazoketone) with 75:25 ethyl acetate:hexanes.

3-PDK: $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.14$ (s, 3 H), 7.36 (m, 1 H), 7.86 (m, 1 H), 8.69 (m, 1 H), 8.81 (m, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.2$, 63.7, 123.3, 133.1, 134.6, 147.9, 151.9, 187.2; UV/Vis (MeOH) nm, ($\varepsilon$, $\text{M}^{-1}\text{cm}^{-1}$): 300.5 (6165), 255.5 (5924), 228.0 (5417); IR ($CCl_4$) $\text{cm}^{-1}$: 3086, 3037, 2964, 2930, 2071, 1628, 1588, 1416, 1340, 1313, 1200, 997; MS (70 eV): $m/z$ (%): 161 (32) [$M^+$], 133 (35), 105 (100), 104 (88), 78 (85), 51 (69); HR-MS: calcd: 161.0589; found: 161.0589.

4-PDK: $^1$H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 2.14$ (s, 3 H), 7.40 (dd, 4.4, 1.7 Hz, 1 H), 8.7 (dd, 4.4, 1.7 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.9$, 63.7, 120.6, 144.0, 150.3, 187.5; UV/Vis (MeOH) nm, ($\varepsilon$, $\text{M}^{-1}\text{cm}^{-1}$): 304.5 (7558), 264 (6578), 220.4 (7000); IR ($CHCl_3$) $\text{cm}^{-1}$: 3075, 3044, 2966, 2930, 2072, 1631, 1551, 1411, 1347, 1311, 1218, 1185, 1006; MS (70 eV): $m/z$ (%): 161 (29) [$M^+$], 133 (35), 105 (74), 104(53), 78 (94), 51 (100); HR-MS: calcd: 161.0589; found: 161.0591.

The platinum single crystal Pt (110) was cut and polished using standard procedures, and cleaned before each dosing experiment by $Ar^+$ sputtering, heating in oxygen, and annealing cycles. The RAIRS experiments were performed in an ultra high vacuum (UHV) chamber pumped to a base pressure below $3.8 \times 10^{-10}$ mbar. The sample was heated with a current of up to 30 A and cooled with liquid nitrogen allowing temperature control between 100 and 1300 K. Samples of 3-PDK and 4-PDK were dosed on the Pt crystal with background pressures of $3.8 \times 10^{-9}$ mbar. The chamber was equipped with a Hiden Analytical Limited 601 Quadrupole Mass Spectrometer for TPD experiments. A Mattson Galaxy Series 5000 FTIR spectrometer was used for RAIRS, and the RAIR spectra were measured at 283 K unless otherwise noted. The data was collected by focusing the IR source from the spectrometer through a KBr window onto the sample at grazing incidence and refocusing into a MCT detector.

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