

Photosublimation of the Novel π -System Photoproduct of Ethyl-4-formyl-1,3-dimethylpyrazole-5-carboxylate

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Photosublimation of the photoproduct of ethyl-4-formyl-1,3-dimethylpyrazole-5-carboxylate (EFDPC) has been observed for the first time at room temperature and normal atmospheric pressure. Steady state absorption spectroscopy and atomic force microscopic studies of EFDPC cast film as a function of UV/visible photoirradiation time revealed that upon photoirradiation EFDPC is converted to photoproduct first, which on further photoirradiation is evaporated from the substrate. This evaporation is a single photon phenomenon which is completely different from the laser ablation (sublimation) process.

The organic photochromic compounds are of potential interest for the development of electronic devices such as switches, photodiodes,¹ optical data memory systems, and photon-mode erasable optical recording.² Discovery of photosublimation and photosublimated photochromic compound will open new era for the further development of optoelectronic devices such as EPROM, EPRAM and etc.

Considerable research has been focused on the UV–visible-laser sublimation (etching) of semiconductor surfaces, such as ZnO, CdTe, HgCdTe, CdS,³ etc. In most cases, etchings by photosublimation are highly nonlinear phenomena with respect to laser power and are generally analyzed in terms of the dynamic interaction of the beam with induced microstructures.⁴ Maycock et al. observed the photosublimation phenomena of three organic explosives, Pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and trinitrotoluene in reduced pressure which was of linear process.⁵ To our knowledge, no report was found up to now for photosublimation of organic compounds in atmospheric pressure and ambient temperature which could be a linear process dealing with single photon interaction.

In this letter, we report the first direct evidence of sublimation of photochromic pyrazole derivatives on UV–visible photoexcitation from high-pressure xenon lamp.

In our recent work,⁶ substantial theoretical and femtosecond laser spectroscopic studies have been done to understand the photochemical behavior of newly synthesized ethyl-4-formyl-1,3-dimethylpyrazole-5-carboxylate (EFDPC) both in solid state and solution phase.⁷ The compound shows remarkable photochromism in its solid state: a prominent color change from colorless to reddish purple upon UV irradiation (~ 350 nm) and thermal (~ 330 K) fading without loss of starting material. The color products have a novel π -system zwitterionic (Scheme 1) form which results in γ -hydrogen abstraction by an excited

formyl group followed by very short-lived singlet 1,4-biradical being identical to that of the tetramethyleneethane biradical. The identification of zwitterionic photoproducts was made by femtosecond through microsecond transient spectroscopic studies and time dependent density functional theory calculation at the B3LYP level of theory and a 6-31G* basis set.⁶

In this study, we have examined the photosublimation of the cast film of EFDPC from chloroform solution onto glass substrate at 296 K and normal pressure. In the wet cleaning process, a 0.12 mm thickness glass substrate was sonicator-washed with acetone and milli-pore water and was dried by gentle flow of nitrogen gas. However, upon 350 nm photoexcitation, the cast film of EFDPC is converted into color photoproduct first, which on further photoirradiation disappears from the substrate. Photoirradiation was performed using a high-pressure xenon arc lamp (Hamamatsu Photocure-200 UV-spot source), which was guided through multimode optical fiber to focus on the sample surface. We have used very weakly intense normal UV light to avoid any nonlinear effect. The incident photon energy density was ~ 0.15 mW/cm² at 350 nm. Photo-selection was done employing a suitable band-pass filter, and an IR cut filter was used removing any unwanted infrared on the film to avoid local heating. Steady-state spectroscopy of the EFDPC film revealed a strong absorption band at 250 nm and a very weak band at 330 nm. Upon photoexcitation of 350 nm by 10 s on the film surface, a new band appeared at 550 nm with little decrease in absorption of 250 and 330 nm band without any change of band structure. Furthermore, the color of the film was also changed from colorless to reddish purple. This color lasts for several days if the film is kept in a dark place. We assigned this new band at 550 nm as the absorption band of photoproducts (Figure 1). Band shape analysis of this absorption band shows two Gaussian peaks, one is at 515 nm and the other is at 566 nm under this broad envelop indicating the coexistence of the photoproduct in two isomeric forms and there could be a fast equilibration between the two isomers.⁶ On further excitation/irradiation either by 350 or 550 nm light, all bands start decreasing with irradiation time, and finally, all bands disappear (Figure 1) which is presumed to the evaporation

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SCHEME 1: Solid State Photochromism of EFDPC and the Proposed Structure of the Photoproduct

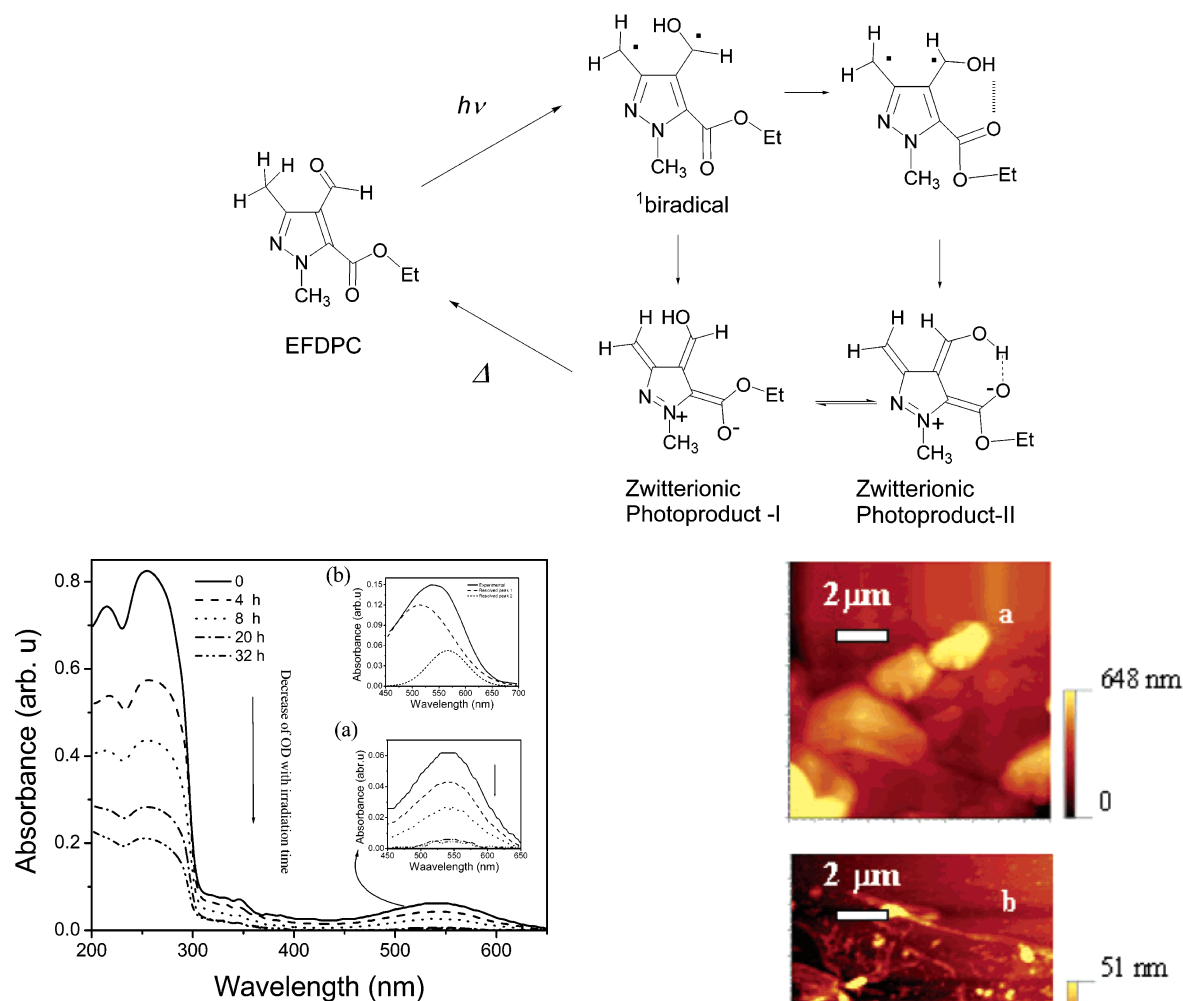


Figure 1. Change of absorption spectra of the cast film of the photoproduct of EFDPC on photoirradiation time (h). $\lambda_{\text{irr}} = 550$ nm. The inset (a) is the enlarged form of the red band. (b) Two resolved Gaussian peaks of the red band found by band shape analysis. A relatively thick film was used to increase the OD of the red band for band shape analysis.

of the molecule from the substrate. We have checked that there is no reversible transformation of the photoproduct of EFDPC by photoirradiation but thermally reversible transformation on heating to 330 K without loss of material. To confirm the evaporation of photoproduct of EFDPC from the substrate, a poly(vinyl alcohol) (PVA) coated film was surveyed for photoexcitation. In this case, the appearance of new band (550 nm) as well as the color change of the film was observed with little decrease of both 250 and 330 nm bands, but no change of absorption spectra was found on further photoirradiation by both 350 and 550 nm light. Furthermore, we also monitored the surface morphology change of EFDPC cast film onto glass substrate as a function of photoirradiation time both for uncoated and PVA coated surfaces by AFM. For the first case, a huge change of the surface morphology was observed on continuous photoirradiation by 350 nm. The size of the micro crystals of the EFDPC photoproduct decreases with irradiation time (Figure 2), and finally, it almost vanishes, whereas for a PVA coated surface, no change was found on photoirradiation (Figure 3). Hence, we are convinced that on photoexcitation EFDPC first converted to zwitterionic photoproduct which on further photoirradiation evaporates from the substrate. These findings could be rationalized on the basis of the following assumptions:

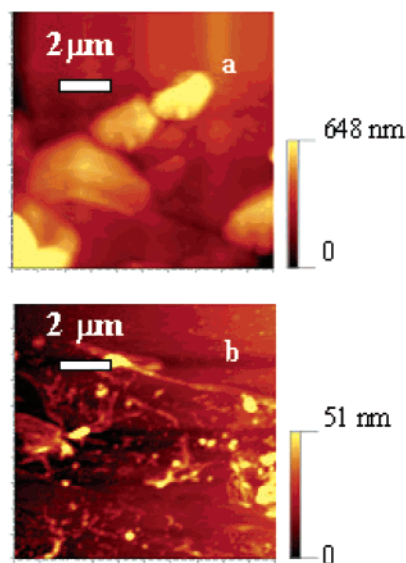


Figure 2. AFM image of the cast film of the EFDPC photoproduct. (a) After 10 s of photoirradiation by UV light (350 nm). (b) After 75 min of photoirradiation, $\lambda_{\text{irr}} = 550$ nm.

(a) The activation energy for photosublimation is much less than that for a thermally induced process as it was observed for organic explosives Pentaerythritol tetranitrate (PETN) and trinitrotoluene.⁸ (b) The inefficient radiative deactivation channel⁹ and, thus, the absorbed photon energy totally converted into heat energy.

On those favorable conditions, the photon energy absorbed by the photoproducts of EFDPC is converted to vibrational energy which could enormously increase the internal temperature of the zwitterionic photoproducts just after photoexcitation. This internal temperature is expected to be as high as that in the merocyanin isomer^{10,11} due to its nonradiative deactivation such that the van der Waals forces holding the molecule together are perturbed due to vibrational–translational energy transfer to the molecule causing photosublimation to occur.

In conclusion, we reported the first observation of true photosublimation of the zwitterionic photoproduct of EFDPC at room temperature and atmospheric pressure by the photoirradiation of a normal UV source. The unprecedented localized heating due to absorbed photon energy exceeds the activation energy for sublimation resulting in evaporation of the molecules from the substrate surface.

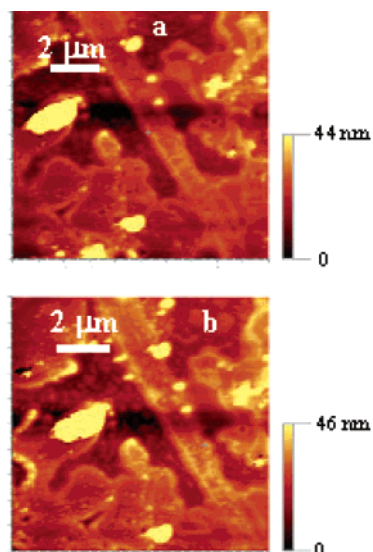


Figure 3. AFM image of the PVA coated cast film of the EFDPC photoproduct. (a) Before photoirradiation. (b) After 8 h of photoirradiation, $\lambda_{\text{irr}} = 350 \text{ nm}/550 \text{ nm}$. The 12 mg/L concentrated aqueous PVA solution was to coat the EFDPC cast film.

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Supporting Information Available: Sequential change of surface morphologies of the EFDPC cast film as a function of photoirradiation time, taken by a CCD camera under microscope and AFM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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