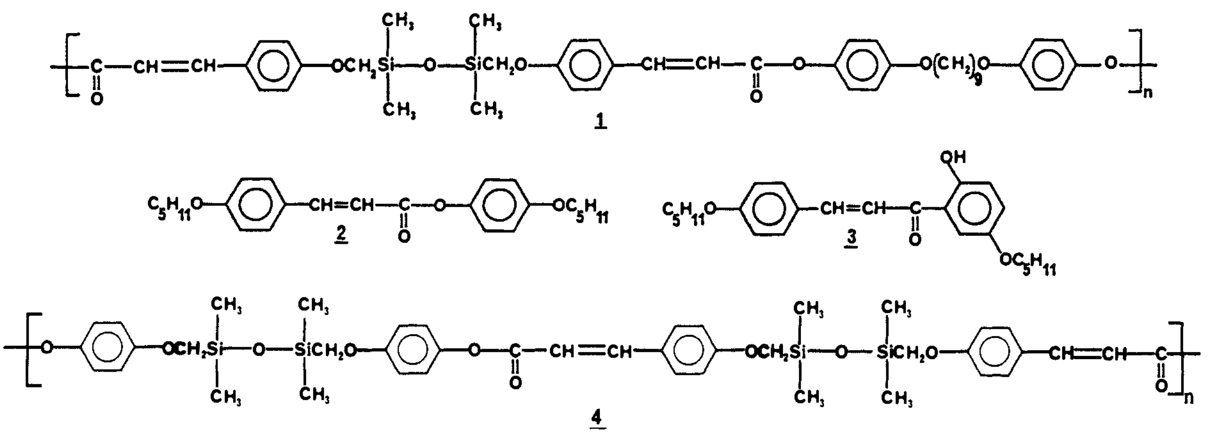
Chart I


1
2
3
4

photochemistry of the isolated aryl cinnamate chromophore has also been explored by using solid solutions of **2** in PMMA. If these solutions are sufficiently dilute, the only reaction observed upon irradiation is the photo-Fries reaction. The isosbestic point observable under these conditions indicates that trans–cis isomerization is not occurring in this highly viscous medium, and this is probably also true for the rigid phases of the polymer although it cannot be excluded in the more mobile nematic phase[2] and in the isotropic melt.

The photochemistry of **1** is wavelength dependent. This effect is quite dramatic in the nematic phases. Irradiation of films at 366 nm, where virtually all the light energy is absorbed by aggregates, leads to the UV–vis changes attributable to cinnamate photodimerization and almost none of the long wavelength absorption increase attributable to photo-Fries reaction. However, irradiation at 313 nm produces both the dimer and the Fries products (Figure 1). Upon exhaustive 366-nm irradiation, not all the absorption due to the aryl cinnamate chromophores disappears. That this residual absorption is due to unreacted aryl cinnamate can be shown by the appearance of the absorption due to the photo-Fries product upon 313-nm irradiation of these exhaustively 366 nm irradiated films. All of these observations tend to suggest that a significant fraction of chromophores is present in aggregates and that dimerization is the only photochemical process that occurs upon specific excitation of these aggregates. Exhaustive irradiation at 366 nm converts all aggregated pairs to dimers, and the remaining isolated chromophores, having very little absorptivity at 366 nm, are relatively insensitive to further 366-nm irradiation. However, 313-nm irradiation causes them to undergo the alternative, *unimolecular* photo-Fries reaction. This effect is most pronounced in the glassy nematic state, where a greater fraction of chromophores is aggregated. In this state, we estimate, at least 70% of the original chromophores are aggregated on the basis of the cinnamate absorption remaining after exhaustive 366-nm irradiation.

Compared to these dramatic effects, there is no observable wavelength dependence upon 313- compared to 366-nm irradiation of the isotropic melt at 123 °C. This parallels the observation[2] of loss of the hypochromic effect when the UV–vis spectra of films are run in the isotropic melt. Some wavelength dependence is, however, observed upon irradiation of "amorphous" (i.e., nonbirefringent[3]) films of **1** and upon irradiation of a polymer, **4**, with the same chromophore as **1** but which is not liquid crystalline. In these cases, the main evidence for wavelength dependence is a delay between chromophore disappearance and the appearance of the characteristic absorption due to Fries product when irradiation is at 366 nm, and the absence of such a delay upon 313-nm irradiation. Qualitatively this effect is more pronounced in the case of "amorphous" **1** compared to non-LC **4**. In both these cases, short-range ordering of chromophores presumably occurs during casting of the films. Our photochemical observations thus clearly parallel the photophysical observations of Reiser and his coworkers[9] in which ground-state aggregation of *p*-phenylenediacrylate chromophores in a main-chain polyester is apparent from fluorescence intensity and lifetime studies.

We are currently quantitating the photoproduct ratios in the different phases as a function of wavelength and temperature. Preliminary results indicate that the dimer/Fries ratios are higher in the more organized and less mobile phases. This may be advantageous for applications such as the development of biaxially strengthened films or photoresists, for which photochemical cross-linking is the most important reaction.

Acknowledgment. We thank Armstrong World Industries, the National Science Foundation (Grant No. RII-8902064), the State of Mississippi, and the University of Southern Mississippi for their support of this work and Professor R. G. Weiss for helpful discussions.

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(8) Photocycloaddition is the principle photoprocess observed upon irradiation of a related, main-chain, non liquid crystalline polymer of *p*-phenylenediacrylic acid. Eggerton, P. L.; Trigg, J.; Hyde, E. M.; Reiser, A. *Macromolecules* **1981**, *14*, 100–104.

(9) Graley, M.; Reiser, A.; Roberts, A. J.; Phillips, D. *Macromolecules* **1981**, *14*, 1752–1757.

Structure, Dynamics, and Reactivity of an Alkoxy Intermediate Formed from Acetylene on Zeolite Catalysts: An in Situ Solid-State NMR Study

Noel D. Lazo, Jeffery L. White, Eric J. Munson,
Marsha Lambregts, and James F. Haw*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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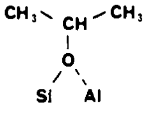
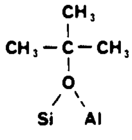
Recently, there has been much interest in reactive intermediates formed by the adsorption of organic compounds on zeolites and alumina.[1-3] In a low-temperature in situ NMR study of the oligomerization of propene on zeolite HY, Haw and co-workers[1] proposed that alkoxy species of type I, formed between protonated alkenes and the zeolite framework, are long-lived intermediates.[4]


I


II

$Al{-}O{-}CH_2{-}(CH_2)_2{-}CH_3$

III

$Al{-}O{-}CH{=}CH_2$

IV

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* Author to whom correspondence should be addressed.

(1) Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052.

(2) Aronson, M. T.; Gorte, R. J.; Farneth, W. E.; White, D. *J. Am. Chem. Soc.* **1989**, *111*, 840.

(3) Chin, Y. H.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 7653.

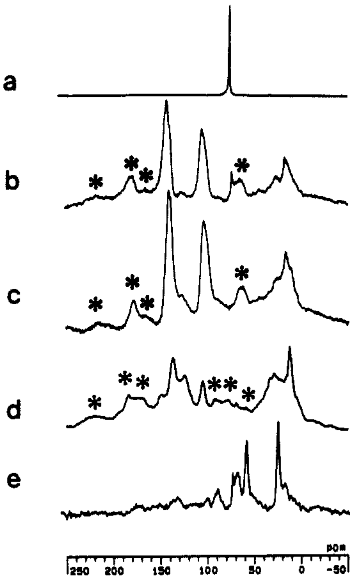


Figure 1. ^{13}C CP/MAS spectra showing in situ reactions of acetylene on various catalysts: (a) zeolite HY, 296 K; (b) zeolite HY, 473 K; (c) zeolite HY, 503 K; (d) zeolite HZSM-5, 503 K; (e) γ-alumina, 393 K. All spectra were taken with 400 transients. The cross-polarization contact time was 2 ms, and the pulse delay was 1 s. Asterisks (*) denote spinning sidebands.

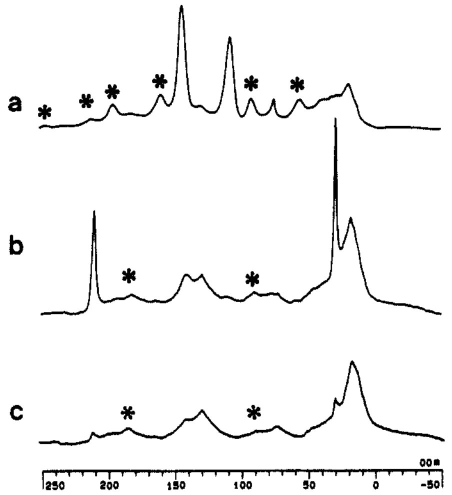
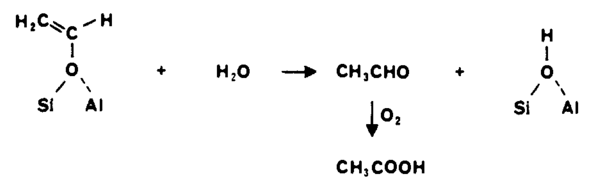


Figure 2. ^{13}C CP/MAS spectra probing the reactivity of species V: (a) species V and tars in zeolite HY at 296 K after heating to 503 K; (b) spectrum obtained after exposure of the sample in spectrum a to water and oxygen; (c) spectrum of the tars obtained after further exposure of the sample in spectrum b, showing only tars. Asterisks (*) denotes spinning sidebands.

Scheme I

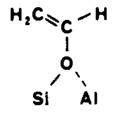


Upon the adsorption of 2-methyl-2-propanol-*2*-^{13}C on zeolite HZSM-5 and evacuation to remove water, Aronson and co-workers[2] observed the formation of the alkoxy intermediate II. Chin and Ellis[3] recently showed that species III and IV could form from the adsorption of acetylene on γ-alumina at room temperature. In this communication, we present evidence for a vinyl alkoxy species, analogous to IV, which is formed at high temperatures from acetylene on zeolites HY and HZSM-5. Upon exposure of the catalyst to water, the intermediate was converted quantitatively to acetaldehyde.

Zeolites HY and HZSM-5 were employed in this investigation.[5] Active catalysts were prepared from the ammonium-exchanged forms by a multistep activation procedure.[1] Adsorptions were carried out by exposing the catalysts to 60 Torr of acetylene-*1,2*-^{13}C (99.2 atom % ^{13}C, MSD Isotopes) at room temperature to achieve loadings of ca. 3.3 mmol/g (HY) or 2.8 mmol/g (HZSM-5). Acetylene uptakes were measured by using a standard vacuum line and manometer arrangement. ^{13}C NMR spectra were acquired on a Chemagnetics CMX-300 spectrometer using cross polarization and magic-angle spinning (CP/MAS).

Parts a–c of Figure 1 show spectra obtained after adsorption of acetylene-*1,2*-^{13}C on zeolite HY. No reaction was observed at 298 K. After the sample temperature was raised to 473 K, however, acetylene was partially consumed, and two equally intense signals formed at 143 and 107 ppm (Figure 1b). Less intense signals corresponding to aromatic and aliphatic carbons also formed (vide infra). At 503 K (Figure 1c), most of the acetylene reacted, and the spectral features described above increased. Essentially identical results were also obtained when the alternate Y zeolite obtained from UOP Corporation was used.[5] The 143- and 107-pm resonances also formed in an identical experiment on HZSM-5 (e.g., Figure 1d), except that their intensities were lower, consistent with the lower number of active sites on zeolite HZSM-5. Gas-phase reactions of acetylene to form benzene and other hydrocarbons are known to occur to a small extent at temperatures exceeding 673 K,[6] well in excess of the temperatures used in this study. This possibility was ruled out by a control experiment using inactive NaY zeolite, on which no reaction was observed at 503 K.

Consideration of model compound chemical shifts[7] and the above observations suggest that the 143- and 107-ppm resonances correspond to the vinyl alkoxy species V, analogous to species IV[8]



V

described by Chin and Ellis. The other peaks in Figure 1a–c are consistent with alkyl-substituted aromatics (tars or coke) formed either by an alternate reaction pathway from acetylene[9] or indirectly from acetaldehyde (vide infra).

A similar experiment was performed on γ-alumina, and resonances similar to those assigned by Chin and Ellis to saturated alkoxy species such as III were observed (Figure 1e).

When the zeolite samples were cooled to room temperature, the peaks assigned to V remained (Figure 2a). To verify the structure of species I, Haw and co-workers exposed catalyst samples to atmospheric water and observed loss of the alkoxy resonance with the formation of a new signal consistent with secondary alcohols. In a similar vein, the sample in Figure 2a was briefly exposed to the atmosphere, and the spectrum in Figure 2b was obtained.[10] That figure shows that the 143- and 107-ppm resonances were completely replaced with two sharp signals at 207 and 30 ppm. Similar results were obtained with HZSM-5 (spectrum not shown). The reaction product was determined to be acetaldehyde on the basis of comparison with spectra obtained

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(4) Similar conclusions were reached in a quantum chemical study by Malkin and co-workers: Malkin, V. G.; Chesnokov, V. V.; Paukshtis, E. A.; Zhidomirov, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 666.

(5) Y type zeolites were obtained from two sources: (1) NaY (Strem), 63.5 wt % SiO_2, 23.5 wt % Al_2O_3, and BET surface area of 550 m^2/g; (2) NH_4Y (UOP Corporation), 70.2 wt % SiO_2, 23.1 wt % Al_2O_3, and BET surface area of 848 m^2/g. NH_4ZSM-5 (Mobil Corporation) had a Si/Al ratio of 70.

(6) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

(7) For example, the vinyl group of $CH_2{=}CHOC(O)CH_3$ has ^{13}C chemical shifts of 142 and 96 ppm.

(8) Species IV was reported in ref 3 to have chemical shifts of 148 and 88 ppm.

(9) Tsai, P.; Anderson, J. R. *J. Catal.* **1983**, *80*, 207.

(10) Similar results were obtained when the sample was exposed to water in a glove box from which oxygen was excluded.

J. Am. Chem. Soc. **1990**, *112*, 4052-4054

following direct adsorption of acetaldehyde on the zeolite catalysts.[11] Further exposure of the catalyst to the atmosphere allowed the acetaldehyde to diffuse out and permitted a spectrum of the tars to be obtained (Figure 2c). Alternatively, further heating of adsorbed acetaldehyde in the presence of oxygen resulted in the formation of acetic acid (Scheme I).

Control experiments in which water was coadsorbed onto the zeolite with acetylene yielded spectra similar to Figure 2b. The highly paraffinic nature of these tars suggests that the required source of hydrogen may be water. Indeed, in samples that were not deliberately exposed to water, the amount of tars formed correlated with the catalyst activation temperature and thus the degree to which water was present in the catalyst. Furthermore, similar tars were observed to form when authentic samples of acetaldehyde on HY catalyst were subjected to analogous high-temperature studies.[12]

The dynamics of V were probed by dipolar dephasing[13] experiments at 298 and 143 K. At 298 K, the 143-ppm peak survived 50 μs of interrupted decoupling. At 143 K, however, the intensity of the 143-ppm peak was greatly attenuated. The 107-ppm resonance was completely suppressed at both temperatures. These results suggest that V undergoes rapid rotation at 298 K about the C–O axis, with the effect that the dipolar coupling to the directly bound proton is attenuated.[14] At low temperatures, this rotation is slowed down, and the 143-ppm peak is attenuated.

Acknowledgment. This work was supported by a grant from the National Science Foundation (Grant CHE8700667). E.J.M. is a National Science Foundation Predoctoral Fellow. J.L.W. and M.L. are Department of Education Fellows.

Registry No. H_2O, 7732-18-5; CH_3CHO, 75-07-0; acetylene, 74-86-2; alumina, 1344-28-1.

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[11] The chemistry is analogous to the hydrolysis of vinyl ethers. See, for example: Salomaa, P. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: New York, 1966.

[12] Chang and Silvestri also observed the conversion of acetaldehyde to alkyl aromatics: Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249.

[13] Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

[14] Elementary considerations of the bond angles for sp^2 carbons suggest that the angle between the C–H bond vector for the carbon attached to oxygen in species V and the axis of rotation (the C–O bond vector) is 60°, which is close to the "magic angle" of 54.7°, which is effective in averaging dipolar couplings.

Photoreduction of Palladium Radical Cations. Transient Absorbance Kinetics of Electron Transfers to Photogenerated $[Pd(CNMe)_3]^{\bullet+}$ Radicals

Frederick R. Lemke,[1] Robert M. Granger,
David A. Morgenstern, and Clifford P. Kubiak*,[2]

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received June 1, 1989

The photochemical deposition of metal films provides the basis for a wide variety of imaging processes.[3] Laser direct writing of conducting metal features has received considerable attention as a means of defining and "wiring" a micron-scale circuit in a single step.[4-6] We report the photoreduction of organometallic radical cations by electron transfers to photogenerated $[Pd(CNMe)_3]^{\bullet+}$ radicals. It is generally recognized that photogenerated $^{\bullet}ML_n$ radicals are potentially stronger both as oxidants and as reductants than their parent ground-state, metal–metal-bonded $L_nM{-}ML_n$ complexes.[7-9] The complex $[Pd_2(CNMe)_6][PF_6]_2$ (**1**) was found previously to exhibit photochemical σ,σ^* Pd–Pd bond homolysis.[9,10] Photogenerated $[Pd(CNMe)_3]^{\bullet+}$ radicals derived from photolysis of **1** are rapid and potent reductants of a variety of electron acceptors,[9] A, eq 1. We now report our findings

$$[Pd(CNMe)_3]^{\bullet+} + A \xrightarrow[\text{solvent}]{k_e} [Pd(CNMe)_3(\text{solvent})]^{2+} + A^{\bullet-} \qquad (1)$$

relating to the role of $[Pd(CNMe)_3]^{\bullet+}$ radicals as photogenerated oxidants. The $[Pd(CNMe)_3]^{\bullet+}$ radical system provides a rare example for direct observation of both reductive and oxidative behavior of an organometallic radical. A key finding is that transfer of an electron to the d^9, Pd(I) radical produces a Pd(0) complex which spontaneously deposits palladium as a metal film.

Table I. Electron-Transfer Rate Constants for the Reduction of $[Pd(CNMe)_3]^{\bullet+}$ by Substituted Ferrocenes with Determined $E_{1/2}$ Values

ferrocene	$E_{1/2}$, V vs SCE	$[Pd(CNMe)_3]^{\bullet+}$ k_e, M^{-1} s^{-1}
$Fe(C_5Me_5)_2$	−0.09	9×10^7
$Fe(C_5H_5)(C_5Me_5)$	+0.13	6×10^7
$Fe(C_5H_4Me)_2$	+0.31	3×10^7
$Fe(C_5H_5)(C_5H_4CH_2OH)$	+0.38	3×10^6
$Fe(C_5H_5)_2$	+0.42	2×10^6
$Fe(C_5H_4I)(C_5H_5)$	+0.54	5×10^4
$Fe(C_5H_4Cl)_2$	+0.77	$<4 \times 10^4$

Irradiation (λ = 313 nm) of an acetonitrile solution of **1** (0.013 mmol) and $Fe(C_5Me_5)_2$ (0.027 mmol) leads to the disappearance of **1** at 307 nm and the appearance of a band at 777 nm characteristic of $[Fe(C_5Me_5)_2]^{\bullet+}$, as observed by UV–vis spectrophotometry. A new absorbance at 410 nm also appears and corresponds to $[Pd(CNMe)_2]_n$.[11,12] This band vanishes over a period of several minutes as metallic palladium is deposited within the quartz photolysis cell. We note that palladium(0) isocyanide oligomers $[Pd(CNR)_2]_n$ (R = Pr^i, C_6H_{11}, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) are known to decompose in polar solvents.[11,12] Irradiation of an identical sample at 438 nm, within the $Fe(C_5Me_5)_2$ absorbance band, produced no reaction. Similarly, no reaction was observed in refluxed samples of **1** and $Fe(C_5Me_5)_2$. These results indicate that decamethylferrocene is oxidized by photolysis of **1**, producing a Pd(0) isocyanide species which is unstable in acetonitrile with respect to the formation of palladium metal.

Laser flash photolysis (7 ns, 355 nm) of **1** (1 mM in acetonitrile) produces an intense transient absorbance at 405 nm. The disappearance of transient absorbance corresponds to second-order recombination of $[Pd(CNMe)_3]^{\bullet+}$ radicals (eq 2). Recombination

$$2[Pd(CNMe)_3]^{\bullet+} \xrightarrow{k_r} \underset{\mathbf{1}}{[Pd_2(CNMe)_6]^{2+}} \qquad (2)$$

of $[Pd(CNMe)_3]^{\bullet+}$ radicals occurs with a rate constant, $k_r = 1 \times 10^9$ M^{-1} s^{-1}, near the diffusion-controlled limit in acetonitrile.[9] The addition of decamethylferrocene (10 μM) to a solution of **1** (1 mM in acetonitrile) dramatically accelerates the observed rate of disappearance of $[Pd(CNMe)_3]^{\bullet+}$ radicals. The synchronous appearance of the decamethylferricinium ion indicates that the disappearance of $[Pd(CNMe)_3]^{\bullet+}$ is due to electron transfer. The kinetics of electron transfer to photogenerated $[Pd(CNMe)_3]^{\bullet+}$ radicals was examined for each of the ferrocenes, $Fe(C_5Me_5)_2$, $Fe(C_5H_5)(C_5Me_5)$,[13] $Fe(C_5H_4Me)_2$, $Fe(C_5H_5)(C_5H_4CH_2OH)$,

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[1] Present address: Department of Chemistry, Ohio University, Athens, OH 45701.

[2] Research Fellow of the Alfred P. Sloan Foundation, 1987-1991.

[3] *Proceedings of the Seventh International Symposium on the Photochemistry of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berling, Heidelberg, 1987.

[4] Ehrlich, D. J.; Tsao, J. Y. *J. Vac. Sci. Technol., B* **1983**, *1*, 969.

[5] Montgomery, K. R.; Mantei, T. D. *Appl. Phys. Lett.* **1986**, *48*, 493.

[6] (a) Gross, M. E.; Appelbaum, A.; Gallagher, P. K. *J. Appl. Phys.* **1987**, *61*, 1628. (b) Harriott, L. R.; Cummings, K. D.; Gross, M. E.; Brown, W. L. *Appl. Phys. Lett.* **1986**, *49*, 1661.

[7] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[8] Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.

[9] Metcalf, P. A.; Kubiak, C. P. *J. Am. Chem. Soc.* **1986**, *108*, 4682.

[10] Reinking, M. K.; Kullberg, M. L.; Cutler, A. R.; Kubiak, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 3517.

[11] Malatesta, L. *J. Chem. Soc.* **1955**, 3924.

[12] Fischer, E. O.; Werner, H. *Chem. Ber.* **1962**, *95*, 703.