the experimental data (even after scaling the frequencies as proposed[5]).

To summarize the IR data unequivocally suggest 1,2-dithiete to be the most stable isomer, whereas the computed total energies indicate *trans*-dithioglyoxal should be the most stable. The computed energies however do predict that **1** and **2** should be similar in energy. It is not surprising that there is not better quantitative agreement of the computed relative energies with the apparent experimental results, since errors of this magnitude for isomers are not uncommon at this level of calculation.[12]

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(12) See, e.g., Tables 6.69 and 6.70 in the following: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Solid-State NMR Study of Acetylene Adsorbed to Platinum on Alumina As Followed by Direct Observation Using CP MAS Methods. Differentiation between Acetylene Adsorbed to Alumina and Platinum

Yu-Hsing Chin and Paul D. Ellis*

Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

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In a recent series of papers Slichter and co-workers[1] have reported solid-state ^{13}C and ^{195}Pt NMR investigations of small molecules, e.g., acetylene and ethylene, adsorbed to platinum on η-alumina. Of particular interest to us is the work involving the adsorption of acetylene.[1a] This work is significant because it verified that the principal species on the surface was not the ethylidyne, $\equiv CCH_3$, species proposed by Somorjai et al.[2] Rather, what Slichter and co-workers deduced from their analysis was that the principal component could be described as a species of the type CCH_2 (77 ± 7)% and to a lesser amount (23 ± 7)% HCCH. The C–C bond length of CCH_2 was estimated to be midway between a single and double bond. Slichter and co-workers arrived at their conclusions by a careful analysis of the "slow beats" present in spin-echo amplitudes in the free induction decay and not by direct observation of the high-resolution solid-state ^{13}C spectra via CP MAS methods. Hence, because of the importance of their observations we wanted to confirm them by using more conventional CP MAS methods. Of more concern, however, was the apparent implicit assumption that the acetylene does not react with the alumina support. Such an assumption, if incorrect, would have a striking influence on their structural conclusions. It is apparent from the surface literature that such an assumption is not valid.[3] We confirm that ethylidyne species are not present on Pt/γ-Al_2O_3 surfaces. However, we also prove that acetylene *does* chemisorb to alumina in the presence and absence of platinum metal. Further, the presence of such species adsorbed to the alumina clearly biases the structural conclusions of Slichter and co-workers. Finally, we conclude the principal species bound to the platinum is such that the bonding between the carbon atoms is intermediate between double and triple bonds. This latter conclusion is supported by IR experiments on the Pt/γ-alumina surface.

The samples were prepared by standard methods,[4] and the solid-state ^{13}C data were obtained on a Varian XL-300 by using conventional CP MAS methods.[5] Presented in Figure 1 is the ^{13}C CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed to γ-alumina and platinum surfaces. Comparison of spectra of adsorbed acetylene on γ-alumina obtained at several spinning speeds and variable temperatures, we can extract four isotropic carbon resonances from spectra a–d in Figure 1. Their chemical shifts are 148, 88, 58, and 23 ppm.[6] These chemical shifts[7] most likely correspond to a mixture of two chemical species on the γ-alumina surface, e.g.

$$\mathrm{Al{-}O{-}CH_2{-}(CH_2)_2{-}CH_3} \tag{1}$$

$$\mathrm{Al{-}O{-}CH{=}CH_2} \tag{2}$$

Figure 1e illustrates the ^{13}C CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed to 5% Pt/γ-Al_2O_3 at room temperature. Additionally, in Figure 1f we present the results of adsorbed acetylene on platinum surfaces where we have subtracted the spectrum in Figure 1d from that of Figure 1e. The criteria employed for the scaling was that the peaks at 148 and 88 ppm would be removed from the difference spectrum. As a result of this procedure four isotropic peaks due to the presence of Pt metal are evident in Figure 1f. Their chemical shifts are 129, 59, 23, and 14 ppm. Clearly, the principal species present on the Pt/γ-alumina surface is represented by the resonance at 129 ppm. The peaks at 59, 23, and 14 ppm may arise from an increase in the population of species[1] in the presence of γ-alumina on platinum surface. This may simply result from the increased loading of acetylene in the presence of the platinum. However, the minor isotropic peaks at 23 and 14 ppm could also possibly arise from the chemical species, Pt–CH_2CH_3.[8] Further, the application of the interrupted ^{1}H-decoupling sequence[9] demonstrates the resonances at 59, 23, and 14 ppm have directly bonded ^{1}H's, and the resonance at 14 ppm can be assigned to a methyl resonance. That is, this resonance is reduced in intensity but not eliminated by the interrupted decoupling sequence.

The results of the interrupted ^{1}H-decoupling experiments show the resonance at 129 ppm has a more complicated behavior. That is, the resonance loses about 50% of its intensity and is narrowed approximately by a factor of two. Hence, we ascribe this resonance to two carbons, one protonated and the other nonprotonated. The

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(1) (a) Wang, P. K.; Slichter, C. P.; Sinfelt, J. H. *Phys. Rev. Lett.* **1984**, *53*, 82. (b) Wang, P. K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1985**, *89*, 3606.

(2) Koestner, R. J.; Van Hove, M. A.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 203.

(3) (a) Yates, D. J. C.; Lucchesi, P. J. *J. Chem. Phys.* **1961**, *35*, 243. (b) Bhasin, M. M.; Curran, C.; John, G. S. *J. Phys. Chem.* **1970**, *74*, 3973. Highly transparent γ-alumina aerogel (60–85% in the region of 2000–4000 cm^{-1}) used by Bhasin, Curran, and John was predried at a specified temperature between 400 and 900 °C for about 2–6 h. Adsorption bands of ethyl groups and C=C stretching on the surface of γ-alumina observed by Bhasin and his co-workers are not in agreement with Yates and Lucchesis' work. The appearance of alkyl groups and the adsorption band of C=C stretching are consistent with the results reported here, even though our surfaces were not pretreated in the same way.

(4) The sample is cleaned on vacuum line by alternating H_2 and O_2 flow for about 5 h and then evacuated overnight at 298 °C. The ^{13}C-enriched acetylene is loaded, after the sample is cooled down to room temperature in vacuum. In about 40 min, evacuation is performed again to remove any physisorbed C_2H_2. The sample is frozen and stored with liquid N_2 to avoid any possible thermal decomposition during sealing. The sample is packed in a 7-mm zirconia rotor in a vacuum atmospheric drybox with a N_2 atmosphere.

(5) Pines, A.; Gibby, M. E.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569. Hartmann–Hahn cross-polarization magic angle spinning is applied. The rotor is spun typically at a speed of 4.5 kHz. The probe used for the CP MAS experiments was purchased from Doty Scientific Co.

(6) Chemical shifts are externally referenced to TMS. The resonances in our ^{13}C spectra were referenced to the most shielded resonance in adamantane which has a chemical shift at 29.2 ppm with respect to TMS.

(7) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *In Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience Publication: New York, 1980; p 50.

(8) (a) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1975**, *97*, 721. (b) Hall, P. W.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1974**, *71*, 145.

(9) (a) Fyfe, C. A. In *Solid State NMR for Chemists*; C.F.C. Press: Ontario, Canada, 1983; p 474. (b) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

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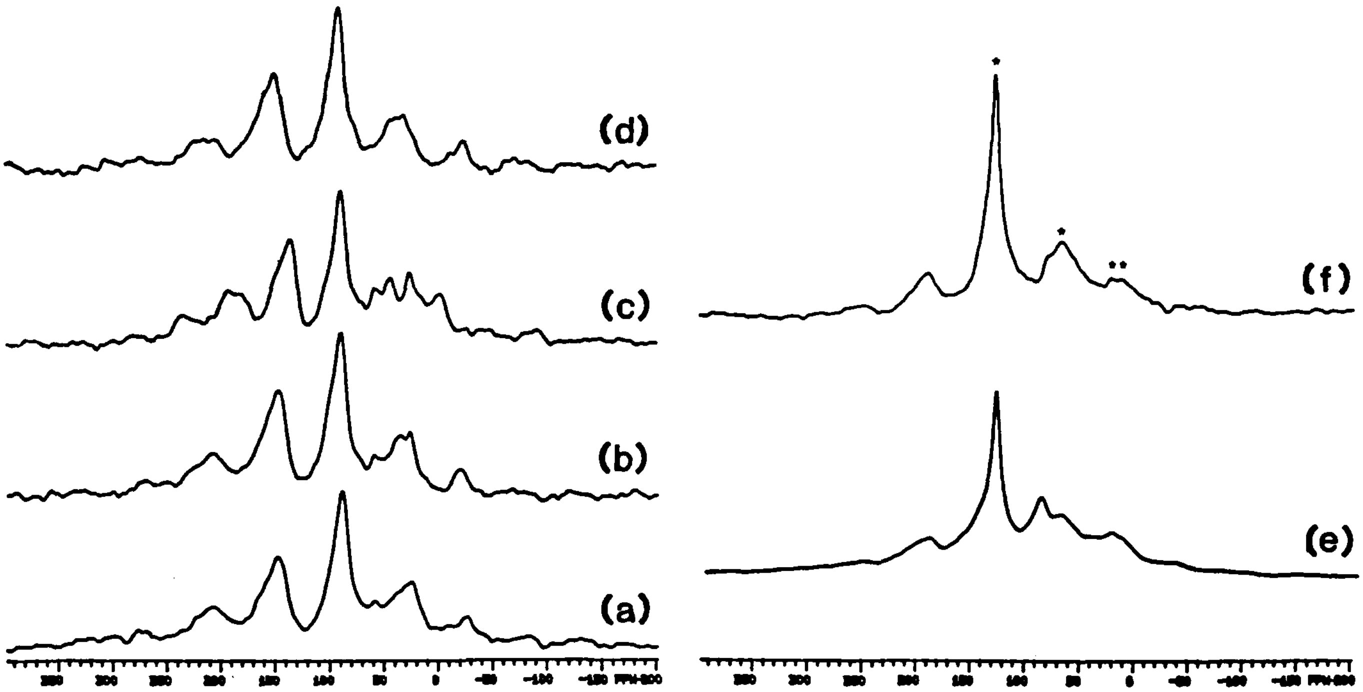

Figure 1. 75.43-MHz ^{13}C solid-state CP MAS NMR spectra of [1,2-^{13}C]acetylene, 90%, adsorbed on γ-alumina surface at (a) −54 °C, spinning speed is 4.3 KHz; (b) −25 °C, spinning speed is 4.2 KHz; (c) −0.5 °C, spinning speed is 3.4 KHz; (d) room temperature, spinning speed is 4.4 KHz; (e) adsorbed on 5% Pt/γ-Al_2O_3 at room temperature, spinning speed is 4.5 KHz; and (f) obtained by subtraction of the ^{13}C spectrum of γ-alumina, Figure 1d, from spectrum of 5% Pt/γ-Al_2O_3, Figure 1e. Scaling employed is such that the peaks at 148 and 88 ppm are cancelled (see text for details). Each spectrum results from 20 000 scans. Line broadening of each spectrum is 400 Hz. Scale is in parts per million with respect to TMS. Asterisks (*) in Figure 1f represent isotropic peaks due to the presence of Pt metal.

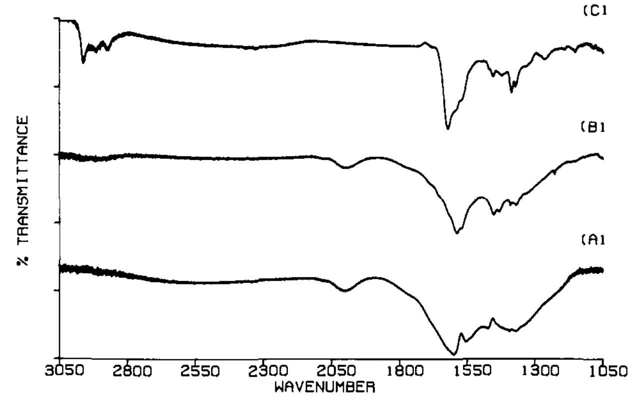

Figure 2. Infrared spectra of adsorbed C_2H_2 at room temperature on (A) 10% Pt/γ-Al_2O_3, (B) 5% Pt/γ-Al_2O_3, and (C) γ-Al_2O_3. All of infrared spectra were obtained with Nicolet Model 740 spectrometer. The sample used to study the chemisorption of acetylene on alumina and platinum by infrared spectroscopy in the region of 3050–1050 cm^{-1} is cleaned in vacuum by alternating H_2 and O_2 flow at 298 °C. The acetylene is injected to sample cell at room temperature in vacuum. In about 5 min after sample loading the cell is evacuated again to remove any residual of C_2H_2. Spectra of the sample have been ratioed with background after loading.

resonance at 129 ppm is indicative of the formation of platinum π-complexed species in the form of a monoanion of acetylene, i.e.

(3)

The partial triple-bond nature of the species is supported in the IR spectra of the same sample in Figure 2.[10] From a comparison of the room temperature and −54 °C spectra of the 5% Pt/γ-Al_2O_3 sample we observed a loss of intensity and increase of line width of the resonance at 129 ppm. This observation strongly suggests that dynamics are involved. The exact nature of these dynamics will be the topic of further investigations.

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(10) Green, M.; Grove, D. M.; Howard, J. A.; Spencer, J. L.; Stone, F. G. *J. Chem. Soc., Chem. Commun.* **1976**, 759. (IR $\nu_{C\equiv C}$ 1881 cm^{-1}, acetylenic carbon resonance of bis(acetylene)platinum(0) at 124.8 ppm).

Determination of the Rate Constant of Self-Exchange of the $O_2/O_2^{\bullet -}$ Couple in Water by $^{18}O/^{16}O$ Isotope Marking

J. Lind,[*,†] X. Shen,[†] G. Merényi,[*,‡] and B. Ö. Jonsson[§]

Royal Institute of Technology
S-10044 Stockholm, 70, Sweden

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The apparent self-exchange rate of the dioxygen/superoxide couple as estimated from the Marcus cross relationship[1] varies by about 16 orders of magnitude.[2] The present work is the first experimental measurement of this parameter.

The measurements utilize as a probe ^{18}O during the exchange reaction 1

$$^{36}O_2^{\bullet -} + {}^{32}O_2 \rightarrow {}^{36}O_2 + {}^{32}O_2^{\bullet -} \qquad (1)$$

which occurs prior to the second-order dismutation reaction 2.

$$O_2^{\bullet -} + HO_2^{\bullet} \rightarrow O_2 + HO_2^{-} \qquad (2)$$

The rate of reaction 2 is strongly pH dependent[3] and is rather

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[†] Department of Nuclear Chemistry.

[‡] Department of Physical Chemistry.

[§] Department of Physics.

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(2) McDowell, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 2232.

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