



Figure 1. Calculated 90% probability densities for solvent molecules in the first solvation shell of *trans*-glyoxal in the system $[(\text{HCO})_2]_{\text{aq}}$ at 25 °C. (a) Total molecule, (b) oxygen atom, (c) carbon atom, and (d) hydrogen atom.

The envelope containing the probability of finding primary coordinated water molecules around *trans*-glyoxal in aqueous solution is shown in Figure 1a. The solvent density is seen to be space filling as expected but not otherwise readily interpretable. The probability density of the primary coordinated solvent was then decomposed into contributions identified with the various solute atoms by using the proximity criterion, with the following results.

For the carbonyl oxygen, the average coordination number was found to be 2.30. The probability density distribution for solvation of the carbonyl oxygen is shown in Figure 1b. The statistical state solvation sites here are well localized into two specific regions, corresponding to the pair of solute-solvent hydrogen bonds involving the carbonyl oxygen unshared electron pairs.

The average primary coordination number of the glyoxal carbon atom was calculated to be 0.73. This relatively low value is a consequence of the reduced solvent accessibility of the carbon atom. The statistical state solvation sites, Figure 1c, are localized above and below the molecular plane and correspond to the interaction of water molecules with the π electrons of the carbonyl group. This and all other density plots should be symmetric with respect to the molecular plane; this is not completely realized in the level of convergence reported here.

The glyoxal hydrogen atom was found to have a primary coordination number of 5.78. The solvent probability density associated with the solute hydrogen by the proximity criterion is shown in Figure 1d. The density envelope for the hydrogen solvation was found to encompass a large spatial region around the atom, and here the statistical state solvation of the hydrogen is a single site, broad and diffuse in character.

The localized nature of the solvation of the carbonyl oxygen and the more diffuse character of the CH group solvation emerge clearly and quantitatively from this analysis. The former illustrates how the statistical state solvation site concept accommodates directional hydrogen bonding. The latter indicates that incipient evidence of hydrophobic hydration is present for even the smallest hydrocarbon fragment in a molecule. The essential features of the aqueous hydration of glyoxal are thus well represented in terms of statistical state solvation sites. We feel that statistical state solvation sites are a highly promising basis for the development of a comprehensive descriptive structural chemistry of aqueous solutions.

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Molybdenum(0)/Dehydroxylated Alumina Catalysts

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Heterogeneous catalysts consisting of highly dispersed group 8 metals supported on such high area oxides as silica gel and alumina have been extensively employed and investigated. However, very little work has been reported on supported group 6 metals. Although catalysts starting as $\text{MoO}_3/\text{Al}_2\text{O}_3$ have received considerable attention, it has appeared impracticable to reduce them to $\text{Mo}(0)/\text{Al}_2\text{O}_3$. Hydrogen at 500 °C reduces the Mo only to an average oxidation number (ON) of about +4.^{1,2} Catalysts of $\text{Mo}(0)$ supported on alumina have not been prepared and studied in the past because of the apparent difficulty in the reduction of $\text{MoO}_3/\text{Al}_2\text{O}_3$, because the extraordinary stability of $\text{Mo}(0)/\text{Al}_2\text{O}_3$ in hydrogen at 950 °C (see later) was not anticipated, and probably because of a feeling that hydrocarbons would react with the surface of molybdenum to form unreactive and deactivating deposits. We report here that $\text{Mo}(0)/\text{Al}_2\text{O}_3$ is readily prepared and that it exhibits some remarkable catalytic activity.

We had investigated catalysts that start as $\text{Mo}(\text{CO})_6/\gamma\text{-Al}_2\text{O}_3$ in which the molybdenum is initially in ON = 0. The surface layer of conventional, partially dehydroxylated alumina (PDA) contains both O^{2-} and OH^- ions ($\sigma\text{-OH}$).³ When $\text{Mo}(\text{CO})_6/\text{PDA}$ is heated in flowing ultrapure helium, complete loss of CO starts at about 200 °C to generate $\text{Mo}(0)$ which is immediately oxidized to Mo^{2+} by $\sigma\text{-OH}$ with concomitant liberation of H_2 .⁴ Above 400 °C, ON's from +4 to +6 appear. Thus, $\text{Mo}(0)/\text{PDA}$ could exist only at low temperatures. However, flowing helium at 950–1000 °C converts PDA to a dehydroxylated alumina (DA) with a low content in $\sigma\text{-OH}$. Heating $\text{Mo}(\text{CO})_6/\text{DA}$ in helium to 300–500 °C generates a material in which the ON of Mo is about +0.3 and in which residual carbon, C/Mo, is 0.3–0.4. This material is an active catalyst for the hydrogenation of carbon monoxide,⁵ the isotopic exchange between alkanes and deuterium at 20 °C,⁶ the hydrogenolysis of cyclopropane at 0 °C,⁷ and the hydrogenation of propylene at –46 °C.⁸

$\text{H}_2, 650^\circ, 1$ (which expression indicates heating in flowing hydrogen at 650 °C for 1 h) reduced C/Mo in the material just described to ~ 0.01 . The carbon was liberated as methane which was measured. $\text{H}_2, 950^\circ, 0.25$ liberated the remaining carbon as methane, since a subsequent $\text{H}_2, 950^\circ, 1$ liberated no more methane. Most of the carbon remaining after $\text{H}_2, 650^\circ, 1$ was removed by $\text{H}_2, 800^\circ, 1$. Exposure of $\text{Mo}(\text{CO})_6/\text{DA}, \text{He}, 300\text{--}500^\circ$ to hydrogen even at 500 °C substantially increased the activity for hydrogenation of propylene. Thus, in a flow reactor at –46 °C using 0.2 mg of Mo ($2 \mu\text{mol}$) on 0.2 g of DA, treated $\text{He}, 500^\circ$, conversion to propane was 28%. After subsequent exposure to $\text{H}_2, 500^\circ$ the conversion became 100%, corresponding to a turnover frequency per atom of Mo (N_f) $> 1.7 \text{ s}^{-1}$.

Although molybdenum metal prepared by reduction of MoO_2 has been reported to be relatively inactive in the hydrogenolysis

(1) Gajardo, P.; Grange, P.; Delmon, B. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 929–938.

(2) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265–310.

(3) Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 211–219.

(4) Burwell, R. L., Jr.; Brenner, A. *J. Mol. Catal.* **1975**, *1*, 77–84.

Brenner, A.; Burwell, R. L., Jr. *J. Catal.* **1978**, *52*, 353–363.

(5) Bowman, R. G.; Burwell, R. L., Jr. *J. Catal.* **1980**, *63*, 463–475.

(6) Defosse, C.; Laniecki, M.; Burwell, R. L., Jr. *Proc. Int. Congr. Catal.*, **7th** **1980**, in press.

(7) Merta, R.; Ponec, V. *Proc. Int. Congr. Catal.*, **4th** **1968**, 896–918. They reported that evaporated molybdenum film was an active catalyst for this reaction.

(8) Activity for the hydrogenation of olefins on activated $\text{Mo}(\text{CO})_6/\text{PDA}$ was first reported by Brenner, A., Ph.D. Dissertation, Northwestern University, 1975. See also: Brenner, A. *J. Mol. Catal.* **1979**, *5*, 157–61. In our work at –46 °C, $\text{Mo}(\text{CO})_6/\text{DA}, \text{He}, 300^\circ$ is about 10 times more active than $\text{Mo}(\text{CO})_6/\text{PDA}, \text{He}, 300^\circ$.

of ethane,⁹ we find that Mo(0)/DA such as Mo(CO)₆/DA, He, 500°; H₂, 650° exhibits remarkable activity for the hydrogenolysis of alkanes. At 200–300 °C in runs at low conversion with a flow reactor, total flow rates of 30–400 cm³ min⁻¹, pressures of H₂ and propane of 0.96 and 0.04 atm, and usually about 4 μmol of Mo on 0.05 g of DA, reactions 1 and 2 were observed. At



250 °C on He, 500°; H₂, 650°, 1, N_t was 0.070 s⁻¹ initially, 0.067 s⁻¹ after 1 h, and 0.064 s⁻¹ after runs for 1 h each at 200 and 300 °C. Initially, $N_t(1)$ (for reaction 1) was 0.053 and $N_t(2)$ was 0.017 s⁻¹; $E_a(1)$ was 105 kJ mol⁻¹ and $E_a(2)$ was 142 kJ mol⁻¹. N_t 's were almost the same when 2 μmol of Mo on 0.2 g of DA was used and also with Mo(CO)₆/DA, He, 500°; H₂, 650°, 0.5; H₂, 950°, 0.25. For Mo(CO)₆/DA which had been first treated with He, 300°, 1, detectable activity was exhibited after H₂, 300° and activity rose steadily up to H₂, 650 °C.

The catalysts were very sensitive to contamination. In a pulse reactor at 300 °C, Mo(CO)₆/DA, He, 500°; H₂, 950° gave a conversion of 12.9% per pulse. A pulse of O₂ (O₂/Mo = 2.4) completely poisoned the catalyst for the hydrogenolysis of propane. Subsequent treatment by H₂, 450° led to 0.03% conversion, H₂, 650° to 3.05%, H₂, 800° to 7.6%, and H₂, 950° to 12.6%. A pulse of carbon monoxide (CO/Mo = 9.6) at 300 °C reduced the activity to zero and a pulse of H₂O (H₂O(adsorbed)/Mo = 1.05) led to 41% of the initial activity.¹⁰ Even nitrogen poisoned the hydrogenolysis. A pulse with N₂/Mo = 1.3 on a catalyst containing 31 μmol of Mo reduced the hydrogenolysis from 99 to 79% and 3 more pulses reduced it to 40%. After H₂, 950°, the conversion had become 100%.

As measured in the pulse reactor, the rate of hydrogenolysis of ethane was about 0.13 that of propane at 250 °C and 0.5 at 300 °C. Relative to propane, the rates for butane, pentane, and neopentane at 250 °C were 1.2, 1.7, and 0.3, respectively.

The experiments so far described started with DA. One might suspect that similar material would result from heating Mo(CO)₆/PDA in hydrogen to temperatures which would lead to the formation of dehydroxylated alumina. Mo(CO)₆/PDA, He, 300°, 1; H₂, 650°, 1; He, 650°, 0.25 was titrated with oxygen at 500 °C by a pulse method. The average ON calculated from the oxygen consumption assuming Mo⁶⁺ resulted was near +2. After exposure to H₂, 800 °C, 0.25 h, ON was zero to within an uncertainty of ±0.2. Materials so prepared were investigated for the hydrogenolysis of propane at 300 °C. After H₂, 500°, N_t was about 0.001; after H₂, 650°, 0.011; after H₂, 800°, 0.34; and after H₂, 950°, 0.24 s⁻¹. In these experiments, one sample of catalyst was activated to successively higher temperatures. In another run, Mo(CO)₆/PDA, H₂, 800°, 0.5 gave N_t at 250 °C = 0.079 s⁻¹. Similar results were obtained in the pulse reactor.

A MoO₃/γ-Al₂O₃ containing 4 μmol of Mo per 0.05 g of alumina was prepared in the conventional fashion by impregnating alumina with ammonium molybdate followed by calcination at 500 °C. It was activated in H₂, 800°, 0.5. In the flow reactor this material gave N_t = 0.058 s⁻¹ at 250 °C. Relative yields in reactions 1 and 2 and E_a 's were close to those of activated Mo(CO)₆/DA

(9) Sinfelt, J. H. *Adv. Catal.* 1973, 23, 91–119. See also: Boudart, M.; Oyama, S. T.; Leclercq, L. *Proc. Int. Congr. Catal.* 7th 1980, in press. A catalyst, Mo(CO)₆/DA, He, 500°, 1; H₂, 950°, 0.25 gave for the hydrogenolysis of propane at 250 °C, N_t = 0.054 s⁻¹. After exposure to the stream of C₃H₈ + H₂ at 580 °C for 0.5 h and then to H₂, 580°, 0.08 (a treatment which might be expected to give carbiding), N_t was 0.042 s⁻¹. After H₂, 950°, 0.5, N_t was 0.050 s⁻¹.

(10) After CO poisoning, the catalyst still led to hydrogenation of 99% of a pulse of propylene at 25 °C. However, Mo/Al₂O₃ catalysts other than clean Mo(0)/DA are effective catalysts for several reactions. Clearly, the methanation of CO at 300 °C on Mo(CO)₆/DA, He, 300–500° in which both CO and H₂O are present does not proceed on clean Mo(0). The rate of hydrogenolysis of cyclopropane at 60 °C on Mo(CO)₆/DA, He, 300° is little affected by the additional pretreatment of the catalyst with H₂ at 300–950 °C, and Mo²⁺/PDA also exhibits high activity for this reaction. However, the ratio, single/double hydrogenolysis, decreases substantially as the ON of Mo increases.

as were those of Mo(CO)₆/PDA activated in hydrogen at 800 and 950 °C.

A few experiments have been run with W(CO)₆/DA. W(CO)₆/DA, He, 300°, 1; H₂, 760°, 1 was an active catalyst for the hydrogenolysis of propane in both reaction 1 and reaction 2 with an activity in the vicinity of that of Mo(CO)₆/DA with the same pretreatment.

It has not yet been possible to characterize well these Mo(0)/DA catalysts, but they might consist of molybdenum metal particles with nearly 30% exposed, supported on DA.⁵ It is also probable that the Mo²⁺ present after He, 300–500° is reduced to Mo(0) by exposure to hydrogen at high temperatures. We have no secure information as to the degree of interaction, if any, between Mo(0) and the support.

Sinfelt⁹ reported that the highest activity for the hydrogenolysis of ethane of metals which had been studied was exhibited by ruthenium and osmium. He also reported that metallic molybdenum made by reduction of MoO₂ had only a very slight activity. From his data, N_t per Ru_s would be 0.035 s⁻¹ at 250 °C under our conditions. In our work, per total Mo, N_t was 0.007 for the hydrogenolysis of ethane at 250 °C, or, if the percentage exposed of Mo is 30, N_t per Mo_s would be 0.02 s⁻¹. The origin of the apparent discrepancy between Sinfelt's work and ours is unclear. Perhaps, in the experiments of Sinfelt, MoO₂ was reduced at too low a temperature to remove surface contamination. Alternatively, the activity of our catalysts may be higher than that of bulk metallic Mo either because a much larger activity characterizes small particles of Mo or because of some kind of interaction between Mo(0) and the support.

Burch and Mitchell¹¹ have reported that a mixture of Mo and MoO₂ made by the partial reduction of MoO₂ is a very active catalyst for the skeletal isomerization of alkanes but a poor one for hydrogenolysis. Our catalysts exhibit a remarkably high activity for hydrogenolysis, but, even at 300 °C, activity for isomerization of butane, pentane, and hexane was negligible. In the work of Burch and Mitchell, the surfaces of particles of Mo(0) were unlikely to have been clean.

(11) Burch, R.; Mitchell, P. C. H. *J. Less-Common Met.* 1977, 54, 363–372.

Gas-Phase Nucleophilic Addition Reactions of Phenylnitrene Anion Radical with Certain Carbonyl-Containing Molecules¹

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Gas-phase studies of nucleophilic addition reactions to carbonyl groups with closed-shell, singlet anions are difficult unless an anionic leaving group is present in the carbonyl compound, e.g., with acid halides,² esters,³ etc. We recently reported the use of phenylnitrene anion radical (PhN⁻) to observe competitive 1,2- and 1,4-addition processes with certain α,β-unsaturated molecules.¹ We now wish to report preliminary results of ion-molecule reactions of PhN⁻, an open-shell, doublet reagent, with several simple carbonyl-containing compounds which establish the nucleophilic addition mechanism for adduct formation.⁴

(1) (a) Paper 9 in the series "Hypovalent Radicals"; for paper 8, see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.*, 1980, 102, 6146.

(b) Presented in part at the Fifth IUPAC Conference on Physical Organic Chemistry, University of California, Santa Cruz, CA, Aug 17–22, 1980.

(2) (a) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* 1979, 101, 3715.

(b) Asubiojo, O. I.; Blair, L. K.; Brauman, J. I. *Ibid.* 1975, 97, 6685.

(3) (a) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* 1976, 98, 2049. (b) Fukuda, E. K.; McIver, R. T. *Ibid.* 1979, 101, 2498.