initiation step consists of excitation of the quinone and generation of the radical cation $1^{+}\cdot$ by electron transfer from the cage compounds. The ring cleavage process of the radical cation $1^{+}\cdot$ giving the radical cation $2^{+}\cdot$, followed by a subsequent electron transfer from **1** to $2^{+}\cdot$, comprises the propagation steps. Then, the radical cation $1^{+}\cdot$ reenters the chain cycle. Reaction 4 can be considered to be reversible, because there is no gap in the oxidation potentials between **1** and **2**. However, reaction 3 involving the bond cleavage reaction releases much strain energy and cannot be reversible. Thus, the propagation sequence is promoted. The termination step involves a quenching reaction of the radical cations $1^{+}\cdot$ and $2^{+}\cdot$ with the radical anion $Q^{-}\cdot$. The absence of sensitizer radical ion from the propagation sequence probably allows the long chain lengths observed.

The detailed mechanism for the type 1 and 2 reactions is still ambiguous, but the key step must be electron transfer from the cage compounds to the electron acceptors in both cases. Since the type 2 reaction also involves a chain process, there seems no essential differentiation between the type 2 and 3 reactions. When the electron-transfer reaction occurs thermally from the cage compounds to TCNE or quinone, type 1 reaction might result. On the other hand, if the reaction requires excitation of charge-transfer complexes or sensitizers, type 2 and 3 reactions will occur.

More recently, we have discovered that the type 3 reactions of **1d** also take place with quantum yields over unity when dye sensitizers such as triphenylpyrylium and trityl salts[21] or semiconductors such as ZnO and CdS were used.[22] Thus, it could be concluded that electron-releasing properties of the cage compounds which are ascribed to their strain energies and oxidation potentials might be important factors for the cycloreversion reactions which are induced to occur by electron transfer.

Acknowledgment. Financial support was provided from the Ministry of Education, Science and Culture.

(21) K. Okada, K. Hisamitsu, T. Miyashi, and T. Mukai, to be published.
(22) K. Okada, K. Hisamitsu, and T. Mukai, *J. Chem. Soc., Chem. Commun.*, in press.

Statistical State Solvation Sites

P. K. Mehrotra, Francis T. Marchese, and David L. Beveridge*

Department of Chemistry
Hunter College of the City Univrsity of New York
New York, New York 10021
Received July 31, 1980

The structural organization of solvent molecules around a dissolved solute in solution has been discussed extensively in the recent literature in terms of solvation sites. In aqueous solutions, solvation sites are the regions in which water molecules are likely to be found in the vicinity of a dissolved molecular solute. The solvation site concept can be extended straightforwardly to molecular solutions in general.

Up to this point, solvation sites have been equivalenced with local minima in the solute–solvent potential energy hypersurface, as advanced by Pullman, Pullman, and co-workers.[1] Calculations of solvation sites based on molecular quantum mechanics have been reported for diverse biological molecules and used to discuss aqueous hydration and solvent effects on biomolecular conformational structure. The Pullman approach has generated useful insight into aqueous solvation processes but can be improved upon by including solvent–solvent interactions, temperature effects, and consideration of the statistical weight of solvation sites in the N-particle molecular assembly.[2] We offer here a new definition of solvation sites expressed on the statistical state of an N-molecule system at a given temperature in which all of the above critical points are accommodated. The procedure is illustrated by the determination of solvation sites for *trans*-glyoxal from an analysis of computer simulation results on the dilute aqueous solution, $[(HCO)_2]_{aq}$, at 25 °C.

All information about the structure of molecular solutions is in principle contained in the generic molecular distribution functions for the system, and information on solvation sites follows in principle from the analysis of these functions in the region of the first solvation shell of a solute. A general procedure for the analysis of the local solution environment of a dissolved solute from molecular distribution functions has recently been proposed from this laboratory.[3] Here the solvent molecules in the various N-molecule configurations of the system are assigned to the closest or most proximal solute atom (the proximity criterion). The subsequent analysis is organized in the general framework of quasicomponent distribution function theory.[4] By use of this approach the primary and higher order solvation of each solute atom is determined. The spatial extent of the first coordination shell of the solute can be well defined from the solute–solvent radial distribution for primary solvation. The probability density distribution for solvent molecules in the first shell can thus be determined, and the spatial probability distribution of solvent molecules in the immediate vicinity of the solute can be displayed. The further resolution of this density according to solute atoms or functional groups can be achieved by using the proximity criterion, and the analysis of these results leads to the determination of solvation sites. These sites are defined on the statistical state of the system with N-molecule interactions, temperature factors, and statistical weights taken into account and are henceforth called "statistical state solvation sites". Alternative uses of probability density maps to analyze simulation results on aqueous solutions have been described by Hagler et al.[5] and Romano and Clementi.[6]

To examine the viability of the statistical state solvation site concept, we have carried out a liquid state (T, V, N) ensemble Monte Carlo computer simulation on $[(HCO)_2]_{aq}$, represented by 1 glyoxal molecule and 215 water molecules under periodic boundary conditions at 25 °C. Ensemble averages in the calculation of properties and in the structural analyses were formed from $1000K$ configurations after equilibration, chosen on the basis of the Metropolis method. General aspects of the calculations and related recent results are reviewed in ref 7 and 8 and literature cited therein.

The primary coordination number of glyoxal in $[(CHO)_2]_{aq}$ was found to be 17.77 water molecules. The 90% probability density distribution of these molecules was determined and displayed by using computer graphics by means of the program PSI/77 by Jorgensen.[9] The results are collected in the composite Figure 1.

(1) A. Pullman and B. Pullman, *Q. Rev. Biophys.*, **7**, 505 (1975).
(2) D. L. Beveridge and G. W. Schnuelle, *J. Phys. Chem.*, **78**, 2064 (1974).
(3) P. K. Mehrotra and D. L. Beveridge, *J. Am. Chem. Soc.*, **102**, 4287 (1980).
(4) A. Ben-Naim, "Water and Aqueous Solutions", Plenum Press, New York, 1974.
(5) A. T. Hagler, D. J. Osguthorpe, and B. Robson, *Science* **298**, 599 (1980).
(6) S. Romano and E. Clementi, *Int. J. Quantum Chem.*, **17**, 1007 (1980).
(7) D. L. Beveridge, M. Mezei, S. Swaminathan, and S. W. Harrison, *ACS Sym. Ser.*, **No. 86**, 191 (1978).
(8) D. L. Beveridge, M. Mezei, P. K. Mehrotra, F. T. Marchese, V. Thirumalai, and G. Ravi-Shanker, *Ann. N.Y. Acad.* Sci., in press.
(9) W. L. Jorgensen, *QCPE*, **11**, 340 (1979).

0002-7863/81/1503-672$01.00/0

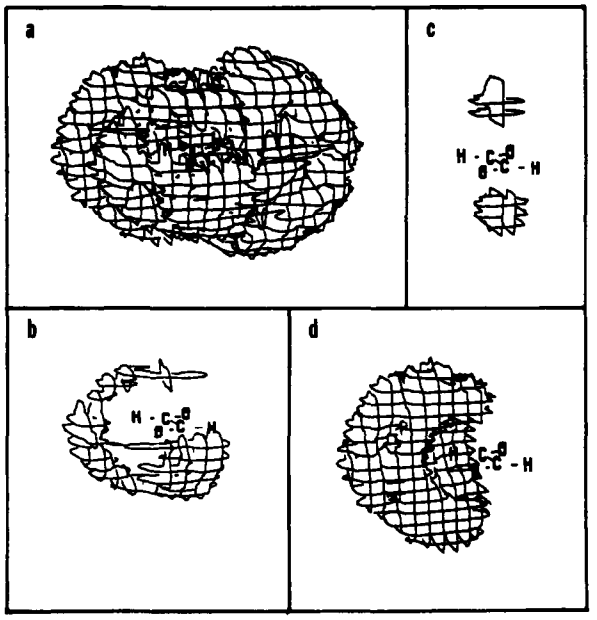

Figure 1. Calculated 90% probability densities for solvent molecules in the first solvation shell of *trans*-glyoxal in the system $[(HCO)_2]_{aq}$ at 25 °C. (a) Total molecule, (b) oxygen atom, (c) carbon atom, and (d) hydrogen atom.

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.

Acknowledgment. This research was supported by NIH Grant No. GM-24149 and a CUNY Faculty Research Award.

Molybdenum(0)/Dehydroxylated Alumina Catalysts

Ryu-ichi Nakamura, Robert G. Bowman, and Robert L. Burwell, Jr.*

Ipatieff Laboratory, Department of Chemistry Northwestern University, Evanston, Illinois 60201

Received October 6, 1980

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 MoO_3/Al_2O_3 have received considerable attention, it has appeared impracticable to reduce them to $Mo(0)/Al_2O_3$. Hydrogen at 500 °C reduces the Mo only to an average oxidation number (ON) of about +4.[1,2] Catalysts of Mo(0) supported on alumina have not been prepared and studied in the past because of the apparent difficulty in the reduction of MoO_3/Al_2O_3, because the extraordinary stability of $Mo(0)/Al_2O_3$ 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 $Mo(0)/Al_2O_3$ is readily prepared and that it exhibits some remarkable catalytic activity.

We had investigated catalysts that start as $Mo(CO)_6/\gamma\text{-}Al_2O_3$ 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 (σ-OH).[3] When $Mo(CO)_6$/PDA is heated in flowing ultrapure helium, complete loss of CO starts at about 200 °C to generate Mo(0) which is immediately oxidized to Mo^{2+} by σ-OH with concomitant liberation of H_2.[4] Above 400 °C, ON's from +4 to +6 appear. Thus, Mo(0)/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 σ-OH. Heating $Mo(CO)_6$/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]

H_2,650°,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. H_2,950°,0.25 liberated the remaining carbon as methane, since a subsequent H_2,950°,1 liberated no more methane. Most of the carbon remaining after H_2,650°,1 was removed by H_2,800°,1. Exposure of $Mo(CO)_6$/DA,He,300–500° 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 μmol) on 0.2 g of DA, treated He,500°, conversion to propane was 28%. After subsequent exposure to H_2,500° the the conversion became 100%, corresponding to a turnover frequency per atom of Mo (N_t) > 1.7 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 $Mo(CO)_6$/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, $Mo(CO)_6$/DA,He,300° is about 10 times more active than $Mo(CO)_6$/PDA,He,300°.

0002-7863/81/1503-673$01.00/0