The progress of the digestion was followed by LC[7] and by enzymatic assay for AMP[8] and appeared to be complete in 65 h. The resulting solution contained (millimoles) AMP (80), GMP (60), UMP (81), and CMP (31). Active enzyme could be recovered from the digest by ultrafiltration and reused.

An aliquot of this solution (280 mL, 50 mmol of AMP) was cooled to room temperature and diluted to 2.25 L. The pH of the solution was adjusted to pH 7.6 with 2 M Na_2CO_3, and a pH-stat was employed to maintain this pH through the subsequent reaction by addition of 2 M Na_2CO_3. Acetate kinase (E.C. 2.7.2.1, 100 U) and adenylate kinase (E.C. 2.7.4.3, 300 U) immobilized in ~200-μm particles of cross-linked poly(acrylamide-*co*-*N*-acryloxysuccinimide) gel[9] were added, together with magnesium acetate (75 mmol), ATP (0.1 mmol), and dithiothreitol (0.3 g). Diammonium acetyl phosphate (1.0 M solution) was added at 2.2 mmol h^{-1} to the stirred solution. After 44 h of addition, the reaction mixture contained (millimoles) ATP (41), ADP (5), and AMP (1).[8] These quantities correspond to a 90% selectivity for conversion of acetyl phosphate into ATP and ADP. The remainder of the acetyl phosphate was lost by hydrolysis; no di- or triphosphates of other nucleotides were detected.

This mixture was used directly in enzyme-catalyzed reactions requiring ATP recycling. For example, an aliquot (250 mL) was used to provide 7 mmol of ATP for a reaction mixture originally containing, inter alia,[10] glucose (1.0 mol), hexokinase (E.C. 2.7.11, 120 U), and acetate kinase (100 U) in 1.6 L of solution. Addition of AcP over 136 h, followed by workup as described previously,[2] yielded 110 g of solid, of which 90% (by weight) was accounted for by enzymatic assay as Ba G-6-P·$7H_2O$. The yield of G-6-P based on AcP was 51%. Similarly, 170 g (420 mmol, 97% pure by weight, 70% based on acetyl phosphate) of dicyclohexylammonium *sn*-glycerol 3-phosphate was isolated following procedures described elsewhere[3] after 72 h of operation of a reactor originally containing glycerol (500 mmol), glycerol kinase (800 U, E.C. 2.7.1.30), acetate kinase (420 U), and a 90-mL aliquot of the nucleotide solution (1.7 mmol of ATP). Both of these reactions followed a course which was qualitatively indistinguishable from that observed with similar reactions carried out with pure ATP: this observation establishes that the crude, ATP-containing, nucleotide solution serves as a satisfactory substitute for pure ATP.

Much of the expense of commercial ATP is determined by its purification. High purity is not necessary for cofactors to be used in recycling schemes, but any impurities must not interfere with the reactions nor degrade the enzymes, cofactors, reactants, or products. The mixture of nucleotides generated by this procedure contains no more than 27 mol % ATP, but, since *no* purification steps are required prior to its use in procedures involving cofactor recycling, it provides a particularly convenient source of ATP for organic synthetic use. We note, however, that pure ATP can be isolated from this mixture by conventional techniques, if required. This preparation of ATP is superior to one reported earlier based on phosphorylation of adenosine:[10] the enzymes required are all commercially available, and the cost of the starting adenosine moieties is lower.

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Photoreaction of Hexacarbonylmolybdenum(0) and Tricarbonyl(η^5-cyclopentadienyl)hydridomolybdenum(II) in the Presence of Cyclopentadiene. Substitution, Oxidative Addition, and Hydrometalation

Sir:

We report here new results pertaining to photoreaction of low-valent metal carbonyls in the presence of olefins. The systems reported on here are $Mo(CO)_6$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ irradiated in the presence of cyclopentadiene, C_5H_6. These particular systems are important inasmuch as $Mo(CO)_6$ is a known catalyst precursor under photochemical conditions for the isomerization of olefins[1] and 1,4-hydrogenation of 1,3-dienes,[2] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ is reported to be a stoichiometric reducing agent for converting 1,3-dienes into alkenes.[3] Further, C_5H_6 is a source of $\eta^5\text{-}C_5H_5$ in metal complexes, when reacted with an appropriate precursor. Generally, using light to effect an individual step in a catalytic or stoichiometric process may provide for greater specificity or rate or change the course of events altogether. In the systems under consideration here, Mo-CO dissociation is likely a thermally rate-limiting process at room temperature which can be substantively altered by optical excitation.[4,5]

Our first interest in the $Mo(CO)_6/C_5H_6$ system actually began some years ago when we attempted the photoassisted 1,4-hydrogenation of C_5H_6 to cyclopentene under the conditions[2] giving efficient hydrogenation of those 1,3-dienes which can easily achieve, or are held in, an *s*-cis conformation. Little catalytic chemistry occurred using $Cr(CO)_6$ as the catalyst precursor in the attempted hydrogenation of C_5H_6, though large spectral changes obtained upon irradiation. We now present the results of a study of the irradiation of $Mo(CO)_6$ or $Cr(CO)_6$ in the presence of C_5H_6. Irradiation (355 ± 20 nm, 2×10^{-6} einstein/min) at 25 °C of 5×10^{-3} M $Mo(CO)_6$ in a degassed isooctane solution of freshly distilled 0.1 M C_5H_6 rapidly yields chemical reaction which can be monitored by IR spectroscopy in the CO-stretching region. In accord with very early findings associated with irradiation of $M(CO)_6$ (M = Cr, Mo, W) in the presence of olefins,[6] the IR spectral changes initially correspond to formation of $Mo(CO)_5(\eta^2\text{-}C_5H_6)$ with IR bands as given in Table I (eq 1). This primary

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photoproduct, however, absorbs in the near-UV and is itself photosensitive under the conditions used to produce it.

$$\mathrm{Mo(CO)_6} \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{Mo(CO)_5} + \mathrm{CO} \xrightarrow{\mathrm{C_5H_6}} \mathrm{Mo(CO)_5(\eta^2\text{-}C_5H_6)} \quad (1)$$

Continued irradiation of the $Mo(CO)_6/Mo(CO)_5(\eta^2-C_5H_6)/C_5H_6$ mixture results in the further decline of $Mo(CO)_6$ and growth of other Mo-carbonyl species. IR bands of greater and lesser importance appear at 2043 (w), 2029 (w), 1961 (s), and 1912 (w) cm^{-1} and, ultimately, two prominent features at 1880 and 1950 cm^{-1} appear. The strong 1961-cm^{-1} feature is attributable to *trans*-$Mo(CO)_4(\eta^2-C_5H_6)_2$ on the basis of its intensity dependence in time and the fact that *trans*-$Mo(CO)_4(\eta^2$-1,3-butadiene$)_2$ has a similar feature at 1965 cm^{-1}.[6] The bands at 2043 and 1912 cm^{-1} may be due to $Mo(CO)_4(\eta^4-C_5H_6)$ or to *cis*-$Mo(CO)_4(\eta^2-C_5H_6)_2$; presumably the other two features for such complexes[7] in the 1965-1940-cm^{-1} range are obscured by the 1961- and 1957-cm^{-1} absorptions of *trans*-$Mo(CO)_4(\eta^2-C_5H_6)_2$ and $Mo(CO)_5(\eta^2-C_5H_6)$, respectively. The weak band at 2029 cm^{-1} identically matches the highest energy CO-stretching absorption of an authentic sample of $(\eta^5-C_5H_5)Mo(CO)_3H$,[8] but the 1946-cm^{-1} band of this complex is obscured. The bands at 1950 and 1880 cm^{-1} identically match those from an authentic sample of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$.[9] This product is somewhat photosensitive, and it, too, ultimately reacts. Yields of up to ~20% (based on IR absorption) $Mo(CO)_2(\eta^5-C_5H_5)\eta^3-C_5H_7)$ can be realized starting with $Mo(CO)_6$. Interestingly, the irradiation of $Cr(CO)_6$ in the presence of C_5H_6 results in IR bands at 1942 and 1880 cm^{-1} which we attribute to $Cr(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$.[10] The formation of such a product possibly accounts for our inability to effect the 1,4-hydrogenation of C_5H_6 at 1 atm of H_2 pressure, since it is formed under these conditions.

Equations 1-4 represent a plausible sequence of photochemical reactions leading to the formation of the $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$. Irradiation of $Mo(CO)_4(\eta^2-C_5H_6)_2$ may also give rise to this product; isolation and characterization of both tetracarbonyl species is of interest. However, whatever the mechanism, the product reflects the fact that C_5H_6 binds, oxidatively adds, and undergoes hydrometalation. The reactive, doubly allylic C-H bonds and the stability of $\eta^5-C_5H_5$ complexes promotes the formation of the $(\eta^5-C_5H_5)Mo(CO)_3H$ upon photogeneration of coordinatively unsaturated intermediates in the presence of C_5H_6.

$$\mathrm{Mo(CO)_5(\eta^2\text{-}C_5H_6)} \xrightarrow{h\nu} \mathrm{Mo(CO)_4(\eta^4\text{-}C_5H_6)} + \mathrm{CO} \quad (2)$$

$$\mathrm{Mo(CO)_4(\eta^4\text{-}C_5H_6)} \xrightarrow{h\nu} \mathrm{(\eta^5\text{-}C_5H_5)Mo(CO)_3H} + \mathrm{CO} \quad (3)$$

$$\mathrm{(\eta^5\text{-}C_5H_5)Mo(CO)_3H} + \mathrm{C_5H_6} \xrightarrow{h\nu} \mathrm{Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)} + \mathrm{CO} \quad (4)$$

Irradiation of an authentic sample of $(\eta^5-C_5H_5)Mo(CO)_3H$[11] in the presence of C_5H_6 leads to the clean formation of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$[12] according to eq 4. Inasmuch as the hydride is conveniently synthesized, eq 4 represents the synthetic procedure of choice for $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$. The 355-nm quantum yield is 0.12 ± 0.02. Figure 1 shows the IR spectral changes accompanying a typical photoreaction. We conclude that the formation of product proceeds via photogeneration of $(\eta^5-C_5H_5)Mo(CO)_2H$ followed by thermal reaction with C_5H_6. An alternative mechanism involving $(\eta^5-C_5H_5)Mo(CO)_3$ radicals as in the simple substitution of $(\eta^5-C_5H_5)Mo(CO)_3H$[13] appears to be ruled out by the following experiment. Visible light (514.5 nm) irradiation of $(\eta^5-C_5H_5)_2Mo_2(CO)_6$ in the presence of $(\eta^5-C_5H_5)Mo(CO)_3H$ and C_5H_6 does not lead to $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$. $(\eta^5-C_5H_5)_2Mo_2(CO)_6$ is a known photochemical source of $(\eta^5-C_5H_5)Mo(CO)_3$ radicals.[14] Irradiation of $(\eta^5-C_5H_5)Mo(CO)_3H$ in the presence of other dienes such as *trans*-1,3-pentadiene, *trans,trans*-2,4-hexadiene, 1,4-pentadiene, and 1,2,3,4,5-pentamethylcyclopentadiene results in IR spectral changes consistent with the formation of $Mo(CO)_2(\eta^5-C_5H_5)(\eta^3$-allyl) complexes. Establishing the role of such complexes in the formation of alkenes from 1,3-dienes using $(\eta^5-C_5H_5)Mo(CO)_3H$ is the object of continuing studies in this laboratory.

Table I. Infrared Spectral Band Maxima for Pertinent Complexes

complex	band maxima, cm^{-1} (ϵ, M^{-1} cm^{-1})[a]
$Mo(CO)_6$	1988 (53 800)
$\eta^5-C_5H_5)Mo(CO)_3H$	2029 (5340); 1946 (9190)
$Mo(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7)$	1950 (6290); 1880 (6010)
$Mo(CO)_5(\eta^2-C_5H_6)$	2079 (*1*), 1957 (*8*), 1944 (*4*)
trans-$Mo(CO)_4(\eta^2-C_5H_5)_2$	1961 (. . .)
$Cr(CO)_6$	1987 (51 700)
$Cr(CO)_2(\eta^5-C_5H_5)(\eta^3-C_5H_7$	1942 (*1.14*), 1880 (*1.0*)

[a] All data were recorded at 25 °C in alkane solvent employing a Perkin-Elmer 180 IR spectrometer. Numbers in parentheses which are italicized represent relative absorbance for that complex.

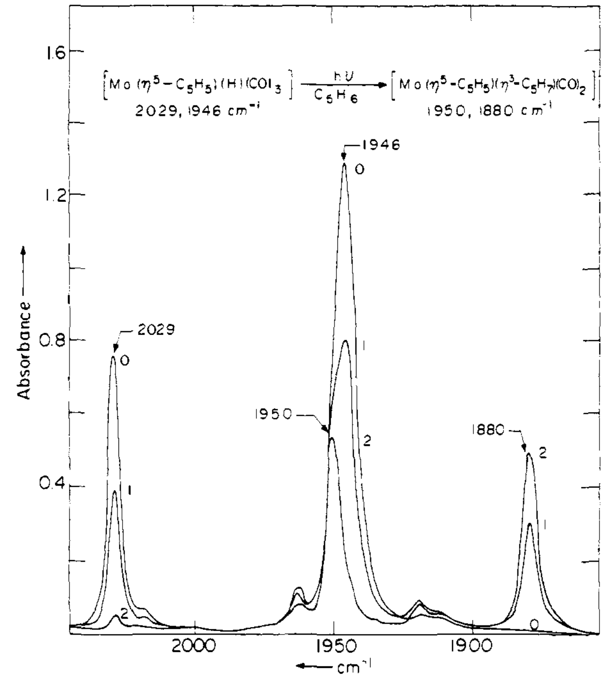

Figure 1. Infrared spectral changes accompanying 355 ± 20 nm irradiation (2×10^{-6} einstein/s) of degassed 1.0-mL isooctane solutions of 1.4×10^{-2} M $(\eta^5-C_5H_5)Mo(CO)_3H$ and 0.6 M C_5H_6. Trace 0 was before exposure to the irradiation and curves 1 and 2 are after 0.5 and 4.0 h of irradiation, respectively. IR spectra were recorded in 0.1-mm path-length NaCl cells.

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(11) (η^5-C$_5$H$_5$)Mo(CO)$_3$H was prepared according to the literature procedure:[8]

$$\mathrm{Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \xrightarrow{Na/Hg} 2[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^-}$$
$$\mathrm{\xrightarrow{H^+} 2[(\eta^5\text{-}C_5H_5)Mo(CO)_3(H)]}$$

(12) The Mo(CO)$_2$(η^5-C$_5$H$_5$)(η^3-C$_5$H$_7$) isolated from the photoreaction was characterized by IR, ^{1}H NMR, and mass spectroscopy.
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Monte Carlo Computer Simulation of Hydrophobic Bonding

Sir:

The tendency of nonpolar solutes to associate spontaneously in aqueous solution at ordinary laboratory and physiological temperatures is presently recognized as one of the primary organizing principles of structural biochemistry and biology. A theoretical account of this phenomena, the hydrophobic interaction, was advanced by Kauzmann[1] some years ago and is now widely accepted.[2] However, it is clear from diverse recent contributions to the problem[3-5] that some detailed theoretical aspects of the process remain controversial. We report herein the first fully ab initio theoretical calculation of the hydrophobic interaction of nonpolar molecular solutes in liquid water, and comment on one currently debated point, the behavior of the solvent averaged interaction between hydrocarbon moieties as a function of separation. The prototype molecular system for the theoretical study of hydrophobic bonding is the dilute aqueous solution of two methane molecules, $[(\mathrm{CH_4})_2]_{\mathrm{aq}}$.

In a series of recent contributions to this journal,[6-8] we reported statistical thermodynamic Monte Carlo computer simulation studies of the structure of liquid water and the dilute aqueous solution of methane, $[\mathrm{CH_4}]_{\mathrm{aq}}$, at 25 °C. The calculations were based on pairwise additive analytical potential functions representative of quantum mechanical calculations of intermolecular interactions.[9,10] The calculated structure of liquid water corresponded most closely to the energetic continuum model, and produced an average water coordination number of 4.2.[6] For $[\mathrm{CH_4}]_{\mathrm{aq}}$, clathrate-like contributions to the local solution environment of methane were directly identified, and the average methane coordination number was calculated to be 19.35.[7] The solvent in the vicinity of the solute was found to be ordered and energetically stabilized with respect to bulk water, independently confirming the prevalent conceptual model of hydrophobic hydration. For later reference, the aqueous phase effective radii for water and methane are $R_{\mathrm{H_2O}} = 1.38$ and $R_{\mathrm{CH_4}} = 2.2$ Å, estimated from the position of the first minima in our calculated radial distribution functions.[6,7]

We have recently extended our studies of water structure and hydrophobic hydration to problems in hydrophobic bonding. In computer simulation, the essential features of the hydrophobic interaction can be described in terms of a solvent averaged mean force $\langle F_z(R)\rangle$ between solute molecules as a function of the intersolute center-of-mass separation, R, and by the corresponding potential of mean force, $W(R)$. Recently, Pratt and Chandler[4] studied the interaction of spherical apolar species in a model water based on an integral equation method and predict an oscillatory behavior in $\langle F_z(R)\rangle$, implicating this result in a novel proposal for the folding of hydrocarbon chains. This contravened early Monte Carlo work on the problem by Dashevsky and Sarkisov[11] and the recent theoretical study by Clark et al.[5] based on the hypernetted chain approach. Pangali et al.[12] note a similar behavior for $\langle F_z(R)\rangle$ in molecular dynamics on Xe$_2$ in ST2 water. The calculations on $[(\mathrm{CH_4})_2]_{\mathrm{aq}}$ reported herein introduce independent molecular level information on this problem and, by reference to our corresponding work on $[\mathrm{H_2O}]_{\mathrm{l}}$ and $[\mathrm{CH_4}]_{\mathrm{aq}}$, provide a structural interpretation of the $\langle F_z(R)\rangle$ results.

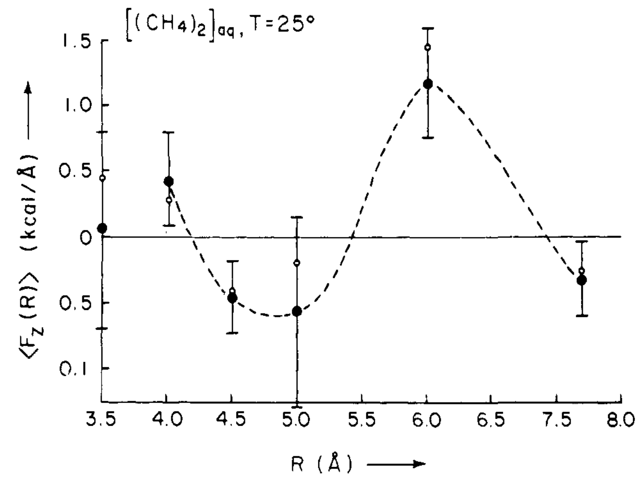

Figure 1. Calculated $\langle F_z(R)\rangle$ vs. R for $[(\mathrm{CH_4})_2]_{\mathrm{aq}}$. The dots represent values computed by the direct procedure of ref 14. The circles represent values determined in an independent check based on finite differences. The error bars were established for each solid point from the corresponding maximum $[F_X(R), F_Y(R)]$.

Our computer simulation on $[(\mathrm{CH_4})_2]_{\mathrm{aq}}$ involved a system of two methane molecules and 214 water molecules at a temperature of 25 °C and a density calculated from the observed[13] partial molar volumes of methane (37 cm^3/mol) and water (18.06 cm^3/mol). The water-water and methane-water intermolecular potential functions and other characteristics of the calculations on $[(\mathrm{CH_4})_2]_{\mathrm{aq}}$ were chosen to correspond as closely as possible to previous calculation on $[\mathrm{CH_4}]_{\mathrm{aq}}$, and the formalism and further detail is available in ref 8. The principle additional quantities computed here are the solvent-averaged forces $\langle F_i(R)\rangle$ ($i = x, y, z$) experienced by the center-of-mass of solute methane, determined here by the procedure suggested by McDonald and Rasaiah.[13] In an exact calculation, $\langle F_X(R)\rangle$ and $\langle F_Y(R)\rangle$ would be expected to be zero, while $\langle F_z(R)\rangle$, the force along the intersolute coordinate, may be nonvanishing, and will be zero at the maxima and minima points in $W(R)$. In numerical calculations the residual magnitudes of $\langle F_X(R)\rangle$ and $\langle F_Y(R)\rangle$ can be used to estimate error bounds on the calculated $\langle F_z(R)\rangle$ (Figure 1). The solvent averaged force is expected to be the dominant contribution to total force between nonpolar species in aqueous solution, as in the model system in ref 14.

Separate calculations were carried out for six solute intermolecular separations between 3.5 and 7.20 Å. The force calculations are each based on 800K to 1000K Monte Carlo Metropolis configurations after equilibration of the system. Each calculation required ~12 h on the CUNY IBM 370/168

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