Table I. Second-Order Rate Constants $k_{ex}^{(2)}$ for Electron Exchange in the Ion Radicals $1\text{-}C_2H_5N^{-\cdot}$ and $n\text{-}C_4H_9PI^{-\cdot a,b}$

T	η	$10^{-8}k_{ex}^{(2)}$	$10^{-8}k_{diff}$	T	η	$10^{-8}k_{ex}^{(2)}$	$10^{-8}k_{diff}$
$1\text{-}C_2H_5N^{-\cdot}$ in DME–2% HMPA^c				$1\text{-}C_2H_5N^{-\cdot}$ in HMPA^c			
-60	1.69	0.88	24	30	3.03	7.1	22
-30	0.93	2.3	58	15	4.24	5.0	15
0	0.61	4.2	100	0	6.23	3.0	10
$E_a = 3.0$ kcal/mol				$E_a = 4.0$ kcal/mol			
$n\text{-}C_4H_9PI^{-\cdot}$ in DME–2% HMPA				$n\text{-}C_4H_9PI^{-\cdot}$ in HMPA			
0	0.61	1.2	100	0	6.23	1.8	10
20	0.48	1.8	130	15	4.24	2.7	15
40	0.39	2.9	180	30	3.03	4.2	22
$E_a = 3.6$ kcal/mol				$E_a = 5.2$ kcal/mol			
$E_{a,diff} = 2.7$ kcal/mol				$E_{a,diff} = 4.5$ kcal/mol			

^{a} 1-Ethylnaphthalene: *N*-butylphthalimide. Data from ref 1b and 2b. ^{b} Appropriate units are T in K, $k_{ex}^{(2)}$ and $k_{diff}^{(2)}$ in M^{-1} s^{-1}, η, solvent viscosity, in cP; $k_{diff}^{(2)}$ calculated from $k_{diff}^{(2)} = 8RT/3000\eta$. ^{c} DME is 1,2-dimethoxyethane; HMPA is hexamethylphosphoramide.

Table II. First-Order Rate Constants $k_{ex}^{(1)}$ for Electron Exchange in the Ion Radicals $N\text{-}(CH_2)_m\text{-}N^{-\cdot a}$

M	6	8	10	12	16	20	η
At 0 K							
$10^{-7}k_{ex}^{(1)}$(DME)^b	2.5	1.3	1.1	0.88	0.56	0.42	0.61
$10^{-7}k_{ex}^{(1)}$(HMPA)	2.3	1.8	1.6	1.1	0.70	0.55	6.23
At 15 K							
$10^{-7}k_{ex}^{(1)}$(DME)^b	3.3	1.7	1.5	1.3	0.70	0.52	0.51
$10^{-7}k_{ex}^{(1)}$(HMPA)	4.4	2.8	2.3	1.8	1.1	0.74	4.24

^{a} $k_{ex}^{(1)}$ in s^{-1}, viscosity (η) in cP. ^{b} DME–2% HMPA.

As Halpern[6] has pointed out, this model is valid only for groups on the ends of a freely jointed chain. Hydrocarbon chains have fixed bond angles and limited rotational angles. Chains of this length have access to only a relatively small number of conformations. Thus while the chains serve to keep the end groups from separating, they also tend to keep them apart. Experimental values for C_{eff}, from the work of Mandolini and Illuminati,[7] are often much smaller than C_{min}. For their reactions, by an S_N2 mechanism, $k^{(2)}$ is 10 to 12 orders of magnitude slower than the diffusion-controlled rate constant.

Diffusion processes are sensitive to solution viscosity. Over limited viscosity domains, diffusion rates are inversely proportional to solution viscosity. This behavior has been observed for k_{diff}[8] for rotational diffusion,[9] for internal motion in hydrocarbon chains,[10] and for end-to-end cyclization dynamics probed by fluorescence techniques in polypeptides,[4c] polystyrene,[11] and poly(ethylene oxide).[12] Even more important is recent evidence that conformational transitions both in small molecules[13] and polymers[14] depend upon solvent viscosity. The definitive test as to whether $k_{ex}^{(1)}$ is sensitive to cyclization dynamics is whether it is sensitive to the viscosity of its environment.

For PI–$(CH_2)_m$–PI$^{-\cdot}$, Shimada and Szwarc point out that there is no sensitivity to solvent viscosity. For N–$(CH_2)_m$–N$^{-\cdot}$, electron exchange occurs slightly faster in HMPA than in DME–HMPA for all chain lengths and temperatures examined (Table II) in spite of the tenfold higher viscosity of the former solvent. These results are best explained in terms of a conformationally controlled reaction, which, because of ion–pair effects, has a larger reactive volume in HMPA than in DME.

Hydrogenations with Molybdenum Hydrides Formed in the Reaction of Molybdenum Atoms with Tetrahydrofuran
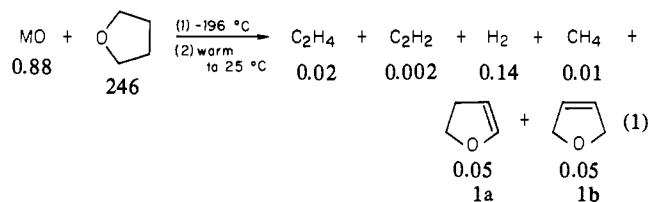
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There have been several investigations in which the high reactivity of metal atoms[1] has been utilized to effect insertion of a metal into carbon–hydrogen[2,3] and carbon–carbon bonds.[2] Studies of the deposition of metal atoms into inert matrices in order to create slurries with high catalytic activity for processes such as hydrogenation have also been reported.[4] In this communication, we report the reaction of molybdenum atoms with tetrahydrofuran (THF) in which molybdenum hydrides are formed and may be used to effect hydrogenations of added olefins.

When Mo atoms, generated in an apparatus similar to that described by Dobson, Remick, Wilburn, and Skell,[5] are cocondensed with THF at −196 °C, the volatile products shown in eq 1 along with their millimolar yields have been identified.[6] An

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Table I. Hydrogenations of Alkenes by the Mo-THF Matrix[a]

	reactants, mmol				products, mmol					
	Mo	THF	alkene							
1	1.85	184	⌇	0.571	⌇	0.027	⌇	0.013	⌇	0.475
2	2.25	172	⌇	0.540	⌇	trace	⌇	0.008	⌇	0.428
3	1.90	172	⌇	0.524	⌇	0.017	⌇	0.063	⌇	0.309
4	2.28	221	⌇	0.588	⌇	0.281	⌇		⌇	0.132
5	3.03	172	⌇	0.691	⌇	0.004	⌇	0.002	⌇	0.592
						0.101				
6	0.928	209	==	0.540	==	0.018	⌇	0.085	⌇	0.032
7	1.04	218	1-octene	0.410	1-octene	0.071	*n*-octane	0.085		
8[b]	1.37	308	⌇	0.717	⌇	0.025	⌇	0.003	⌇	0.029
					⌇	0.047	⌇	0.027	⌇	0.138

[a] The olefin was added at -196 °C after condensation of the Mo-THF was completed. In all cases except entry 8 the reaction vessel was then warmed to 25 °C and allowed to stand 1.5 h, and the products were analyzed. [b] In this case the mixture was allowed to stand 1.5 h at -78 °C and products volatile at this temperature were pumped off and analyzed. The second line of this entry shows product distributions after standing an additional 1.5 h at 25 °C.

interesting feature of this system is the fact that relatively large amounts of hydrogen are formed. This hydrogen is not simply the result of pyrolysis of THF during condensation; if this were the case, the majority of the hydrogen would be pumped out during condensation at the low pressures (10^{-5} torr) employed for Mo vaporization.[7] In our experiments, the hydrogen does not appear until condensation is complete and the reactor is warmed to approximately -78 °C.

We propose that the hydrogen results from insertion of the Mo into a C–H bond of THF to generate molybdenum hydride **2** which may be stabilized by coordination to additional THF molecules (eq 2). A subsequent β-hydrogen transfer generates
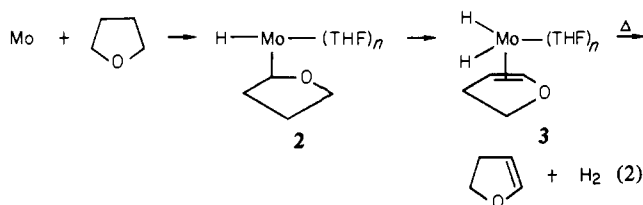

dihydride **3** which can lose hydrogen and the dihydrofurans **1a** and **1b** on warming. The fact that yields of **1a** and **1b** are not as high as that of the hydrogen is most likely a result of the fact that these species are not released from the Mo as easily upon warming as is hydrogen.

In view of the fact that metal hydrides have often been utilized to effect hydrogenations of alkenes,[8,9] we have investigated the possibility that hydrides formed by the sequence in eq 2 would hydrogenate added olefins. We have found that cocondensation of Mo with THF followed by addition of 1-butene to the matrix *after* condensation of the metal brings about hydrogenation of the alkene.

This hydrogenation occurs in the absence of added hydrogen gas with THF serving as the source of hydrogen. We feel that this reaction proceeds via initial coordination of the alkene to **2** followed by insertion of the alkene into the Mo–H bond. A subsequent β-hydrogen transfer generates an alkylmolybdenum hydride coordinated to dihydrofuran, **4**. A reductive elimination

of the alkene completes the process which is summarized in eq 3. Although the sequence in eq 3 represents only a working
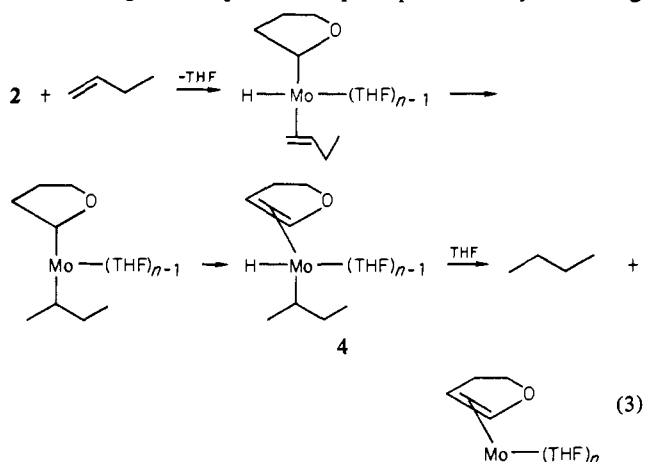
hypothesis at this time, it is analogous to the mechanism of hydrogenation that has been proposed for many metal hydrides.[8a] The process presumably has as its thermodynamic driving force the fact that the double bond in dihydrofuran is more stable than that in 1-butene by ~7 kcal/mol. Table I shows that we have been able to reduce a number of unsaturated hydrocarbons in this manner, even at temperatures as low as -78 °C (entry 8).[6] The results of hydrogenation of both 1,3-butadiene and 1,2-propadiene, shown in Table I, demonstrate that conjugated and cumulated dienes may also be reduced. The mechanisms of these interesting hydrogenations are currently under study. The fact that 2-methylpropene undergoes less hydrogenation than the other butenes may be a result of steric inhibition by the geminal methyl groups.

Control experiments indicate that we are not simply observing a catalytic hydrogenation over Mo. Thus, Mo (1.7 mmol) was cocondensed with THF (246 mmol), the matrix was warmed to 25 °C, and the volatile materials were pumped out. The residue in the reaction vessel was cooled to -196 °C and 1-butene (0.610 mmol) and hydrogen (10.6 mmol) were added. Analysis of the contents of the vessel after 1.5 h at 25 °C revealed butane (0.108 mmol), 1-butene (0.386 mmol), (*E*)-2-butene (0.017 mmol), and (*Z*)-2-butene (0.010 mmol). Thus the recovered hydrocarbons contain only 20% butane when a 17-fold excess of hydrogen is added. This result is in contrast to entry 1 in Table I in which the butene is added before warming and no hydrogen is added, and the recovered hydrocarbons contain 92% butane. The addition of a large excess of 1-butene (40 mmol) and H_2 (40 mmol) to the Mo–THF matrix before warming does not result in any more hydrogenation of the butene than is observed with 0.571 mmol of 1-butene and no added hydrogen.

(6) Hydrogen was pumped from the reactor, trapped on activated charcoal at -196 °C, and analyzed by gas chromatography. Other products were quantitated by gas chromatography and their structures confirmed by infrared spectroscopy and/or mass spectrometry.

(7) Control experiments demonstrate that H_2 will not stick to a preformed Mo surface at -196 °C under the rapid pumping conditions employed in these studies.

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The mechanisms postulated in eq 2 and 3 invoke the intermediacy of both metal–hydrogen and metal–carbon σ bonds. Since the reduction of CCl_4 to $CHCl_3$ is a reaction characteristic of transition-metal hydrides,[10] we have added an excess of CCl_4 to the Mo–THF matrix at -196 °C. This reaction yields 0.15 mmol of $CHCl_3$ when 1.79 mmol of Mo is vaporized. Direct evidence for the intermediacy of carbon–molybdenum σ bonds in these reactions has not been obtained. Hydrolysis with D_2O cannot show deuterium incorporation in the hydrogenation products as water inhibits the hydrogenation. A search for deuterium incorporation in THF recovered after addition of D_2O to the Mo–THF matrix is hampered by the fact that a large excess of THF is employed. Skell, Williams-Smith, and McGlinchey[11] were able to overcome this problem in the reaction of metal atoms with propene by removing the excess propene before hydrolysis. However, in the present case, the Mo–THF complex appears to decompose at a lower temperature than is convenient for removal of THF. In any case, the search for molybdenum carbon σ bonds using hydrolysis techniques may not be conclusive, since the metal alkyl **2** may represent only a small component of the equilibrium in eq 2.

The mechanism in eq 3 involves a series of equilibria in which ligands are added to and removed from the molybdenum. If this is the case, addition of a ligand which forms strong bonds to molybdenum(0) should displace the equilibria in such a way as to produce a stable molybdenum complex. Accordingly, we have added carbon monoxide to the matrix after cocondensing Mo and THF. Upon warming the matrix to 25 °C, $Mo(CO)_6$ is isolated in 8.5% yield based on vaporized Mo. Although eq 3 depicts intermediates which are monomeric in molybdenum, we cannot be sure that this is the case. The fact that $Mo(CO)_6$ can be isolated may implicate a monomeric molybdenum species.

Although there is ample evidence for the formation of hydrides in metal atom reactions,[2,3,12] this is the first report of the utilization of such hydrides to effect hydrogenation of olefins. Klabunde, Davis, Hattori, and Tanaka[13] have condensed Ni atoms with various solvents to obtain substances which are effective hydrogenation catalysts upon addition of H_2. Klabunde and Murdock[14] have observed that alkyl halides can be partially reduced by a Ni–THF slurry with THF serving as the source of hydrogen. We are currently extending our investigations to other ethers in order to develop a system in which catalytic transfer of hydrogen from ether to olefins will occur.

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Regiospecific A,C- and A,D-Disulfonate Capping of β-Cyclodextrin

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Received August 19, 1980

Cyclodextrins exhibit unique and significant characteristics to provide hydrophobic recognition sites in aqueous solution, which are often conveniently and successfully utilized as (part of) enzyme models.[1] However, preparation of more refined and sophisticated

Scheme I[a]

β-CD-A, D-I$_2$ + β-CD-A, C-I$_2$
5   6
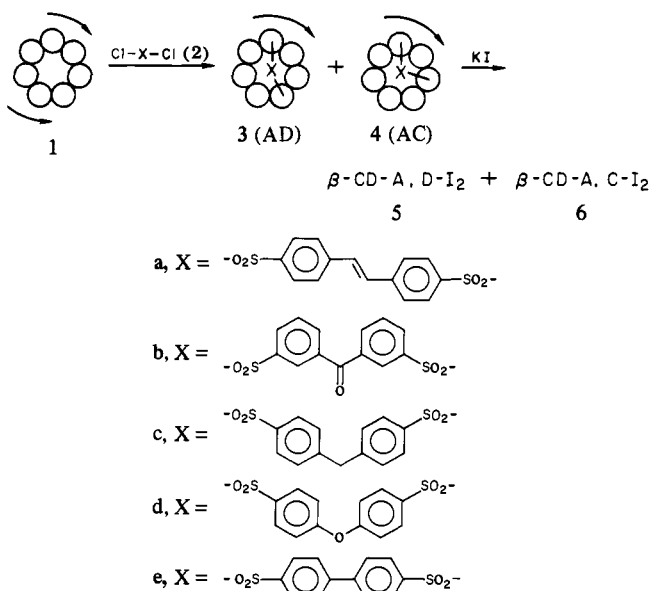
[a] Arrow indicates molecular asymmetry.

Table I. Positional Isomer Distribution of the Capping

capping reagent 2	capped β-cyclodextrin	
	3 (AD)	4 (AC)
a	nearly exclusive	very small
b	small	nearly exclusive
c	nonselective	
d		

enzyme models requires the introduction of efficient catalytic sites onto the recognition sites, mostly consisting of two or more cooperating functional groups in appropriate spacial arrangements, as found in the enzyme catalysis, for instance in the so-called charge-relay system, Asp^{102} . . . His^{57} . . . Ser^{195} of chymotrypsin.

This type of bifunctionalization was investigated by us, leading to the successful preparation of transannularly bifunctionalized β-cyclodextrins[2] through rigid capping[3] with 1,1'-methylenebis-(benzene-4-sulfonyl chloride) (**2c**). Starting from our capped cyclodextrin as well as Breslow's,[4,5] beautiful enzyme models of bifunctional catalysis with hydrophobic recognition were provided.[4–6]

This transannular capping with **2c** is not regiospecific but gives isomers AC, substituted at A,C rings, and AD[4] (see Scheme I). Now we wish to report that regiospecific disulfonate capping was first achieved with *trans*-stilbene-4,4'-disulfonyl chloride (**2a**) for A,D and benzophenone-3,3'-disulfonyl chloride (**2b**) for A,C positions, respectively.

Thus, 2 g of β-cyclodextrin dissolved in 50 mL of pyridine was treated with 0.68 g of **2b** at 60 °C. After 1 h, crude capped cyclodextrin **4b** was obtained by the usual workup and purified by repeated flush column chromatography to give pure **4b** in 40% yield. Spectra: NMR (Me_2SO-d_6) δ 3.3 (42 H), 4.73 (C_1–H, 7 H), 4.30, 5.53 (C_2, C_3, C_6–OH, 19 H), 7.70, 7.87 (aromatic,

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