Concerted Dihydrogen Exchange between Methanol and Formaldehyde. A Theoretical Study

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Abstract: A detailed examination of the concerted dihydrogen transfer mechanism which transfers hydrogens from methanol to formaldehyde has been carried out at ab initio levels (3-21G, 6-31G*) and semiempirical levels (MNDO, MNDOC). The transition structure has C_{2v} symmetry at the ab initio and MNDO levels, and the reaction has a 30 kcal/mol enthalpic barrier predicted at the 6-31G* level including correlation effects and zero point correction. The MNDO method predicts thermodynamic properties and kinetic isotope effects (KIE) in good agreement with ab initio results. However, the MNDO enthalpic barrier disagrees with the ab initio barrier by over 50 kcal/mol. The catalytic effect of water on the mechanism has been studied by both methods and is found to have an enthalpic barrier similar to the uncatalyzed mechanism at the 3-21G and 6-31G* levels. Thermodynamic properties are calculated at elevated temperatures in order to predict reaction conditions under which evolution of products might be expected. Kinetic isotope effects and tunneling coefficients are also calculated and discussed.

The intermolecular concerted dihydrogen transfer, as exemplified by the hydrogenation of ethylene by ethane in eq 1, is of considerable interest to both theoreticians and experimentalists.

$$H_3CCH_3 + H_2C{=}CH_2 \rightarrow H_2C{=}CH_2 + H_3CCH_3 \quad (1)$$

The well-known hydrogenation of olefins by diimide,[1] the hydrogen exchange between *cis*-9,10-dihydronaphthalene and various olefins[2] and the transfer of hydrogen from hydroxymethylene to alkenes[3] are examples of this reaction. The reaction in eq 1 has been used as an example of Woodward–Hoffman symmetry allowed reactions.[4] A quantitative theoretical analysis of this reaction has been carried out by Feller, Schmidt, and Ruedenberg[5] who found a barrier of between 69 and 77 kcal/mol which was relatively insensitive to basis set at the SCF or MCSCF-FORS levels. The symmetric structure was determined to be a transition structure at the 3-21G level. A theoretical study[3] of the reaction of hydroxymethylene with ethylene found that at the 3-21G level both hydrogens have transferred to approximately the same extent in the transition structure. Other studies[6–12] of coupled hydrogen motion include the free base porphine,[6–8] azophenine,[6,10] and acetic acid/methanol.[6,9] Most analogous to the present work is an experimental study[11] of the oxidation of glucose 6-phosphate by a reactant that accepts a hydride ion and is catalyzed by an enzyme which simultaneously accepts a proton.

Another example of a degenerate dihydrogen exchange is that between methanol and formaldehyde (eq 2) which has been predicted[13] by MNDO to have a high barrier of 87.2 kcal/mol.

$$H_3COH + H_2C{=}O \rightarrow H_2C{=}O + H_3COH \quad (2)$$

In the present investigation, a detailed study of this reaction is carried out at the ab initio as well as the MNDO levels. These investigations reveal a significant difference between the barriers calculated by semiempirical and ab initio methods. MNDO has been used extensively for studies of reaction mechanisms and found to yield reasonable results. The present disagreement in predicted barrier heights between the two methods may have implications for types of reactions which may not be accurately modelled by the MNDO method.

Method of Calculation

The semiempirical calculations were carried out by using the MNDO[14] or MNDOC[15] programs. The MNDO method has been used to calculate a number of properties including activation energies,[14,16a] frequencies,[16b] electronic excited states,[16c] isotope effects,[16d] electron affinities,[16e] proton affinities,[16f] and others.[16g] MNDOC[15b] is a reparameterized version of MNDO which explicitly includes the effects of correlation via the BWEN perturbational approach. Although ground-state properties are similarly well reproduced, MNDOC seems to do much better than MNDO in predicting activation energies.[15c]

The ab initio calculations were carried out at several different levels.[17] Initially geometries were optimized at the 3-21G level. By using the

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Table I. Calculated Energies (–hartrees), Zero Point Energies (kcal mol^{-1} at 0K), Entropies, and Heat Capacities (cal deg^{-1} mol^{-1} at 298 K, 1 atm) at the MNDO and ab Initio Levels

parmtr	H_2O	$H_2C{=}O$	H_3COH	TS_2[a]	TS_7[b]
			MNDO geometry		
ΔH_f[c]	-60.9	-33.0	-57.4	-3.2	-41.0
ZPE	14.43	17.99	33.95	49.72	67.81
S	44.93	52.23	57.02	67.09	91.30
			3-21G geometry[d]		
3-21G	75.58596	113.22182	114.39802	227.55013	303.15232
6-31G	75.98454	113.80827	114.98760	228.71210	304.69944
6-31G*	76.00977	113.86529	115.03378	228.81046	304.80983
MP2/6-31G	76.11295	114.02473	115.20295	229.16998	305.28980
ZPE	13.67	18.18	34.19	51.97	67.66
S	45.09	52.14	56.64	66.40	78.53
C_v	5.99	6.25	8.42	13.90	21.39
			6-31G* geometry[e]		
6-31G*	76.01075	113.86633	115.03542	228.81380	304.81434
MP2/6-31G*	76.19837	114.17259	115.35217	229.47278	305.67265
ZPE	14.42	18.32	34.72	51.61	66.10
S	44.99	52.10	56.56	67.03	76.36
C_v	5.99	6.26	8.34	14.15	20.78

[a] Transition structure for eq 2. [b] Transition structure for eq 7. [c] Heats of formation in kcal/mol. [d] Thermodynamic properties (ZPE, S, C_v) are calculated at the 3-21G//3-21G level. [e] Thermodynamic properties are calculated at the 6-31G*//6-31G* level.

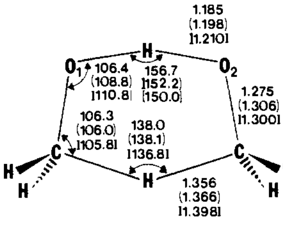

Figure 1. Structural parameters for the transition structure of eq 2. Values are for the 6-31G* basis, (3-21G), and [MNDO].

3-21G geometries, single point calculations were made at the 6-31G* and MP2/6-31G levels in order to determine relative energies at the additivity level[18] (i.e., [MP2/6-31G*]//3-21G). In the next level of approximation, geometries were optimized at the 6-31G* level, and single point calculations were made at the MP2/6-31G* level. Further, frequency calculations were made at the 3-21G and 6-31G* levels in order to determine zero point energy[19a] and other thermodynamic properties.[19b,c] Table I contains various molecular properties (energies, heat capacities, zero point energies) for species calculated at different levels while Table II contains activation parameters calculated at different levels.

Results and Discussion

Ab initio and semiempirical methods agree on the geometry of the C_{2v} transition structure (Figure 1), predicting that the C–O distances in the transition structure are nearly the same as the average CO distances in formaldehyde and methanol (Table III). The hydrogen transferring between two oxygens is nearly linear (156.7°, 6-31G*) in contrast to the hydrogen transferring between two carbons which is more bent (138.0°, 6-31G*).

Comparing the Mulliken charges of the transferring hydrogens in the transition structure to the charges in methanol, one sees a 0.145*e* decrease (more positive) in the charge of the hydrogen between the two oxygens at the 6-31G* level (0.114*e*; 3-21G) and a 0.188*e* increase (more negative) in the charge of the hydrogen between the two carbons (0.161*e*; 3-21G). Clearly the changes in the charges are in the direction of a proton transfer between oxygens and hydride transfer between carbons.

Table II. Thermodynamic Properties[a] and Isotope Effects[b] in Concerted Dihydrogen Transfer Reactions

	MNDO	[MP2/6-31G*]// 3-21G	MP2/6-31G*// 6-31G*
		Reaction 2[c]	
$\Delta H^‡$	87.2	38.8	31.2
$\Delta S^‡$	-42.2	-42.1	-41.6
$\Delta C_p{}^‡$		-2.8	-2.4
KIE(6D)	3.31	2.5	3.0
KIE(ODO)	2.19	1.7	2.0
KIE(ODO, CH_2DCH_2)	3.36	2.7	3.2
KIE(CH_2DCH_2)	1.48	1.6	1.6
KIE(CD_2HCH_2)	0.76	0.9	0.9
		Reaction 7[d]	
$\Delta H^‡$	110.2	44.8	30.3
$\Delta S^‡$	-62.88	-75.0	-77.3
$\Delta C_p{}^‡$		-3.3	-3.8
KIE(8D)[e]	2.10	3.4	5.0
KIE(2ODO)	1.06	2.4	3.3
KIE(CH_2DCH_2)	1.83	1.5	1.6

[a] $\Delta H^‡$ in kcal mol^{-1} at OK and $\Delta S^‡$, $\Delta C^‡$ in cal deg^{-1} mol^{-1} at 298 K, 1 atm. [b] Evaluated for all the hydrogen case compared to a deuterium substituted case (number and location of deuteriums are given in parentheses) at 700 K. Isotope effects are evaluated at the 3-21G//3-21G and 6-31G*//6-31G* levels. [c] $H_3COH + H_2C{=}O \rightarrow H_2C{=}O + H_3COH$. [d] $H_3COH + H_2C{=}O + H_2O \rightarrow H_2C{=}O + H_3COH + H_2O$. [e] For purposes of calculating isotope effects at the 6-31G*//6-31G* level, the smaller imaginary mode of 167i cm^{-1} was treated as a real mode.

Table III. Comparison of Geometric Parameters (Å) in the Reactants and Transition Structure of the Reaction $CH_2{=}O + CH_3OH \rightarrow CH_3OH + CH_2{=}O$

comparison	MNDO	3-21G	6-31G*
av C–O distance in $CH_2{=}O$ and H_3COH	1.304	1.324	1.292
C–O distance in transtn structure	1.300	1.306	1.275

One of the most significant results of the present study is the relatively low barrier for this reaction as predicted by ab initio methods. The barrier is calculated to be 38.8 kcal/mol at the additivity level with zero point correction ([MP2/6-31G*]//3-21G + ZPC//3-21G) and decreases to 31.2 kcal/mol at the MP2/6-31G*//6-31G* + ZPC//6-31G* level. In contrast the MNDO and MNDOC methods drastically overestimate this barrier with values of 87.2 and 84.5 kcal/mol, respectively.

Since both the hydrogen transfer from ethane to ethylene in eq 1 and the hydrogenation of formaldehyde by methanol in eq 2 are symmetry allowed σ2s + π2s + σ2s cycloadditions,[4] the

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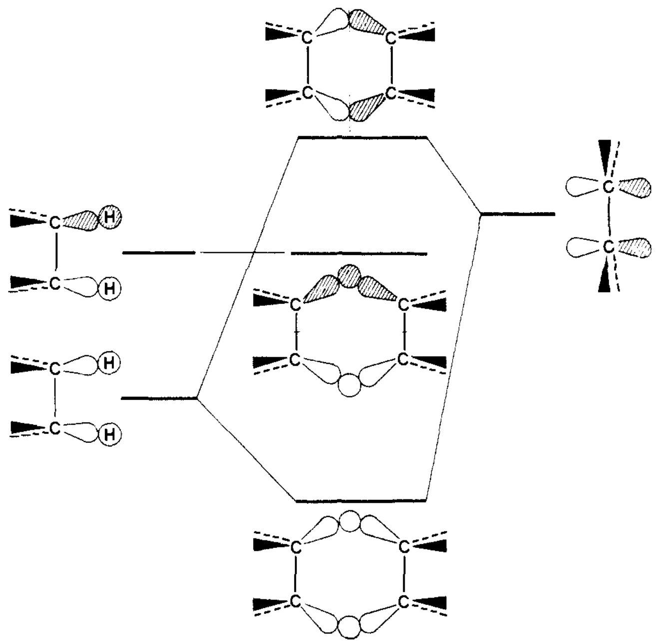

Figure 2. Partial correlation diagram for the formation of the transition structure in the concerted dihydrogen exchange between ethane and ethylene.

reason for the large differences in their activation energies is of interest. In the ethane + ethylene reaction, the relevant orbitals are a symmetric and antisymmetric C–H combination and the π orbital. When these orbitals are combined to form the transition structure orbitals for the pericyclic reaction as shown in Figure 2, the HOMO of the activated complex has a node between the two transferring hydrogens leading to antibonding interactions in the transition structure. A discussion of the reasons for the high barrier in the symmetry allowed ethane–ethylene reaction has led to the conclusion that this antibonding interaction is a major factor.[5] The fact that the dihydrogen transfer from diimide to ethylene is facile was ascribed to the thermodynamic driving force associated with the exothermicity of N_2 formation.

While there is no doubt that thermodynamic factors affect the heights of the barriers in these dihydrogen transfers, the results of the present study argue that this cannot be the whole story. Although the hydrogen transfers in eq 1 and 2 are both isoenergetic, the reaction in eq 2 is predicted to proceed with less than half the barrier of that in eq 1. An inspection of the molecular orbitals of the transition structure for the process in eq 2 reveals significant differences from the situation encountered in eq 1. In the former case, the highest occupied orbitals are not those orbitals in the plane of the molecule involving the transferring hydrogens; rather they consist mainly of a symmetric and an antisymmetric combination of the out-of-plane p orbitals on oxygen. These are followed in order of decreasing energy by the in-plane orbitals involving the transferring hydrogens. It is interesting to note that the orbital of b_2 symmetry (Figure 3a) in which there is a node on the transferring hydrogen is lower in energy than the a_1 combination (Figure 3b), a situation exactly opposite to that in the ethylene–ethane reaction. Thus, although this orbital has a node on the transferring hydrogens, it is lower in energy than the analogous orbital in the ethylene–ethane transition structure and exerts a smaller deleterious effect on the barrier. The reason that this three-center bond is favorable in the present case is undoubtedly due to the fact that the electronegative oxygen atoms bear the greatest electron density in the b_2 orbital and thus serve to stabilize this orbital. This type of four-electron, three-center bond with electrophilic atoms at the termini has long been thought to be a factor in hydrogen bond formation.[20] From this perspective, we may view the transition structure as one which has been stabilized by the formation of a hydrogen bond. Although the type of hydrogen bond proposed here differs from the normal hydrogen bond in that both O–H distances are equal at 1.185 Å, the short O–H bond lengths and the relatively open O–H–O angle of 156.7° in the transition structure for the process in eq 2 indicate a bonding interaction.[21] In contrast, the C–H–C distances of 1.356 Å indicate the antibonding character of this orbital. The importance of the heteroatoms in stabilizing the transition structure for the diimide reduction of ethylene is demonstrated by the fact that the N–H bonds are calculated to be rather short (0.993 Å) while long (1.64 Å) C–H bonds are predicted.[22]

Table IV. Comparison of ab Initio Enthalpic Barrier (kcal/mol) and Geometric Parameters (Distance from Carbon or Oxygen to Transferring Hydrogen) in the Transition Structure with MNDO and MNDOC

thermodynamic or geometric values	MNDO	MNDOC	"best"
	Reaction 1[a]		
$\Delta H^\ddagger$	73.5	62.9	69.3[d]
C–H	1.379	1.366	
	Reaction 2[b]		
$\Delta H^\ddagger$	87.2	84.5	31.2[e]
O–H	1.210	1.206	
C–H	1.398	1.388	
	Reaction 5[c]		
$\Delta H^\ddagger$	39.0	38.8	4.3[f]
O–H	1.223	1.233	

[a] Equation 1; $CH_2{=}CH_2 + CH_3OH \rightarrow CH_3CH_3 + CH_2{=}CH_2$. [b] Equation 2; $CH_2{=}O + CH_3OH \rightarrow CH_3OH + CH_2{=}O$. [c] Equation 5; $HC(OH){=}CHC(H){=}O \rightarrow O{=}C(H)CH{=}CH(OH)$. [d] DZ basis MCSCF; ref 5. [e] MP2/6-31G*//6-31G* + ZPC present work. [f] MP4/6-31G**//MP2/6-31G* ref 26.

In order to investigate why MNDO overestimates the barrier to concerted dihydrogen transfer, the MNDO and MNDOC methods were compared for the reactions in eq 1 and 2. The MNDOC method includes correlation explicitly through the BWEN perturbational method[15b] while the MNDO method includes correlation through parameterization.[14a] A recent comparison has shown that the MNDOC method performs quite well when comparing properties of transition structures (barrier heights, geometries, and zero point energies) with high level ab initio calculations.[15c] In eq 1 both hydrogens are transferred between carbons while in eq 2 one hydrogen is transferred between carbons and the other between oxygens. Both methods, MNDO and MNDOC, perform similarly for eq 1 and in agreement with a MCSCF-FORS calculation using a DZ basis set.[5] For eq 2 MNDO and MNDOC predict very high barriers, which are in disagreement with ab initio predictions (Table IV).

Our explanation for the discrepancy involves the basic approximation itself. In MNDO and MNDOC (and MINDO/3) the core–core repulsion for the O–H and N–H pairs were estimated by using an arbitarily different empirical function from all other core–core repulsions (eq 3 and 4) but which was found

$$E_{AB} = Z_A Z_B (1 + e^{-\alpha_A R_{AB}} + e^{-\alpha_B R_{AB}}) \tag{3}$$

$$E_{XH} = Z_A Z_B (1 + (R_{XH}/\text{Å}) e^{-\alpha_X R_{XH}} + e^{-\alpha_H R_{XH}}) \tag{4}$$

to improve overall results.[14a] In most compounds the O–H and N–H distances are close to 1 Å, and therefore the core–core repulsion integrals are only slightly modified. In the present reaction the much larger O–H distances yield overestimated core–core repulsion integrals and therefore lead to the calculated higher barriers.[23]

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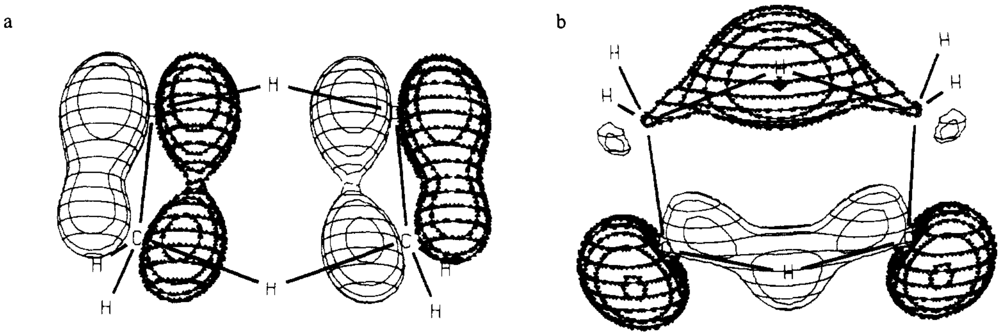
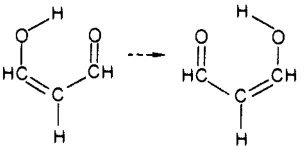


Figure 3. (a) Jorgensen orbital contour plot (STO-3G//3-21G) for the highest occupied b_2 (HOMO-3) in the transition structure of eq 2. (b) Jorgensen orbital contour plot (STO-3G//3-21G) for the highest occupied a_1 (HOMO-2) in the transition structure of eq 2.

If our explanation is correct, one would expect that the barrier to intramolecular hydrogen migration in malonaldehyde (eq 5) would be overestimated by MNDO and MNDOC. An accurate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ab initio calculation (MP4/6-31G**//MP2/6-31G*)[26] predicts a barrier of 4.3 kcal/mol which is in good agreement with an experimentally estimated barrier height of 4.0–5.2 kcal/mol.[27] In contrast MNDO and MNDOC predict much higher barriers, 39.0 and 38.8 kcal/mol, respectively (Table IV). The transition structure has C_{2v} symmetry as shown by one imaginary mode of 2303 cm^{-1} (MNDO). The active hydrogen–oxygen distance of 1.223 Å predicted by both MNDO and MNDOC is close to ab initio values of 1.188 and 1.203 Å using 6-31G** and MP2/6-31G** basis sets, respectively.

In a recent study[28] of the reaction between ammonia and formic acid, barriers were calculated at the ab initio and MNDO levels for the step-wise proton transfer reactions in eq 6 as well as for

$$\underbrace{NH_3 + HCOOH \xrightarrow{TS_1} H_2N\text{-}CH(OH)_2 \xrightarrow{TS_2} NH_2CHO + H_2O}_{TS_3} \qquad (6)$$

the concerted reaction. The first barrier, (TS_1), represents a transfer from nitrogen to a keto oxygen, the second, (TS_2), between two oxygens, and the concerted barrier, (TS_3), to transfer between nitrogen and a hydroxyl oxygen. MNDO overestimates the three barriers by 19.6, 40.7, and 30.8 kcal/mol, respectively, compared to results at the MP4/6-31G**//3-21G level. Other thermodynamic properties however are well reproduced. The authors' conclusion that "overestimation of the activation energy by MNDO is due mainly to the lack of direct incorporation of correlation effects" may instead be due to the functional form of the O–H and N–H core–core repulsion integral.

One must conclude that MNDO and MNDOC will not be appropriate for calculating *energetics* for reactions involving the transfer of a proton (or hydrogen) between oxygens or probably between nitrogens due to an inherent problem in the core–core repulsion functions used between the two pairs of elements.

Dewar and co-workers have recently developed a new quantum mechanical molecular model called AM1[29] which has overcome the failure of MNDO to reproduce hydrogen bonds. The major difference between MNDO and AM1 is the functional form of the core–core repulsion function which in the new formalism is the same for every element pair. The value of the intramolecular hydrogen migration barrier in malonaldehyde by AM1 is reported[30] as 22.1 kcal/mol.

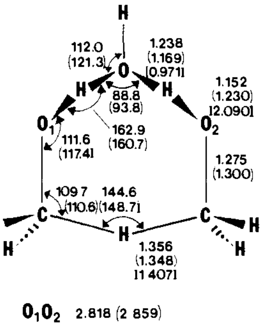

Figure 4. Structural parameters for the transition structure of eq 7. Values are for the 6-31G* basis, (3-21G basis), and [MNDO].

Catalytic Effect of Water. It is known that water may act as an active participant in some reactions. For example, it is found that a molecule of water reduces the barrier to proton transfer in formamide ⇌ amidine tautomerism.[31] In another example, an extra molecule of water significantly reduces the barrier to hydration of carbon dioxide.[32] It was also found[33] that a pathway exists for the hydration of ketene involving a water dimer via a cyclic transition structure. In contrast to rate enhancements afforded by an "active" water molecule (or dimer), water does not reduce the enthalpic barrier in the concerted dihydrogen exchange between methanol and formaldehyde (eq 7).

$$H_3COH + H_2C{=}O + H_2O \rightarrow H_2C{=}O + H_3COH + H_2O \qquad (7)$$

Vibrational calculations were performed to confirm the nature of the concerted stationary structure. At all levels one imaginary frequency was found except at the highest level (6-31G*) where a second imaginary frequency (167i cm^{-1}) indicated a distortion from C_s to a lower C_1 symmetry. The transition structure[34] is unusual in that three bonds (two O–H and one C–H) are being broken simultaneously. The only other proposed mechanism in

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[23] Attempts have been made to modify the core–core respulsion function for MINDO/3[24] and MNDO.[25]

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[34] Although formally a stationary structure of order two at the 6-31G* level, the designation of transition structure will be used. For purposes of computing zero point energy, entropy, and heat capacity at the 6-31G* level, both negative modes are ignored. However, in the calculation of kinetic isotope effects, the smaller imaginary mode is included as a real mode of the same magnitude (167 cm^{-1}).

Table V. Calculated Vibrational Frequencies Compared at Various Levles and with Experiment

molecule	symmetry of mode	frequency (cm^{-1}) MNDO	3-21G	6-31G*	exptl
H_2O	a_1	1960	1800	1827	1648[a]
	a_1	4051	3814	4070	3832
	b_2	4086	3947	4188	3943
$H_2C{=}O$	b_2	1215	1378	1366	1167[b]
	b_1	1210	1337	1384	1249
	a_1	1491	1693	1680	1500
	a_1	2115	1916	2028	1746
	a_1	3255	3162	3159	2783
	b_1	3302	3233	3231	2843
H_3COH	a''	269	360	348	295[c]
	a'	1168	1092	1164	1033
	a'	1416	1153	1188	1060
	a''	1235	1254	1289	1165
	a'	1438	1480	1508	1345
	a'	1504	1638	1638	1455
	a''	1417	1686	1652	1477
	a'	1565	1698	1664	1477
	a'	3228	3177	3185	2844
	a''	3198	3217	3231	2960
	a'	3390	3294	3305	3000
	a'	4007	3868	4117	3681
TS_2[d]	b_2	2652i	2003i	2339i	
	a_2	158	169	141	
	b_1	366	402	320	
	a_1	536	518	512	
	b_2	552	637	643	
	a_1	691	680	698	
	b_1	932	1038	993	
	a_2	799	1041	1021	
	b_2	989	1371	1297	
	a_2	1212	1313	1327	
	b_1	1213	1315	1330	
	a_1	1277	1384	1378	
	b_l	1352	1587	1478	
	b_2	1450	1502	1505	
	a_1	1442	1430	1533	
	a_1	1721	1594	1583	
	a_1	1758	1717	1731	
	b_2	1621	1725	1750	
	a_1	1784	1960	1893	
	b_2	1884	1956	1937	
	a_1	3274	3214	3217	
	b_2	3278	3215	3220	
	a_2	3244	3290	3295	
	b_1	3247	3292	3297	
TS_7[e]	a''	1013i	2038i	2304i	
	a''	52	126	167i	
	a'	97	122	124	
	a'	152	162	199	
	a''	77	481	302	
	a'	249	395	331	
	a''	182	587	499	
	a'	278	469	521	
	a'	301	503	570	
	a'	507	694	610	
	a''	283	587	641	
	a''	440	794	772	
	a''	830	1086	1076	
	a'	1229	1298	1078	
	a''	1225	1272	1287	
	a'	1262	1400	1349	
	a'	1344	1582	1374	
	a''	1468	1351	1388	
	a''	1590	1426	1460	
	a'	1355	1582	1512	
	a'	1313	1440	1521	
	a'	1541	1673	1555	
	a'	1841	1528	1629	
	a''	1884	1713	1708	
	a'	1899	1820	1741	
	a''	2013	1879	1853	
	a''	3163	1997	1950	
	a'	3170	2053	1954	
	a'	3219	3178	3226	
	a''	3226	3179	3228	
	a''	3651	3270	3324	
	a'	3704	3273	3326	
	a'	3831	3959	4129	

[a] Strey, G. *J. Mol. Spectrosc.* **1967**, *24*, 87. [b] Duncan, J. L.; Mallinson, P. D. *Chem. Phys. Lett.* **1973**, *23*, 597. [c] Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards: Washington, DC, 1972; Vol. 1. [d] Transition structure for eq 2. [e] Transition structure for eq 7.

this class is the decomposition of glyoxal to hydrogen and carbon monoxide[35] where three bonds are also being broken in the transition structure.[36]

The ab initio transition structures for eq 2 and 7 (Figure 1, Figure 4) are very similar; only a slight modification being necessary to replace H^+ with H_3O^+. The OC–H–CO moiety is nearly planar while the two hydrogens of H_3O^+ approach from one side. A slightly more linear O–H–O angle is found (162.9°, 6-31G*; 160.7°, 3-21G), and the degree of proton transfer between oxygens is nearly the same (OH distances are 1.238 and 1.152 Å at the 6-31G* level; 1.169 and 1.230 Å at the 3-21G level). The oxygens of methanol and formaldehyde have also "opened up" to accommodate the larger H_3O^+ rather than H^+ (2.321 vs. 2.818 Å, 6-31G*; 2.326 vs. 2.859 Å, 3-21G).

The MNDO transition structure geometry differs principally in the much shorter forming O–H bond and the much longer breaking O–H bond (0.970 and 2.09 Å; Figure 4) and a much smaller O–H–O angle for hydrogen transfer (118.1°, MNDO). The discrepancy in the enthalpic barrier for dihydrogen transfer between MNDO and ab initio actually increases for the water mediated case. The 30 kcal/mol barrier at the ab initio level increases to 110.2 kcal/mol at the MNDO level.

Thermodynamic and Kinetic Properties. It is useful to compare thermodynamic and kinetic data at several levels of approximation. The latter may be of particular value to experimental efforts directed toward observing the hydrogenation of formaldehyde by methanol. Since thermodynamic and kinetic properties are de-

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(36) However, the triple proton transfer between methanol and acetic acid dimer[6,9] could be considered in this class.

Table VI. Thermodynamic Values[a] and Rate Constants[b] at Different Temperatures for Reaction 2 at the 6-31G*//6-31G* Level

T	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	K^{c}	A factor[d]	rate constant
300	−41.6	30.5		3.9×10^{4}	4.8×10^{-19}
500	−42.9	30.0		5.1×10^{4}	4.8×10^{-10}
700	−43.7	29.5	3.1	4.3×10^{4}	9.3×10^{-6}
900	−44.3	29.0	1.8	4.0×10^{4}	7.2×10^{-4}

[a] $\Delta H^{\ddagger}$ in kcal mol^{-1} and $\Delta S^{\ddagger}$ in cal deg^{-1} mol^{-1}. [b] Using the following Eyring equation $k = K(kT/h)(e^{\Delta S^{\ddagger}/R})(e^{-\Delta H^{\ddagger}/RT})$. [c] Tunneling correction from Bell equation; see text. [d] $A = (kT/h)(e^{\Delta S^{\ddagger}/R})$ at 300 and 500 K and $A = K(kT/h)(e^{\Delta S^{\ddagger}/R})$ at 700 and 900 K.

pendent on the calculated vibrational frequencies,[19c] these are compared in Table V.

In order to predict thermodynamic and kinetic properties at elevated temperatures where reaction may be observed, the enthalpy and entropy of activation must be corrected using eq 8 and 9. The heat capacity at constant volume $\bar{C}_v$ is more easily obtained

$$\Delta H^{\ddagger T} = \Delta H^{\ddagger 0\mathrm{K}} + \Delta \bar{C}_p T \tag{8}$$

$$\Delta\Delta S^{\ddagger(T-298\ \mathrm{K})} = \bar{C}_p \ln (T/298\ \mathrm{K}) \tag{9}$$

computationally as the sum of the translational part ($^3/_2R$), rotational part ($^3/_2R$), and vibrational part. For an ideal gas, $\bar{C}_v$ can be corrected to $\bar{C}_p$ by using $\bar{C}_p = \bar{C}_v + R$. In eq 8 and 9 we assume that the heat capacity is constant over the temperature range of interest. The corrected values are given in Table VI.

Tunneling is another effect which may be important in the concerted dihydrogen transfer reaction. To approximate a tunneling correction, a simple approximation given by Bell[37] for tunneling through a parabolic barrier is used (eq 10).

$$Q_t = {}^1\!/_2\mu_{\ddagger}/\sin {}^1\!/_2\mu_{\ddagger} \tag{10}$$

where

$$\mu_{\ddagger} = h\nu_{\ddagger}/kT$$

h = Planck's constant

T = absolute temperature

$\nu_{\ddagger}$ = imaginary frequency for the transition structure

When evaluated at temperatures where reaction might occur, the tunneling correction is rather moderate, resulting in approximately a threefold increase in rate at 700 K and a twofold increase at 900 K (Table VI).

Using the thermodynamic properties evaluated at various temperatures, we can predict a rate constant using the Eyring equation[38] (eq 11). The last term in eq 11, $c^{\Delta n^{\ddagger}}$, is the concentration in the standard state to which the thermodynamic parameters are referred (1 atm, 298 K) raised to one minus the molecularity of the reaction, which lead to the units of atm^{-1} s^{-1} for the rate constant.[39] Rate constants given in Table VI are corrected for tunneling only at 700 and 900 K.

$$k = Q_t(kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}c^{\Delta n^{\ddagger}} \tag{11}$$

Taking realistic reaction conditions, we can estimate the rate for the following reaction (eq 12). Under short reaction times the only likely source of undeuterated formaldehyde would be due to the concerted dihydrogen transfer mechanism. If we assume

$$\mathrm{O{=}CD_2 + H_3COH \rightarrow O{=}CH_2 + D_2HCOH} \tag{12}$$

that 0.001 atm of undeuterated product should be easily detectable and starting with 0.1 atm of $O{=}CD_2$ and 0.9 atm of H_3COH at 700 K, then a reaction time of about $^1/_2$ h is predicted. Experiments to verify this are in progress.

Finally, it should be noted that an alternative to the hydrogenation of formaldehyde by methanol is the formation of the hemiacetal in eq 13. Although this reaction is usually acid

$$\mathrm{H_3COH + H_2C{=}O \rightarrow HOCH_2OCH_3} \tag{13}$$

catalyzed, a recent calculation (4-31G//STO-3G) of the activation parameters indicates that this process should be competitive with the hydrogen transfer in eq 2.[40] However, this fact would not hamper efforts to observe the degenerate hydrogen transfer through the use of isotopic labeling as hemiacetal formation should be reversible at high temperatures, and there will always be a steady state of methanol and formaldehyde available for reaction.

Conclusions

A postulated mechanism of concerted dihydrogen transfer from methanol to formaldehyde has been carefully analyzed at several levels of theory. We predict an enthalpic barrier of approximately 30 kcal/mol and have set out reaction conditions under which the mechanism might be tested. MNDO and MNDOC overestimate the barrier by about 50 kcal/mol, and it is recommended that these methods not be relied upon for the energetics of proton (or hydrogen) transfer between oxygens or between nitrogens.

The catalytic effect of water on the mechanism is small but may be competitive in solution phase.

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Note Added in Proof. Recent experimental atempts[41] to detect the concerted exchange mechanism have led instead to large amounts of CO indicating decomposition of the formaldehyde, possibly by a wall reaction. The activation barrier for formation of CO from formaldehyde pyrolysis has been determined[42] to be 34.4 ± 1.3 kcal/mol with a frequency factor of $10^{11.8\pm0.4}$

Registry No. CH_3OH, 67-56-1; HCHO, 50-00-0; H, 1333-74-0; D, 7782-39-0.

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