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Theoretical Models for Mechanism and Catalysis in Carbonyl Addition

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Abstract: Exploration of potential energy curves, calculated by ab initio procedures at the STO-3G and 4-31G levels, for the systems $H_2O + CH_2O$, $HO^- + CH_2O$, and $H_2O + CH_2OH^+$ produces models for enforced concertedness of proton transfer and heavy-atom reorganization (in the $H_2O + CH_2O$ reaction) and specific-acid–base catalysis (in the two ion–molecule reactions). Thus, in the former case, approach of water to formaldehyde along such directions as to allow formation of the zwitterionic intermediate compound $H_2O^+CH_2O^-$ gives rise to a completely repulsive interaction, so that this structure does not exist as a bound species. A transition state for four-center, concerted addition does, however, exist, and reaction through this state is enforced by nonexistence of the intermediate required along the alternative stepwise route. In the ion–molecule reactions, prior protonation of formaldehyde or prior deprotonation of water leads to formation of the corresponding ionic adducts ($H_2O^+CH_2OH$ and $HOCH_2O^-$), with no barrier to reaction, simulating specific-acid and -base catalysis, respectively.

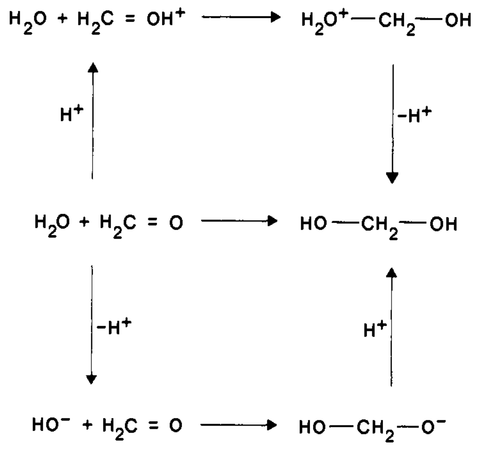
Introduction

Nucleophilic additions to carbonyl groups are of great importance in chemistry and biochemistry and their mechanisms have been widely studied[1] but remain as yet imperfectly understood. A severe complication in most experimental studies is the presence of solvent, which apparently plays a greater role in determining mechanism than is commonly suspected. Recently, gas-phase studies have shed new light on these reactions in the absence of solvent but have also revealed some surprises. The manner in which the intrinsic, gas-phase reactivity of a system is modified by solvation is a question of much interest, and it seems desirable to use theoretical methods to aid in experimental interpretation and prediction of information that is difficult to obtain experimentally.

In this paper we report a theoretical study of formaldehyde hydration and related reactions by using quantum mechanical methods. We have chosen this most simple example of nucleophilic addition to a carbonyl compound to serve as a model for the reaction class in order to facilitate investigation of general mechanistic features. These will eventually include such topics as solvation, various modes of catalysis, and the relationships among structural variables, force constants, and charge distributions in transition states.

Equations representing the hydration of formaldehyde and catalysis of this reaction by acid or base are shown in Scheme I. These reactions correspond to specific-acid–base catalysis, while general-acid–base catalysis is the observed mode in solution.[2] The factors which lead to one or the other mode of catalysis are an object of this investigation. Gas-phase ion–molecule reactions of HO^- with H_2CO and of H_2O with H_2COH^+ have been observed and studied recently,[3,4] although the reactions observed are not necessarily those of Scheme I. Uncatalyzed neutral–neutral addition has not yet been directly observed in the gas phase, although the vaporization behavior has long been interpreted in terms of a gas-phase equilibrium between the reactants and the product methanediol.[5]

Scheme I



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Below we describe theoretical studies of these three additions. Comparison of the ion–molecule calculations with the experimental observations provides a means for testing the theoretical model, while the $H_2O + H_2CO$ calculation provides an opportunity for theory to make predictions in advance of experiment. In this way theory and experiment may be used to their mutual advantage. Furthermore, consideration of the above reactions as models for nucleophilic carbonyl additions allows some qualitative and semiquantitative conclusions to be drawn from the calculated results even for those reactions involving relatively complicated molecules in solution. These results ought, therefore, to be of general mechanistic significance for this class of reaction.

Pseudo-Minimum-Energy Paths

A minimum-energy path (MEP) is usually considered to be the projection onto the coordinate-space base plane of the line on a potential energy surface (PES) running in either direction from the saddle point (corresponding to a transition state) along the valley bottoms toward the reactant and product minima. This path reflects the shape of the PES which is dependent upon the coordinates used to describe the system and which is generally different for each choice of coordinates. Such a path is not invariant to coordinate transformations and may therefore be called a *pseudo-minimum-energy path* (Ψ-MEP).[6] Since structural changes occurring along a Ψ-MEP are dependent upon the particular (but arbitrary) choice of coordinates for a given system, it is clear that detailed statements concerning the nature of these changes, and the relations among them, cannot be made unambiguously. However, a Ψ-MEP may conveniently provide an approximate indication of the energetics and structural changes occurring during the course of a reaction. Structures corresponding to critical points on a PES (including all minima and saddle points) are independent of the choice of coordinates, and so any such structure located on a Ψ-MEP will be unaltered by a change of coordinates even though the Ψ-MEP itself may be radically altered.[7] Determination of the *true* Ψ-MEP for a given PES is extremely difficult, and computational considerations usually dictate that an *approximate* Ψ-MEP be obtained for all but the very simplest of chemical reactions. One popular method involves selection of a *distinguished coordinate*[8] which changes monotonically and by a reasonably large amount during the reaction. This coordinate is appropriately incremented, and at each point the energy of the system is minimized with respect to the remaining internal degrees of freedom, although the constrained nature of the minimization may result in a fallacious approximation to the Ψ-MEP. Problems related to use of this method have been discussed previously.[6]

The extent to which a Ψ-MEP may be physically meaningful depends upon the nature of the forces acting within the system. In an associative process, the Ψ-MEP determined at long range may be of little mechanistic significance since weak intermolecular forces may permit large changes in relative molecular orientation to result in only small changes in potential energy. Thus molecules with any kinetic energy at all may execute trajectories deviating greatly from the Ψ-MEP. Furthermore, gas-phase structures with large intermolecular separations and small interaction energies are unlikely to be of great importance when transferred into solution, owing to the dominating influences of surrounding solvent molecules. A Ψ-MEP is more likely to have some physical significance at close range where stronger intermolecular forces are involved and particularly so in regions about stable minimum-energy structures. In other regions of a PES the Ψ-MEP may be critically dependent upon the choice of distinguished coordinate and thus of questionable physical significance.[9]

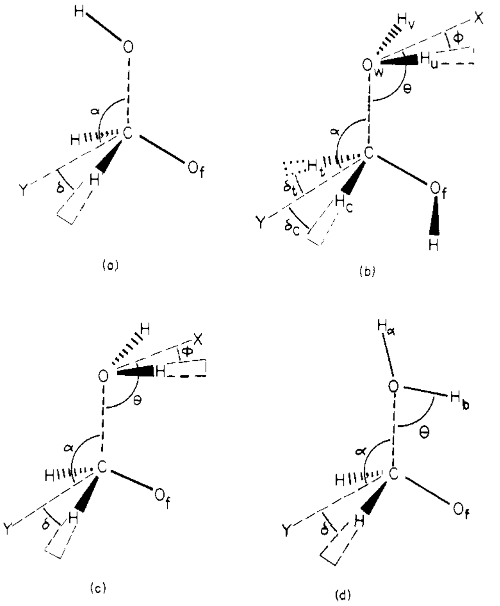

Figure 1. Internal coordinates employed in reaction path calculations. (a) $HO^- + H_2CO$; (b) $H_2O + H_2COH^+$; (c) straddled $H_2O + H_2CO$; (d) coplanar $H_2O + H_2CO$. X and Y are both coplanar with the atoms OCO; X is coplanar also with the atoms of the water molecule, and Y is coplanar also with the methylene fragment.

Table I. Internal Coordinates[a] Employed in Reaction Path Calculations

system	figure	distinguishd coord	coords included in constraind geometry optimizatn
$HO^- + H_2CO$	1a	$O\cdots C$	$C-O_f$, C-H, O-H; $O-C-O_f$, C-O-H, α, δ
$H_2O + H_2COH^+$	1b	$O\cdots C$	$C-O_f$, C-H, O_f-H, O_w-H; O_w-C-O_f, $C-O_f-H$, α, δ_c, δ_t, θ, ϕ; O_w-C-O_f-H
$H_2O + H_2CO$ straddled	1c	$O\cdots C$	$C-O_f$, C-H, O-H; $O-C-O_f$, α, δ, θ, ϕ
$H_2O + H_2CO$ coplanar	1d	$O\cdots C$	$C-O_f$, C-H, $O-H_a$, $O-H_b$; $O-C-O_f$, α, δ, $C-O-H_a$, $C-O-H_b$

[a] Here and throughout this paper, the following representations are used: A-B for a bond, A-B-C for a bond angle, and A-B-C-D for a dihedral angle.

Computational Methods

The distinguished coordinate approach to determination of a Ψ-MEP was adopted for study of each of the reactions in Scheme I. A sensible choice of distinguished coordinate for nucleophilic addition to carbonyl compounds is the distance between the atoms involved in the bond-making process, which in the present cases is the intermolecular distance $O\cdots C$. The internal coordinates used for each reacting system were chosen so as to be complete and without redundancy,[10] although the particular choices were arbitrary. The mirror symmetry found for both $HO^- + H_2CO$ and $H_2O + H_2CO$ at $O\cdots C \approx 3.0$ Å was enforced along the addition path for each of these systems, thereby reducing the number of coordinates (other than $O\cdots C$) to be optimized from 11 to 7 and from 14 to 8, respectively. Although the $H_2O + H_2COH^+$ system possessed no formal symmetry element, constraints were introduced to reduce the number of coordinates optimized for each chosen value of $O\cdots C$ from 17 to 12. The complete sets of internal coordinates employed in the reaction path studies are illustrated

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Table II. STO-3G Optimized Geometries and Interaction Energies for $HO^- + H_2CO$

	distinguished coord O···C[a]								
	spp addition path					app addition path			
	3.0	2.0	1.6	1.5	1.43	3.0	2.0	1.6	1.5
coordinates[a]									
C-O_f	1.22	1.26	1.31	1.33	1.43	1.22	1.26	1.30	1.31
C-H	1.10	1.12	1.14	1.14	1.12	1.10	1.12	1.14	1.15
O-H	1.06	1.02	1.00	0.99	1.20	1.06	1.02	1.00	1.00
O-C-O_f	130	112	113	113	93	126	112	114	114
O-C-H	111	94	100	102	115	71	94	100	102
H-C-H	113	108	103	102	104	114	108	103	102
C-O-H	95	99	100	100	74	92	98	102	104
H-O-C-O_f	0	0	0	0	0	180	180	180	180
interaction energy[b]	−8.9	−59.5	−95.4	−98.2	−82.3	−9.1	−57.9	−90.4	−92.2
energy barrier[c]									
spp → app	0.0	2.1	6.8	8.9					

[a] Bond lengths (Å) and angles (deg) are illustrated in Figure 1a. [b] Energy (kcal/mol) relative to isolated STO-3G optimized HO^- (O-H = 1.068 Å, total energy = −74.06502 hartrees) and H_2CO (C-H = 1.101 Å, H-C-H = 114.5°, total energy = −112.35435 hartrees). [c] Energy difference (kcal/mol) between spp conformer and transition state for internal rotation about O-C.

Table III. STO-3G Optimized[a] Geometries and Interaction Energies for $H_2O + H_2COH^+$

	distinguished coord O_w···C[b]						
	2.94	2.4	2.0	1.8	1.6	1.5	1.4
coordinates[b]							
C-O_f	1.27	1.28	1.31	1.34	1.37	1.39	1.42
C-H	1.11	1.11	1.11	1.11	1.10	1.10	1.11
O_f-H	1.00	1.00	0.99	0.99	0.99	0.99	0.99
O_w-H	0.99	0.99	0.99	0.99	0.99	0.99	0.99
O_w-C-O_f	91	97	104	106	107	107	104
O_w-C-H_c	90	89	93	98	102	105	106
O_w-C-H_t	90	89	93	96	100	102	106
H_c-C-O_f	122	123	122	121	118	117	115
H_t-C-O_f	117	117	116	115	113	113	115
H-C-H	121	120	118	116	113	111	110
C-O_f-H	114	114	111	110	108	108	106
C-O_w-H	130	128	117	113	113	114	114
H-O_w-H	100	102	104	106	107	108	109
O_w-C-O_f-H	90	89	92	93	99	106	180
interaction energy[c]	−11.7	−19.8	−35.8	−49.1	−60.4	−61.3	−55.9

[a] As discussed in the computational methods section, only 12 coordinates are included in these optimizations. [b] Bond lengths (Å) and angles (deg) are illustrated in Figure 1b. [c] Energy (kcal/mol) relative to isolated STO-3G optimized H_2O (O-H = 0.990 Å, H-O-H = 100.0°, total energy = −74.96590 hartrees) and H_2COH^+ (C-O = 1.271 Å, C-H = 1.114 Å, O-H = 1.002 Å, C-O-H = 114.9°, H-C-O(cis) = 123.1°, H-C-O(trans) = 116.4°, total energy = −112.70702 hartrees).

in Figure 1, and those varied in the geometry optimizations are specified in Table I.

The GAUSSIAN 70 program[11a] was used to perform ab initio SCF MO calculations, and interaction energies ΔE were calculated as differences between energies of supermolecular complexes and the combined energies of isolated molecules, $\Delta E = E(\text{complex}) - E(\text{reactants})$, all structures having optimized geometries. Geometry optimization was carried out by the standard GAUSSIAN 70 procedure of finding the minimum in a parabola fitted to three energies calculated for structures in which a single coordinate at a time was appropriately incremented. Several cycles of optimization were usually required in order to achieve convergence in the energy and a stable structure. The STO-3G minimal basis[11b] was used for reaction path calculations for the ion–molecule additions, and for preliminary studies on the neutral–neutral additions, and the 4-31G split-valence basis[11c] was used for the $H_2O + H_2CO$ addition path and for geometry optimization of all stable adducts. We expect the energetic calculations to be least reliable for the negative ions but the structural predictions should be reasonable even for these species.[12]

Neglect of correlation and use of a small basis set are two possible sources of error in these SCF calculations. Kolos[13] has suggested that interaction energies calculated at this level of approximation may be improved by inclusion of a dispersion energy term and by correction for the basis set "superposition" or "extension" error. When a small basis set such as STO-3G is used to evaluate the interaction between two molecules in a supermolecular complex, each molecule borrows a part of the basis set of the other molecule in order to extend its own basis set and so lowers its energy in the complex in a way that is unrelated to physical reality. For intermolecular interactions not involving covalency, this artificial stabilization may be eliminated by the counterpoise method[14] which requires the energy of each separate molecule to be evaluated in the full basis set of both molecules. In preliminary studies in this laboratory this method was applied to interactions between nucleophiles and formaldehyde at relatively large intermolecular separations, but it was found that any decrease in the calculated interaction energy, resulting from removal of the spurious basis set extension energy, was compensated by an increase arising from the dispersion energy as estimated by a modified London expression. The counterpoise method cannot be applied to covalent interactions because it fails to distinguish between those basis set superposition effects implicit in genuine bond formation and those arising from the use of an inadequately

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Table IV. STO-3G Interaction Energies for $H_2O + H_2CO$

distinguished coord O···C, Å	interaction energy (kcal/mol)	
	straddled[a]	coplanar[b]
2.94	-1.10	-1.05
2.4	0.57	0.69
2.0	10.0	10.8
1.8	21.2	23.0
1.6	39.9	42.4
1.5	53.9	55.7
1.4	73.6	-39.3

[a] Straddled configuration is illustrated in Figure 1c. [b] Coplanar configuration is illustrated in Figure 1d.

Table V. 4-31G Optimized Geometries and Interaction Energies for $H_2O + H_2CO$

	distinguished coord O···C[a]						
	2.94	2.4	2.0	1.8	1.6	1.5	1.4
coordinates[a]							
$C-O_f$	*1.21*	1.21	1.22	1.23	1.26	1.28	1.30
C-H	*1.08*	*1.08*	*1.08*	1.08	1.09	1.09	1.09
O-H	*0.95*	0.95	0.95	0.96	0.96	0.96	0.96
$O-C-O_f$	105	101	106	108	109	110	110
O-C-H	82	85	87	91	96	99	101
H-C-H	*116*	115	114	113	110	108	107
C-O-H	104	106	113	114	113	113	113
H-O-H	*111*	*111*	111	111	111	111	111
interaction energy[b]	-3.9	-1.9	8.0	19.3	35.5	45.8	59.1

[a] Bond lengths (Å) and bond angles (deg) for the straddled configuration considered in this table are illustrated in Figure 1c. Italicized values are unoptimized. [b] Energy (kcal/mol) relative to isolated 4-31G optimized H_2O and H_2CO with structures and energies as given in Table VI.

large basis set. Furthermore, the expression used to estimate the dispersion energy contribution to the interaction energy is inappropriate in the region of covalent interaction. For these reasons neither correction has been employed in this work.

Results

Figure 2 shows a plot of interaction energies, for the carbonyl additions of Scheme I, as a function of the distinguished coordinate O···C. Geometries optimized in STO-3G for structures occurring along the Ψ-MEPs for the ion–molecule reactions $HO^- + H_2CO$ and $H_2O + H_2COH^+$ are given in Tables II and III. Table IV contains STO-3G interaction energies for the neutral–neutral reaction $H_2O + H_2CO$, and geometries optimized in 4-31G for this system are given in Table V. Geometries optimized in 4-31G for all stable structures considered in this work are presented in Table VI. The detailed results for each reaction are described below.

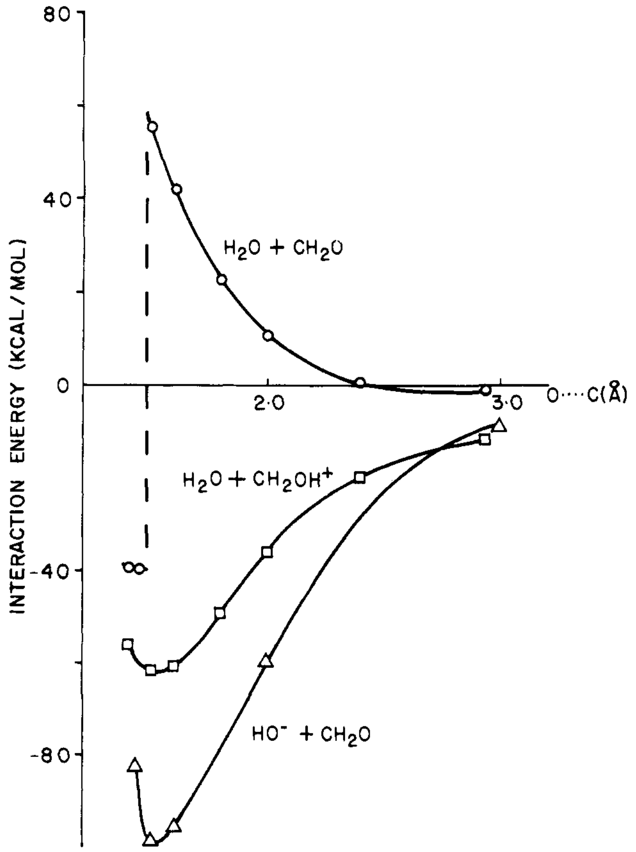

Figure 2. STO-3G interaction energies for $HO^- + H_2CO$, $H_2O + H_2COH^+$, and coplanar $H_2O + H_2CO$ additions as a function of intermolecular O···C distance.

$HO^- + H_2CO$. Bürgi et al.[15] performed calculations which suggested that the preferred approach of H^- to H_2CO for intermolecular separations H···C > 3 Å was along the carbonyl bond axis in the sense H^-···CO, although the potential energy valley for lateral displacement of the nucleophile from this path was extremely shallow. A similar result is obtained for HO^- approach to H_2CO: at O···C = 4 Å an orientation of the two moieties involving collinear HO···CO atoms is very slightly preferred. Behavior analogous to that described by Bürgi et al.[15] is also found for $HO^- + H_2CO$ at closer range in that the nucleophile rotates with respect to the electrophile in the plane bisecting the methylene group so as to attack along a direction making an OCO angle roughly equal to the tetrahedral angle. At O···C = 3.0 Å there are two conformers which differ in energy by only 0.2 kcal/mol and which are separated by a negligibly small potential energy barrier to internal rotation about the O···C axis. Both conformers possess C_s symmetry, but the slightly preferred one has the HO and CO bonds oriented in an antiperiplanar (app) fashion with respect to each other (cf. Figure 1a) and the other has a synperiplanar (spp) relationship between these bonds. The intermolecular forces between HO^- and H_2CO at this relatively large O···C distance are small, and the two moieties are essentially free to adopt any orientation with respect to each other. No mechanistic significance can be attributed to a Ψ-MEP determined in this range of intermolecular separation.

Within the constraint of C_s symmetry, Ψ-MEPs may be determined in STO-3G for O···C < 3.0 Å starting from either the app conformer or the spp conformer. Both Ψ-MEPs are associated with an increasingly attractive interaction between HO^- and H_2CO with no potential energy barrier to formation of roughly tetrahedral adducts. The curve for the interaction energy along the Ψ-MEP for the spp conformer is plotted in Figure 2 and the structures of both conformers are shown in parts a and b of Figure 3. The Ψ-MEPs lead to an app adduct stabilized by 92 kcal/mol and to a spp adduct stabilized by 98 kcal/mol relative to the separated moieties. STO-3G optimized geometries (coordinates in Figure 1a) and interaction energies for structures on both Ψ-MEPs are given in Table II. Interconversion of the two conformers via an in-plane inversion is associated with a very high-energy barrier at all points on the Ψ-MEPs, but the energy barrier to spp → app interconversion by internal rotation about the O···C bond increases gradually to about 9 kcal/mol (cf. the STO-3G results of Lien et al.[16] which predicted a similar barrier to rotational isomerism of the adduct $HOCH_2O^-$). The predicted stabilizations for the rotamers of the $HOCH_2O^-$ adduct are consistent with the 104-kcal/mol stabilization energy calculated in STO-3G by Alagona et al.[17] for the corresponding adduct of HO^- and H_2NCHO. Diverse values for the stabilization energy of $HOCH_2O^-$ are obtained from calculations with semiempirical quantum me-

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Table VI. 4-31G Optimized Geometries and Energies for Stable Structures

species[a]	figure	total energy, hartrees	bond lengths, Å		bond angles, deg		dihedral angles, deg	
OH^-		−75.22979	O-H	0.985				
H_2O (C_{2v})		−75.90864	O-H	0.950	H-O-H	111.2		
H_2CO (C_{2v})		−113.69262	C-O	1.206	H-C-H	116.4		
			C-H	1.081				
H_2COH^+[b] (C_s)		−113.98129	C-O_f	1.246	C-O_f-H_b	124.7	H_c-C-O_f-H_b	0.0
			O-H_b	0.967	H_c-C-O_f	122.0	H_t-C-O_f-H_b	180.0
			C-H_c	1.075	H_t-C-O_f	116.0		
			C-H_t	1.071				
CH_3O^- (C_{3v})		−114.21841	C-O	1.362	H-C-O	115.7		
			C-H	1.122				
$HOCH_2O^-$ spp (C_s)	3b	−189.00536	O-C	1.516	O-C-O_f	112.0	H-O-C-O_f	0.0
			C-O_f	1.325	O-C-H	102.4		
			C-H	1.105	C-O-H	102.6		
			O-H	0.956	H-C-H	106.2		
$HOCH_2O^-$ app (C_s)	3a	−188.98895	O-C	1.545	O-C-O_f	114.0	H-O-C-O_f	180.0
			C-O_f	1.300	O-C-H	101.4		
			C-H	1.116	C-O-H	109.3		
			O-H	0.958	H-C-H	105.5		
$HOCH_2OH_2^+$ (C_1)	3c	−189.93946	O_w-C	1.669	O_w-C-H_f	108.1	O_f-O_w-C-H_c	124.5
			C-O_f	1.321	O_w-C-H_c	100.0	O_f-O_w-C-H_t	−117.1
			C-H_c	1.072	O_w-C-H_t	98.2	O_f-C-O_w-H_u	−87.0
			C-H_t	1.068	C-O_f-H	119.9	O_f-C-O_w-H_v	75.0
			O_f-H	0.956	C-O_w-H_u	123.9	O_w-C-O_f-H	92.0
			O_w-H_u	0.959	C-O_w-H_v	120.0		
			O_w-H_v	0.960				
$HOCH_2OH_2^+$ (C_s)	3d	−189.93214	O_w-C	1.527	O_w-C-O_f	102.8	O_f-O_w-C-H	120.9
			C-O_f	1.367	O_w-C-H	103.0	O_f-C-O_w-H	75.6
			C-H	1.074	C-O_f-H	118.9	O_w-C-O_f-H	180.0
			O_f-H	0.962	C-O_w-H	119.5		
			O_w-H	0.956				
$HOCH_2OH$ (C_2)	3e	−189.62789	C-O	1.441	O-C-O	112.2	O-C-O-H	61.7
			C-H	1.075	H-C-H	110.7	OCO/HCH	95.1
			O-H	0.953	C-O-H	113.1		
$H_2CO\cdots H^+\cdots OH_2$[b] ($C_s$)	3f	−189.95251	C-O_f	1.230	C-O_f-H_b	128.9	C-O_f-O-H	98.1
			O_f-H_b	1.105	H_c-C-O_f	121.5		
			C-H_c	1.076	H_t-C-O_f	118.3		
			C-H_t	1.072	C-O_f-O	130.2		
			O_f-O	2.396	H-O-H	113.1		
			O-H	0.955	O_f-O-H	122.6		

[a] Atomic labeling is as shown in Figure 1, but see note *b*. [b] The methylene hydrogen atoms *cis* and *trans* to the oxygen-bound proton H_b in H_2COH^+ and $H_2CO\cdots H^+\cdots OH_2$ are denoted H_c and H_t, respectively, and the carbonyl oxygen is denoted O_f.

chanical methods: INDO, 254 kcal/mol;[18] MINDO/2, ~70 kcal/mol;[19] MINDO/3, 60 kcal/mol.[18]

Geometries optimized in 4-31G for both conformations of the $HOCH_2O^-$ adduct are presented in Table VI. The low-energy conformer is stabilized by 52 kcal/mol with respect to isolated HO^- and H_2CO and by ~10 kcal/mol with respect to the high-energy conformer. Bürgi et al.[20] calculated a stabilization energy of ~60 kcal/mol for the spp conformer of $HOCH_2O^-$ with partially optimized geometry. They compared this with a 48-kcal/mol stabilization energy calculated for CH_3O^- with respect to H^- and H_2CO by using the same moderately extended basis set. The total energy of H^- and optimized H_2CO is −114.11506 au in 4-31G as compared to −114.0334 au reported by Bürgi et al.,[20] which suggests that 4-31G is the better basis for this system. We have optimized the geometry of methoxide ion in 4-31G (Table VI) and have calculated a stabilization of 65 kcal/mol with respect to H^- and H_2CO as compared to 52-kcal/mol stabilization for the $HOCH_2O^-$ adduct. The relative stabilities of these two adducts are reversed from the order found by Bürgi et al.[20] using a comparable basis set but with only partial geometry optimization. This may indicate the importance of performing full geometry optimizations on the adducts. The 52-kcal/mol stabilization for $HOCH_2O^-$ is consistent with the 56-kcal/mol stabilization for HCO_3^- with respect to HO^- and CO_2 calculated by Jönsson et al.[21] using a slightly more extensive basis set with full geometry optimization.

None of the studies mentioned above, or other quantum mechanical studies,[22] indicate the existence of any potential energy barrier to addition of a negatively charged nucleophile to a neutral carbonyl compound in the gas phase. These theoretical predictions are corroborated by the results of various experimental studies of gas-phase ion-molecule reactions,[3,23-25] although sometimes nucleophlic addition at carbonyl centers is not observed because proton transfer and other reactions predominate.[24,26] Bohme et al.[3] have observed stabilized gas-phase adducts of formaldehyde with anionic nucleophiles; in particular these authors have measured an unusually large rate constant for addition of HO^- to H_2CO, in an inert helium bath, which they argued was consistent with formation of a "tight" adduct $HOCH_2O^-$ through chemical bonding with no energetic barrier. This finding appears to be

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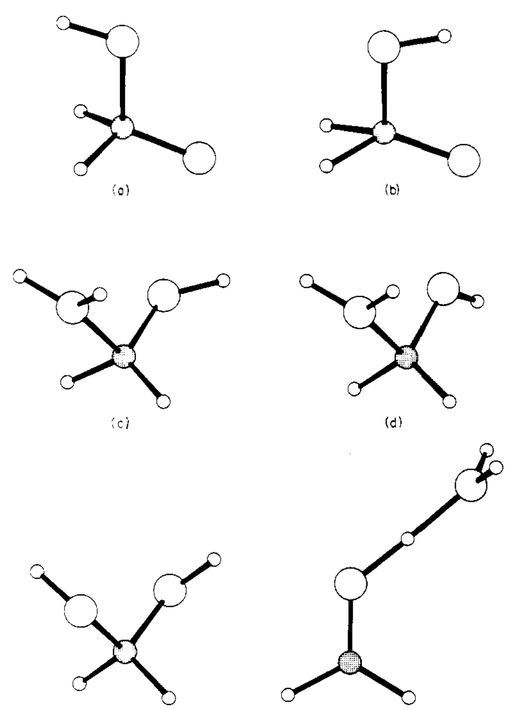

Figure 3. ORTEP drawings of 4-31G optimized structures: (a) $HOCH_2O^-$, app conformer; (b) $HOCH_2O^-$, spp conformer; (c) $HOCH_2OH_2^+$, C_1 conformer; (d) $HOCH_2OH_2^+$, C_s conformer; (e) $HOCH_2OH$, C_2 conformer; (f) $H_2CO{\cdots}H^+{\cdots}OH_2$.

supported by the present theoretical study.

$H_2O + H_2COH^+$. Table III contains geometries and STO-3G interaction energies for structures on the Ψ-MEP for addition of H_2O to H_2COH^+ with O···C as the distinguished coordinate. The ion–molecule interaction is attractive, and there appears not to be any potential energy barrier to formation of a stable adduct with roughly tetrahedral carbon and an energy lower than isolated H_2O and H_2COH^+ by ~62 kcal/mol in STO-3G (see Figure 2). Scheiner et al.[22] used the PRDDO method to study addition of methanol to protonated formic acid and reported a similar interaction to that described here. They found an adduct with O···C ~ 1.62 Å with a stabilization of 48 kcal/mol.

Full geometry optimization in 4-31G, with no symmetry constraints, for this carbonyl adduct $HOCH_2OH_2^+$ yielded a structure (Figure 3c) having C_1 symmetry and a stabilization energy of 31.1 kcal/mol. The geometry of this species is given in Table VI: note the extraordinarily long O_w–C bond (1.67 Å) and the short C–O bond (1.32 Å). Internal rotation about the C–O bond generates a conformer, with C_s symmetry, in which the O_w–C and O–H bonds are antiperiplanar. Geometry optimization in 4-31G, within the constraint of C_s symmetry, gave a structure (Figure 3d) whose geometry is also given in Table VI. In this species the O_w–C bond is shorter (1.53 Å) and the C–O bond is longer (1.37 Å) than in the C_1 conformer, in accord with qualitative theories concerning the orientations of electronic lone pairs (cf. ref 27). The C_s conformer is 26.5 kcal/mol more stable than isolated H_2O and H_2COH^+ but is 4.6 kcal/mol less stable than the C_1 conformer: this result contradicts that obtained by Wipff,[28] who did not consider fully optimized geometries and found the C_s conformer to be *more* stable than the C_1 conformer by 6.3 kcal/mol in 4-31G. The preferred conformation of neutral methanediol has C_2 symmetry,[29] and the 4-31G optimized geometry of this species (Figure 3e) is given in Table VI. Comparison of parts c and d of Figure 3 indicates that the C_1 conformer of $HOCH_2OH_2^+$ is related to the C_2 conformer of $HOCH_2OH$ by simple protonation of an oxygen lone pair unaccompanied by conformational change.

An experiment pertinent to the present work was performed by Caserio et al.,[4] who studied the reaction of $H_2{}^{18}O$ with H_2COH^+ by ICR spectrometry. Addition of the labeled nucleophile to form a cationic tetrahedral intermediate in which internal proton transfer could occur prior to dissociation would have led to $H_2C^{18}OH^+$ as a product ion but surprisingly[30] these authors observed $H_3{}^{18}O^+$ as the only ionic product. The H_2COH^+ ions used in this study were generated by α cleavage of methanol on electron impact and probably possessed about 20 kcal/mol of excess energy[31-33] which would have been more than enough to drive the endothermic proton transfer.[34]

Figure 3f illustrates the structure of a hydrogen-bonded adduct of H_2COH^+ with H_2O whose 4-31G optimized geometry is given in Table VI. This adduct is stabilized by 39.3 kcal/mol in 4-31G and is thus considerably more stable than either of the carbonyl adducts of H_2COH^+ with H_2O. Beauchamp[35] has discussed the importance of strong hydrogen-bonding interactions in gas-phase reaction mechanisms, and Beauchamp and Caserio[36] have noted that much of the ion–molecule chemistry of aliphatic alcohols derives from hydrogen-bonded intermediates involving protonated carbonyl compounds. It would seem that H_2O prefers to act as a proton acceptor in forming a strong hydrogen bond with H_2COH^+ than to act as a nucleophile in forming a carbonyl adduct. Dissociation of the $H_2CO{\cdots}H^+{\cdots}OH_2$ adducts yields either H_2COH^+ or H_3O^+ as the ionic product depending upon which bond to the bridging proton is broken. Cluster ions $H_2COH^+\cdot(H_2O)_n$ with n = 1, 2, and 3 have been observed by Bohme et al.[37] in an inert-gas bath, but the structures of these species are presently unknown. Whether the carbonyl adducts predicted by this theoretical study could exist as stable structures remains an open question.

$H_2O + H_2CO$. The two ion–molecule reactions described above involve simply carbonyl addition unaccompanied by other processes. The predicted structure of the carbonyl adduct of H_2CO^+ with H_2O has the hydrogen atoms of water straddling the OCO plane. By analogy, approach of the neutral nucleophile H_2O to the neutral electrophile H_2CO was considered in such a way that the H_2O hydrogens were symmetrically disposed about an OCO mirror plane as in Figure 1c. Preliminary STO-3G calculations indicated that this "straddled" configuration was slightly preferred over the "coplanar" configuration (Figure 1d) for nucleophilic interaction between H_2O and H_2CO with rigid internal geometries,[38] although overall the most favorable interaction was hydrogen bond formation involving the carbonyl oxygen atom. With O···C as the distinguished coordinate, a Ψ-MEP was determined for the straddled configuration in STO-3G, which yielded the interaction energies given in Table IV.

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(38) STO-3G calculations for H_2O and H_2CO molecules with rigid internal geometries and O–C–O = 90° give interaction energies of −1.10 and −1.05 kcal mol^{-1} for straddled (O···C = 2.93 Å, θ = 110.8°) and coplanar (O···C = 2.955 Å, C–O–H_6 = 94.5°) C_s symmetrical configurations, respectively.

The interaction became increasingly repulsive for $O\cdots C < 2.4$ Å and provided no indication that a zwitterionic intermediate $H_2O^+CH_2O^-$ was formed. Furthermore, rotation of the H_2O moiety about the $O\cdots C$ bond axis failed to indicate the existence of any rotameric structure with other than C_s symmetry as a bound state. In order to establish whether this predicted lack of stabilization was the result of inadequacy of the minimal STO-3G basis, we performed geometry optimization for each value of $O\cdots C$ by using the 4-31G basis, and the structures specified in Table V were obtained. The geometry of the system changes smoothly and sensibly toward a tetrahedral structure as the nucleophile approaches the carbonyl compound, but the trend of the interaction is very considerably repulsive. There is a weak intermolecular attraction to the extent of ~4 kcal/mol at $O\cdots C$ distances close to 3 Å, but at the distance expected for a single bond, $O\cdots C \approx 1.43$ Å, the adduct is unstable by ~55 kcal/mol relative to isolated H_2O and H_2CO molecules.

Calculations in STO-3G for nucleophilic attack of ammonia on formaldehyde were also performed in a manner entirely analogous to that for water addition, and the same repulsive trend was found in agreement with the results of a similar STO-3G study made elsewhere[39] but in contrast to earlier predictions[16,40] obtained by using semiempirical methods (cf. ref 41). At $N\cdots C = 1.5$ Å an interaction energy of +63 kcal/mol was calculated for $NH_3 + H_2CO$ as compared to +54 kcal/mol at $O\cdots C = 1.5$ Å for $H_2O + H_2CO$ in STO-3G. The interaction energies calculated for $NH_3 + H_2CO$ by Scheiner et al.[20] using the PRDDO method fall almost perfectly on a curve drawn through the STO-3G results given in Table IV, and these authors also found an essentially repulsive interaction between methanol and formic acid. Optimized values of $N-C-O = 106°$ and $C-O = 1.23$ Å were found in the present study for an (unbound) $NH_3 + H_2CO$ adduct with $N\cdots C = 2.0$ Å in agreement with values of 105° and 1.23 Å reported by Bürgi et al.[13]

From these results it can be concluded that the behavior of neutral–neutral carbonyl additions in vacuo is very different from that of related ion–molecule reactions; this point does not seem to have been stressed previously. Although a detailed analysis has not been performed, a simple rationalization can be offered in general terms for this behavior. Ion–molecule addition involves net charge dispersal as a relatively charge-localized ion combines with a neutral molecule. As the charge becomes less concentrated, interelectronic repulsion decreases and thus the addition is energetically favorable. In contrast, neutral–neutral addition involves net polarization of charge as reactants combine to form an adduct which may be represented formally as a zwitterion. The separation of opposite charges requires work, and thus the addition tends to be energetically unfavorable. Neutral–neutral addition ought to be facilitated by processes which avoid charge polarization. A concerted process of nucleophilic attack and proton transfer could then lead to formation of a neutral adduct.

The neutral adduct formed by water addition to formaldehyde, concomitant with proton transfer, would be the product methanediol. The Ψ-MEP calculations for $H_2O + H_2CO$ addition along the C_s symmetrical straddled path described above did not predict proton transfer to occur, since the symmetry constraint would have required *both* H_2O protons to have moved together in an unproductive and energetically unfavorable manner. If the water molecule and the carbonyl bond were coplanar then proton transfer would not be prevented by imposition of C_s symmetry. Indeed, Jönsson et al.[42] have reported a transition state for water addition to carbon dioxide, along a C_s symmetry path, in which a proton was appreciably transferred from H_2O to CO_2 in a planar structure. Using a moderately large Gaussian basis of double-ζ type in ab initio SCF-MO calculations, these authors found the transition state to be higher in energy than the reactants by 56 kcal/mol. In contrast, Jean and Lehn[43] studied an addition path for $H_2O + CO_2$ along which C_{2v} symmetry and coplanarity were imposed and found a repulsive trend for the interaction in STO-3G very similar to that found in this work for the straddled C_s symmetrical $H_2O + H_2CO$ system in STO-3G. In the case of Jean and Lehn, transfer of a single proton was prohibited by the C_{2v} symmetry constraint.

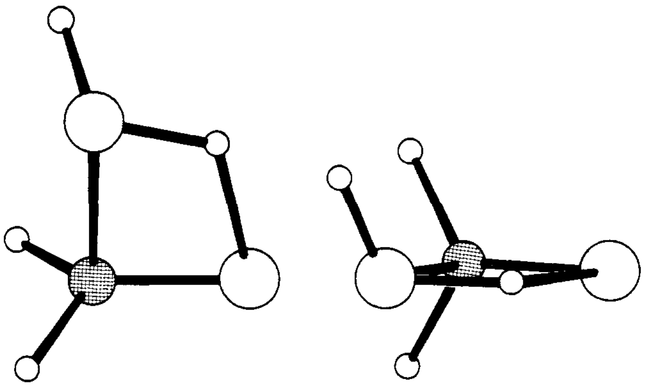

Figure 4. ORTEP drawings of $H_2O + H_2CO$ transition state as viewed from the "side" (left) and from the "top" (right).

As H_2O approaches H_2CO in the straddled orientation, no adduct is formed, even as an intermediate, since the unfavorable interaction between the molecules cannot be compensated by a favorable proton transfer. The species $H_2O^+CH_2O^-$ exists only in an unbound state and dissociates to H_2O and H_2CO within the period of a single vibration.

A C_s symmetrical $H_2O + H_2CO$ addition path has been investigated along which the water moiety is coplanar with the carbonyl bond in the plane bisecting the methylene group. Coordinates for these "coplanar" structures are illustrated in Figure 1d and those varied in constrained optimizations with $O\cdots C$ as the only distinguished coordinate are specified in Table I. Interaction energies calculated in STO-3G along this "coplanar" addition path are given in Table IV. For $O\cdots C > 1.5$ Å, the interaction between H_2O and H_2CO is consistently more repulsive on the coplanar path than on the straddled path. Thus the coplanar path is not the Ψ-MEP as determined by using the STO-3G basis,[44,45] but even at $O\cdots C = 1.5$ Å there is less than 2-kcal/mol difference in energy between structures on the two paths. It appears that the PES for nulceophilic approach of H_2O to H_2CO is rather broad and shallow with respect to angular variation of the H_2O orientation.

As $O\cdots C$ decreases below 1.5 Å on the coplanar addition path, the STO-3G interaction energy falls precipitously by ~95 kcal/mol for a change of less than 0.05 Å in the distinguished coordinate such that the adduct with $O\cdots C = 1.45$ Å is stabilized by ~39 kcal/mol with respect to isolated H_2O and H_2CO molecules as shown in Figure 2. A minimum occurs in the energy profile at $O\cdots C \approx 1.43$ Å and corresponds to a distorted methanediol structure in which a proton has been transferred between the oxygen atoms. Selection of $O\cdots C$ as a single distinguished coordinate for description of reaction progress obscures the crucial involvement of proton transfer in the transformation of reactants into products in addition to O–C bond formation, and the reaction path thus determined is discontinuous. In their study of singlet methylene insertion into a methane C–H bond, Hoffmann and co-workers[46] noted similarly that, in a certain range, the $C\cdots C$

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[44] However, calculations with more extensive bases for rigid, STO-3G optimized geometries[38] of H_2O and H_2CO indicate that the preferred relative orientation of the molecules for nucleophilic interactions is indeed "coplanar", in contrast to the STO-3G prediction (cf. ref 45). Straddled and coplanar C_s symmetrical configurations have interaction energies, respectively, of −3.79 and −3.90 kcal mol^{-1} in 4-31G, and −3.60 and −3.77 kcal mol^{-1} in 6-31G. It is probable that the coplanar addition path is the Ψ-MEP in these bases.

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distance ceased to be a good distinguished coordinate when the most important motion was hydrogen atom transfer.

The discontinuity found in the interaction energy profile (Figure 2) exemplifies the fact that there is no guarantee that a reaction path determined by the distinguished coordinate method must pass through a transition state.[6] In order to locate a transition state for $H_2O + H_2CO$, we must consider motions in all coordinates. Recently a gradient-search procedure (cf. ref 47) has been employed to locate and characterize this transition state[48] whose properties will be discussed in detail elsewhere.[49] It may be noted simply that its structure (Figure 4) involves a proton partially transferred from the nucleophile to the carbonyl oxygen, as distinct from more zwitterionic structures. The transition state is higher in energy than the reactants by 42.2 kcal/mol in STO-3G and by 44.1 kcal/mol in 4-31G, implying a large activation energy for the reaction. This prediction of a large energy barrier to gas-phase $H_2O + H_2CO$ addition is contrary to the results of a CNDO/2 study.[50] Inclusion of correlation effects in the calculations would probably reduce the size of the barrier somewhat but would probably not remove it entirely.

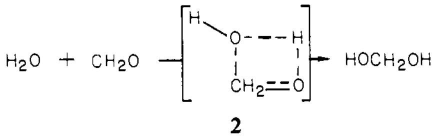
Discussion

Enforced Concertedness of Proton Transfer and Heavy-Atom Reorganization. Many reactions could conceivably occur either (a) in a *stepwise* fashion, with a component process of the overall reaction taking place in each of the steps, or (b) in a *concerted* fashion, in which all component processes are carried out together in a single step. Thus the hydration of formaldehyde might be imagined to proceed in a stepwise manner (eq 1) with formation

$$H_2O + CH_2O \rightarrow \underset{\mathbf{1}}{H_2O^+CH_2O^-} \qquad (1a)$$

$$H_2O^+CH_2O^- \rightarrow HOCH_2OH \qquad (1b)$$

of a C–O σ bond and fission of the carbonyl π bond (heavy-atom reorganization) occurring in a first step (eq 1a) and with the transfer of the proton following in a separate step (eq 1b). The zwitterionic intermediate compound **1** is necessarily formed in this sequence. The same reaction could also be imagined to proceed by the *concerted* mechanism of eq 2, passing through the four-center transition state **2**. Factors which lead to one of these mechanisms instead of the other are of great interest in current mechanisms chemistry.



(2)

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Jencks[51] has clarified one major aspect of this question. When the structure corresponding to **1** has no finite lifetime as a chemical species, there will be no opportunity for the proton transfer of eq 1b to occur, and the stepwise mechanism is then not a feasible reaction route. When the only effective alternative is the concerted route, as in eq 2, the reaction must proceed in that manner and its "concertedness" is said to be *enforced.*

The calculations we report here suggest the structure corresponding to **1** indeed has no finite lifetime in the gas phase, the interaction of water with formaldehyde in the structural region where bonding is expected being entriely repulsive. Furthermore, a four-center transition state like **2** is found to exist on the PES. The reaction thus occurs concertedly, and the concertedness is enforced by the nonexistence of **1** as a bound chemical species.

Stepwise Specific-Acid–Base Catalysis. Although the reaction of neutral water with neutral formaldehyde must proceed through transition state **2**, in which the component process of heavy-atom reorganization (HAR) and proton transfer (PT) are concerted, because the intermediate corresponding to **1** does not exist, the situation can be altered through prior accomplishment of proton transfers.

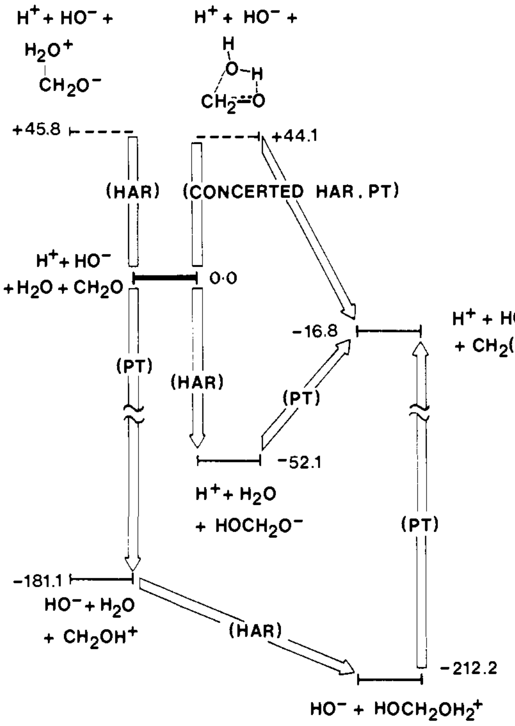

Figure 5. Energy diagram illustrating alternative routes for hydration of formaldehyde. Energies (kcal/mol) are from 4-31G calculations: HAR = heavy-atom reorganization, PT = proton transfer.

As Figure 5 shows, the product methanediol can be reached by the stepwise routes in the lower part of the diagram, as well as by the concerted route in the upper part. These stepwise routes involve prior proton transfer to formaldehyde (*specific-acid catalysis*) or prior proton transfer from water (*specific-base catalysis*).

In specific-acid catalysis, protonation of the formaldehyde results in conversion of the repulsive interaction of neutral formaldehyde with water into a wholly attractive interaction. The cationic adduct $HOCH_2OH_2^+$ is formed with no activation energy in a reaction exothermic by 31.1 kcal/mol. This adduct structure is now a stable species and an intermediate on a feasible mechanistic route. Its structure still contains some of the features that doubtless prevent formation of **1**. For example, the bond from carbon to water-derived oxygen is usually long, 1.67 Å, and the former carbonyl group bond unusually short, 1.33 Å, compared to the corresponding C–O bond length in $HOCH_2OH$ of 1.41 Å. Nevertheless, the presence of the protonic electron sink on the carbonyl oxygen, allowing nucleophilic attack of water without simultaneous generation of unstabilized negative charge at that position, has produced a profound reduction in energy, opening up a stepwise channel to products.

Similarly in specific-base catalysis, the *absence* of a proton from the nucleophilic oxygen means that nucleophilic attack results in dispersal of charge. The anionic adduct $HOCH_2O^-$, like the cationic adduct, is a stable species, formed without activation energy in a reaction exothermic by 52.1 kcal/mol. A long bond to the nucleophile (1.52 Å) and short former carbonyl bond (1.33 Å), relative to the methanediol value of 1.41 Å, appear here again. But the opportunity for nucleophilic binding without charge polarization, produced by prior deprotonation of the nucleophile, has opened a stepwise path to products through a stable intermediate adduct.

The appearance of the specifically catalyzed reactions at lower energy than the concerted, uncatalyzed reaction is a result of the arbitrary choice of the zero of energy, which was taken as the

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(51) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425–432.

energy of an assembly including fully formed H^+ and HO^-. For other purposes, other choices of initial state might be appropriate. As one example, if the zero of energy had been taken as that of the assembly $2H_2O + CH_2O$, the reactions involving H^+ or HO^- would have been displaced vertically upwards by an increment of 426 kcal/mol, with the result that the stepwise processes would no longer be energetically preferred over possible concerted processes.

Factors Leading to Enforced Concertedness. The properties of the stable cationic and anionic adducts, $HOCH_2OH_2^+$ and $HOCH_2O^-$, give a clue to the major reason for the failure of water and formaldehyde to form a zwitterionic adduct **1** and the resulting enforced character of the concerted mechanism through **2**. Both of the ionic adducts have, as noted above, long, weak O···C bonds to the nucleophile and short, strong C–O (former carbonyl) bonds. This suggests a tendency to permit sufficient attachment of the nucleophile and electrophile so that the charge on the ionic partner can be dispersed, but not sufficient bonding that the charge tends to become localized on a single atom (as in the simple valence-bond representations). Dissociation of the ionic adducts then requires work to sever the covalent attachments and reconcentrate the charge within the ionic partner.

Dissociation of the structure corresponding to **1**, in contrast, involves charge depolarization, and thus no energy barrier opposes its decomposition. Expressed differently, the formation of an adduct like **1** would necessarily relocate electron density, resulting in an excess of positive charge in the water fragment and an excess of negative charge in the formaldehyde fragment. The difficulty of achieving such a charge polarization is shown by the fact that when the "bond" to the nucleophilic oxygen is forced to 1.4 Å, the carbonyl group retains a C–O distance of 1.30 Å, substantially shorter than the corresponding distance in either the cationic or anionic adduct. These have equilibrium bond lengths to the nucleophile far longer than 1.4 Å. Adduct formation from neutral molecules must involve charge polarization, while formation of "weak" adducts (with loose nucleophile attachement) in the ion–neutral reactions makes for charge dispersal. This presumably accounts for adduct stability and for the existence of feasible stepwise mechanisms in the ion–neutral reactions but an unbounded character of the "intermediate" and an enforced, concerted mechanism in the neutral–neutral reaction.

The transition state **2**, of course, also dissociates to water and formaldehyde with charge depolarization,[52] a process not resisted by an energy barrier. However, incipient bond formation between one of the hydrogens of the water fragment and the oxygen of the formaldehyde fragment opens another channel for decomposition with charge depolarization, namely, formation of methanediol. This process as well is attended by no opposing energy barrier. Thus **2**, with open, barrier-free pathways to both reactants and products, but bounded in other respects, is a transition state for the concerted reaction. The same physical factors account for the nonexistence of the intermediate **1** and for the fact that **2** exists as a transition state for the concerted reaction.

Conclusions

These results provide models for enforced, concerted carbonyl addition and for stepwise, specific-acid-catalyzed and -base-catalyzed carbonyl addition in the gas phase. Their significance for carbonyl group reactions in more complex environments such as in aprotic solvents, in aqueous solution or in enzyme active sites, remains to be determined by further study. We are currently examining the properties of transition state **2** and the effect of introducing more water molecules into the system.

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[52] In fact, the atomic charge distributions for **2** and for a typical structure resembling **1** are very similar.[49]

The Role of Nonadiabatic Coupling and Sudden Polarization in the Photoisomerization of Olefins

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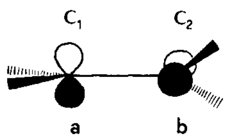
Abstract: Energies, dipoles, and nonadiabatic couplings have been computed for the diradicalic and zwitterionic states of ethylene and propene, in the 3 × 3 CI approximation. The same kind of calculations, and qualitative arguments based on VB theory, are used to elucidate the nature of the perturbation of the zwitterionic states of an olefin, as caused by different kinds of substituents and/or by pyramidalization of a carbon atom adjacent to the double bond. The vibrational problem relative to the twisting coordinate is solved for propene and for ethylene at various pyramidalization angles. The properties of the vibronic states are determined both in the Born–Oppenheimer approximation and in a computational scheme which explicitly allows for nonadiabatic coupling. Finally, quantum mechanical calculations are performed to describe the time evolution of the molecular wave function after a Franck–Condon excitation. The paradigmatic value of the results here presented is discussed, mainly in relation to the open question of the existence of strong polar vibronic states in excited olefins, with a lifetime long enough to play a role in photochemical processes.

Introduction

The problem of the photolysis of olefins has been variously and extensively dealt with by theoretical chemists in the past.

A large number of papers are concerned with the properties of the first electronic states of ethylene and other olefins (see ref 1–18 and references therein).

Chart I



At present the following points seem to be settled more or less definitively. (1) Three VB structures are most relevant to describe

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[1] U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).

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