Table III. Effect of Electron Correlation on the Computed GAPT Atomic Charges. The 6-31G** Basis Set and the Experimental Geometries Used

molecule		Q_{GAPT} HF	Q_{GAPT} MP2	Q_{GAPT} CISD
CH_4	C	0.0830	0.0119	0.0478
(R_{CH} = 1.092 Å)	H	–0.0208	–0.0030	–0.0120
CO	C	0.3712	0.1211	0.2437
(R_{CO} = 1.128 Å)	O	–0.3712	–0.1211	–0.2437
CO_2	C	1.4914	0.9061	1.2587
(R_{CO} = 1.162 Å)	O	–0.7457	–0.4531	–0.6294
HCN	H	0.2777	0.2444	0.2518
(R_{CH} = 1.065 Å)	C	–0.0077	–0.0784	–0.0431
(R_{CN} = 1.153 Å)	N	–0.2700	–0.1661	–0.2086
LiF	Li	0.8379	0.7727	0.7920
(R_{LiF} = 1.564 Å)	F	–0.8379	–0.7727	–0.7920

the computed charges. Our conclusion is that the GAPT charges do not change significantly going from the 4-31G to 6-31G** basis set (the only exception is the NH_3 molecule for which the optimized geometry changes substantially). In ref 20 we have computed the GAPT atomic charges in some lithium compounds using the 6-31++G** basis set. They compare very favorably to the present 6-31G** results. On the other hand, Mulliken net charges vary to a much larger extent. The STO-3G results underestimate ionicity as measured by the magnitude of the GAPT charges. This is caused by the inadequate flexibility of the minimal basis to provide correct dipole moments (see Table I). The STO-3G Mulliken charges have a sign reversed in several cases (CLi_4, HCNO, and LiH molecules).

Our population analysis predicts quite large atomic charges in molecules with multiple bonds (CO, CO_2, C_3O_2, O_3, HCNO, etc.). We found that this is an artifact of the HF wave function rather than an internal failure of our method. We recalculated the atomic charges in the CH_4, CO, CO_2, HCN, and LiF molecules using CISD and MP2 wave functions (with the dipole moments computed as the energy derivatives, Table III). Inclusion of electron correlation reduces the magnitude of atomic charges in all cases. The reduction is larger in the MP2 approach than in CISD. We trust the MP2 results more because CISD lacks the property of size extensivity and therefore might be incapable of accounting for the most part of the effect of the electron correlation on the calculated charges.

Electron correlation does not significantly change the charges in molecules with single bonds. This is true for both covalent (CH_4) and ionic (LiF) bonds. On the other hand, there is a large reduction of the charges in the CO, CO_2, and HCN molecules. The carbon monoxide molecule, which is predicted semipolar at the HF level, becomes almost homopolar according to the MP2 calculations. We conclude that electron correlation is essential for obtaining a correct picture of the electron distribution in molecules with multiple bonds.

In the present paper we have succeedced in proposing a new population analysis that provides insight into the electron distribution in molecules that is not distorted by an arbitrary choice of the reference basis set. Our procedure is simple and feasible for practical calculations. We have demonstrated its validity through numerical calculations on neutral and charged molecules, and molecular complexes.

We are planning to test our population analysis on semiempirical methods. Since they partially account for the electron correlation (through a numerical parametrization), we hope that they would provide reasonable GAPT atomic charges. The field of organometallic compounds and metal complexes can also benefit from our new definition of atomic charges.

Acknowledgment. This research has been performed under the auspices of U.S. D.O.E. All the computations have been carried out on the CRAY X-MP48 digital computer. The author acknowledges inspiring discussions with Drs. P. J. Hay and R. L. Martin.

Base-Initiated Aldol Condensations in the Gas Phase

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Abstract: The enolate anion $CH_2{=}CHO^-$ reacts with acetaldehyde in the gas phase at ca. 0.1 Torr to produce a "stable" adduct that is amenable to study by collisional activation and tandem mass spectrometry (MS/MS). The activated adduct and a reference ion $HCOCH_2CH(CH_3)O^-$ both decompose by elimination of methane and water and by a retro reaction to re-form $CH_2{=}CHO^-$. Although the kinetic energy releases associated with the decompositions and the charge reversed spectra of the adduct and reference are nearly identical, the extent of water and methane loss is considerably attenuated for the ion–molecule reaction adduct. These two losses are assigned to be characteristic of a species of tetrahedral geometry. The adduct undergoes these losses less abundantly because, in addition to existing as a tetrahedral complex, it also is formed as ion–dipole and proton-bound species. The enolate of acetone reacts in a similar way with neutral acetone to give also three adducts: ion–dipole, proton-bound, and tetrahedral complexes.

Aldol condensations, as first reported by Kane in 1838,[1] and later by Wurst in 1872,[2] constitute an important class of organic reactions. A study of the mechanism of the aldol reaction can to some extent lead to a clearer understanding of other condensation reactions that can be described by a priori similar mechanisms. For example, the Claisen, Knoevenagel, Doebner, Perkin, Stobbe, and Reformatsky reactions are all considered to be nucleophilic substitutions at carbonyl carbon.[3]

In the presence of dilute base or dilute acid, two molecules of an aldehyde or a ketone may condense to form a β-hydroxy aldehyde or β-hydroxy ketone. The generally accepted mechanism for the base-catalyzed aldol reaction in the condensed-phase is

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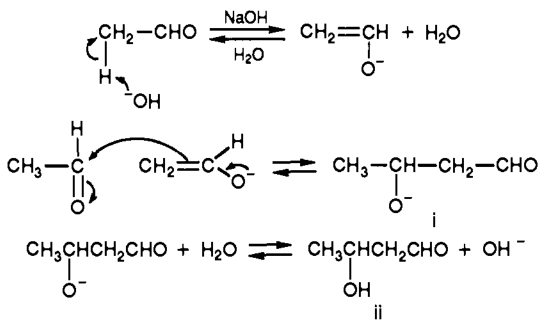
[1] Kane, R. *Ann. Phys. Chem. 2* **1838**, *44*, 475. Kane, R. *J. Prakt. Chem.* **1838**, *15*, 129.

[2] Wurst, A. *Bull. Soc. Chim. Fr.* **1872** *17*, 436.

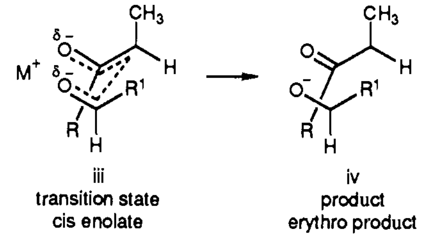
[3] House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1972; p 629. March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 849.

Scheme I



illustrated for acetaldehyde in Scheme I.[4] The entire system of reactions is in equilibrium; the reverse reaction is known as the retrograde aldol reaction.

To control the stereoselectivity of the aldol reaction, pre-formed enolate derivatives have been used.[5] The most common derivatives used are those formed in the presence of lithium, boron, magnesium, or zinc alkoxides. The stereoselectivity of these reactions has been interpreted in terms of the Zimmerman–Traxler transition state (e.g., iii, eq 1).[6] In this transition state, the partial negative charges on both oxygen atoms are directed toward the cation. Moreover, the enolized reactant orientates in such a manner that maximizes the distance between R and R^1. Thus, in the example shown in eq 1, the cis enolate yields the erythro product iv on simple steric grounds. Recent evidence[7] suggests that lithium enolate derivatives exist as tetrameric aggregates in solution. These complexes undergo condensation in an analogous manner to that shown in eq 1.

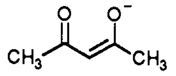


(1)

In contrast, gas-phase aldol condensations are not well understood; in particular, the structures of stable adducts (c.f., i, Scheme I) have not been fully characterized. Wesdemiotis and McLafferty[8] described an acid-catalyzed aldol condensation of acetaldehyde in the gas phase. Evidence for an α,β-unsaturated product was obtained from a comparison of the collisional activation (CA) mass spectrum of this species with that of protonated crotonaldehyde. The structure of the aldol adduct was suggested to be a β-hydroxy aldehyde, but the mass spectral evidence gave support only for a decomposing adduct of tetrahedral geometry and is not indicative of the nature of the stabilized adduct.

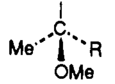
More recently, March et al.[9] and Young and March[10] investigated the acid-catalyzed aldol condensation of acetone by using high-energy collisional activation tandem mass spectrometry. Comparing the CA mass spectrum of an apparent protonated acetone dimer with that of protonated diacetone alcohol, the authors concluded that the structure of the aldol product was a proton-bound dimer. Protonated diacetone alcohol underwent dehydration to yield protonated mesityl oxide.

Bouchoux and Hoppilliard[11] reported the formation of the $(CH_3COCHCOCH_3)^-$ enolate anion following a reaction between acetone and its enolate anion in a high-pressure chemical ionization source. The authors suggest that the observed enolate species is formed by elimination of CH_4 from a condensation adduct of tetrahedral geometry (v). The adduct itself, however, was not observed under the experimental conditions.

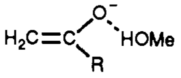


v

Klass and Bowie[12] observed a "stable" adduct in the reaction of the $(M - H)^-$ ion of acetone with acetone in an ion cyclotron resonance (ICR) cell but were unable to determine its structure. Ab initio calculations (at STO-3G and 4-31G levels) support a structure of the stable adduct formed from the nucleophile MeO^- and acetone that is either tetrahedral (vi) or a hydrogen-bonded (proton-bound) enolate complex (vii) as both should be stable with comparable energies.[13]



vi



vii

The structures of stable adducts formed in reactions of nucleophiles with carbonyl compounds in the gas phase are still a matter of conjecture.[12-16] A number of experimental and theoretical studies suggest that simple nucleophile/carbonyl systems (e.g., H^-/H_2CO) give rise to adducts of tetrahedral geometry, whereas reactions of strongly basic nucleophiles (e.g., MeO^-, F^-) with carbonyl compounds, on the basis of both ICR experiments and ab initio calculations, give rise to "stable" proton-bound complexes and "unstable" adducts that decompose through tetrahedral structures.[15] A more recent ab initio study[15] of the HO^-/CH_2O system shows the existence of a small energy barrier (ca. 5 kJ mol^{-1}) to the formation of a tetrahedral structure. Furthermore, the shallow minimum corresponds to an ion–dipole stabilized structure.

Ion–dipole complexes are also thought to play a role in gas-phase anion reactions. Specifically, the 1,2-eliminations of alkanes from activated tertiary alkoxide anions occur through an ion–dipole structure.[17-19] One example of significance to this work is the fragmentation behavior of 2-substituted 2-propoxide anions; viz., the elimination of neutral alkane (RH) occurs over the same double-minimum potential energy surface as that involved in the proton-transfer reaction of R^- with acetone.[19]

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Table I. CA Mass Spectra of $[M - H^+]^-$ from Aldol Condensations of Acetaldehyde and β-Hydroxyaldehydes

			loss [% abundance (kinetic energy release × 10^{-3} eV)^a]					
figure	enolate	neutral	$H^\bullet/D^\bullet$	H_2/D_2	CH4/CD4	H_2O/D_2O	MeCHO	CD_3CDO
1A	CH_2CHO^-	MeCHO	4 (126.2)	6 (241.3)	0.1 (673.8)	2 (61.1)	100 (19.9)	
1B	$HCOCH_2CHMeO^{-b}$		3 (137.2)	5 (245.4)	1 (666.0)	100 (64.5)	14 (18.6)	
	CD_2CDO^-	CD_3CDO	1 (93.7)	0.5 (210.5)	*c*	3 (54.9)^c		100 (17.4)
	$CD_3COCD_2CD(CD_3)O^{-b}$		1 (95.6)	0.5 (219.2)	*c*	3 (53.6)^c		100 (17.9)

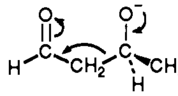
[a] Kinetic energy release = $(m_2^2 eV/16m_1m_3)(\Delta E/E)^2$, where V is the accelerating voltage, ΔE is the peak width at half-height, E_1 is the electric sector voltage of the daughter ion peak center, m_1 is the mass of the parent ion, m_2 is the mass of the daughter ion, and m_3 is the mass of the neutral fragment. [b] β-Hydroxyaldehyde model compound. [c] Composite peak corresponding to losses of CD_4 and D_2O.

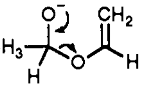
In this paper, we address the following questions: What are the structures of the stable adducts formed in the gas-phase, base-initiated aldol reaction? Are they of tetrahedral geometry, as they have been characterized in the condensed-phase, or are they loosely associated structures (i.e., proton-bound enolates or ion-dipole complexes) as suggested by theoretical calculations? Herein, we turn to the CA mass spectra of adducts from condensations of the enolate anions of acetaldehyde and acetone with acetaldehyde and acetone, respectively, for evidence. We also compare the CA mass spectra of these adducts with those of appropriate model compounds. The structures of the condensation products are discussed on the basis of these comparisons.

Enolate negative ions are easily produced by deprotonation of alkyl carbonyl compounds by using MeO^- (produced by dissociative secondary electron capture of methyl nitrite[20]) in a chemical ionization source.[21] The collision-induced decompositions of a number of enolate negative ions were recently reviewed,[22] and it was demonstrated that the CA mass spectrum is often structurally specific for a particular ion. Moreover, the major fragmentations can be rationalized in terms of simple anion chemistry.

Results

Reaction of Acetaldehyde Enolate Negative Ion with Acetaldehyde. The collisional activation (CA) mass spectrum of an adduct (*m/z* 87) formed in the reaction of acetaldehyde enolate negative ion with acetaldehyde (Figure 1A) shows that the major fragmentation of the adduct is loss of MeCHO to give rise to CH_2CHO^- (*m/z* 43). Loss of MeCHO may arise from an adduct of a structure that is either tetrahedral (viii or ix) by a retrograde mechanism, or from a loosely associated structure (e.g., the proton-bound enolate x or ion–dipole complex xi) by simple dissociation.[23]


viii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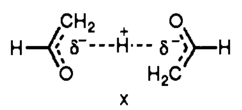
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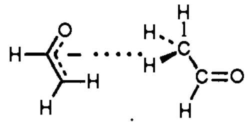
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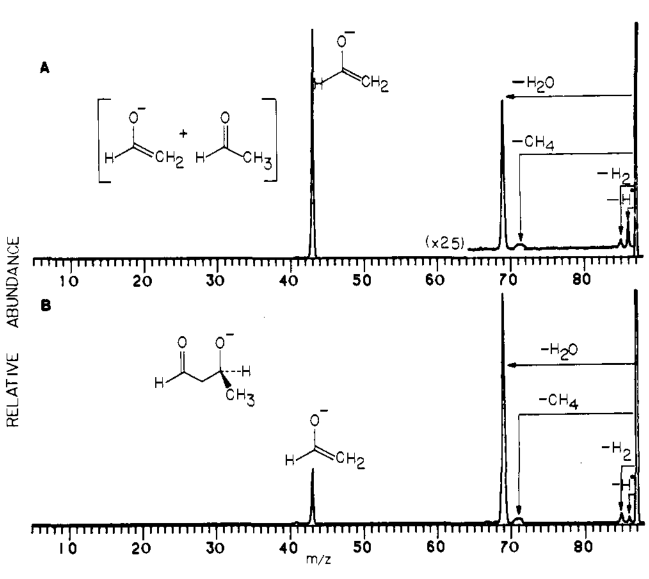
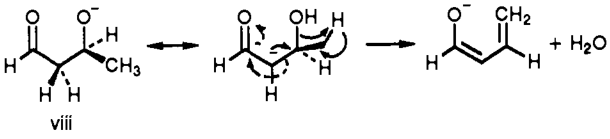


Figure 1. CA Mass spectrum of (A) the adduct(s) formed in the $CH_2{=}CHO^-$/MeCHO system and (B) deprotonated 3-hydroxybutanal. Experimental conditions are given in the Experimental Section.

Two less abundant but structurally more informative fragmentations are the losses of H_2O and CH_4 to give ions of *m/z* 69 and 71, respectively (Figure 1A). The loss of CH_4 is accompanied by considerable kinetic energy release (673.8 meV, Table I) as evidenced in the CA mass spectrum by a "flat-topped" peak shape. The losses of both H_2O and CH_4 are difficult to envision as being simple fragmentations occurring from a loosely associated species, but the resulting products are more likely to arise from the aldol product viii (eq 2 and 3, cf. ref 11). Elimination of H_2O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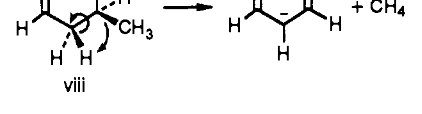
(3)

from the hemiacetal species x (produced by a reaction through oxygen of the ambident enolate nucleophile CH_2CHO^- and acetaldehyde) is unlikely (cf. simple alkoxide anions[17]), whereas the losses of H_2O and CH_4 from viii are analogous to those previously reported for β-dicarbonyl compounds.[24]

Loss of H_2 may also occur through the tetrahedral species viii and ix by the processes shown in Eq 4 and 5. Indeed, the losses of H_2 and CH_4 are indicative of fragmentation through an alkoxide moiety as analogous losses were previously reported for simple

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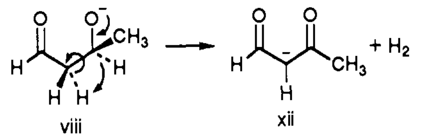
(23) A reviewer has suggested that all of the adducts have a C–H hydrogen-bonded structure, i.e., $CH_2{=}CH{-}O^-{\cdots}H{-}CH_2CHO$. Ab initio calculations for reactions of RO^- (R = alkyl, CF_3) indicate that initial reaction of the nucleophile with the hydrogen of >CH–CO followed by rearrangement to give *stable* enolate ions (e.g., x) is the preferred reaction.[12,14,22] Although, the rearrangement of the initial C–H hydrogen-bonded species to the enolate structure has a substantial energy barrier, the transition states are more negative in energy than reactants, and thus the initial species is likely to collapse rapidly to form the *stable* enolate intermediate. Moreover, collisional activation of a model hydrogen-bonded structure (xvi) yields only the alkoxide anions. No other ions such as from loss of H_2O are observed.

(24) Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *71*, 233.



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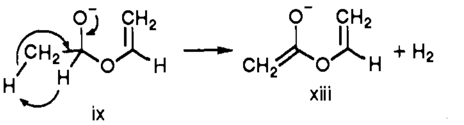
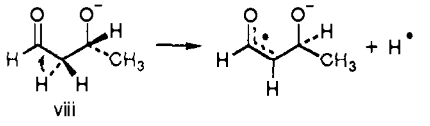


(5)

alkoxide anions.[17] Elimination of H_2 would give either xii (i.e., an β-dicarbonyl anion) or xiii. The $(M - H_2)^-$ ion upon subsequent collisional activation in an MS/MS/MS experiment eliminates predominantly CH_2CO. Smaller losses of H• and CH_4 also occur. This fragmentation pattern is characteristic of β-dicarbonyl compounds as was previously described.[24] Thus, we are reasonably certain that the covalently bound species that eliminates H_2O and H_2 is the aldol product viii and not the hemiacetal species ix.

The loss of H•, also observed in the CA mass spectrum of the gas-phase product, is presumably more a characteristic of viii (eq 6; cf. β-dicarbonyl species[24]) than a fragmentation of a simple alkoxide anion (i.e., ix), which does not eliminate H•.[17]



(6)

The CA mass spectrum of the adduct of m/z 94 formed in the reaction between acetaldehyde-d_3 enolate ion and acetaldehyde-d_4 system shows that analogous losses of CD_3CDO, D_2O, CD_4, D_2, and D• occur. In this case, however, the losses of D_2O and CD_4 are superimposed, giving rise to a peak of composite shape.

The CA mass spectrum (Figure 1B) of deprotonated 3-hydroxybutanal (i.e., the condensed-phase aldol product) shows that losses of MeCHO, H_2O, CH_4, H•, and H_2 take place in a manner similar to those described for the gas-phase adduct. The kinetic energies released for each loss are, within experimental error, the same for both adduct and the corresponding β-hydroxy carbonyl model compound (Table I). Thus, the structures of the decomposing forms, or at least those forms that lose H•, H_2, H_2O and CH_4 from both the adduct and from the β-hydroxy aldehyde model, are the same.[25]

There are, however, differences in the relative abundances of ions arising by losses of neutral aldehyde from the adduct and model compound. The significance of these differences will be addressed later. At this point, however, we suggest that a fraction of the gas-phase adducts have tetrahedral geometry.

Reaction of Acetone Enolate Negative Ion with Acetone. The CA mass spectrum of the adduct formed from a reaction of acetone enolate negative ion with acetone (Table II) shows that the adduct fragments in a manner directly analogous to that described for the adduct formed in the acetaldehyde enolate ion/acetaldehyde system, viz., by means of losses of neutral MeCOMe, H_2O, CH_4, and H• to give ions of m/z 57, 97, 99, and 114, respectively. The kinetic energy releases accompanying each loss are recorded in Table II.

CA mass spectra of the adducts formed in the acetone enolate ion/acetone-d_6 and acetone-d_5 enolate ion/acetone systems (Figure 2, A and B, respectively) show that, in each system, fragmentation occurs by means of losses of neutral MeCOMe *and* $(CD_3)_2CO$; the more abundant enolate ion so formed is the species that is initially the reactant. That is, the adduct formed in the acetone-d_5 enolate/acetone system (of m/z 120) fragments to give more abundant acetone-d_5 enolate ion (of m/z 62) and less abundant acetone enolate ion (of m/z 57) (Figure 2B). Fragmentation to form the initial reactant enolate species is consistent with an adduct of tetrahedral geometry (e.g., xiv) that undergoes retrograde aldol elimination of ketone. The fact that the adducts undergo fragmentations to yield both isotopic enolate anions, however, is understandable only if at least two forms of an adduct are formed, viz., a tetrahedral (e.g., xiv) *and* a proton-bound species (e.g., xv).

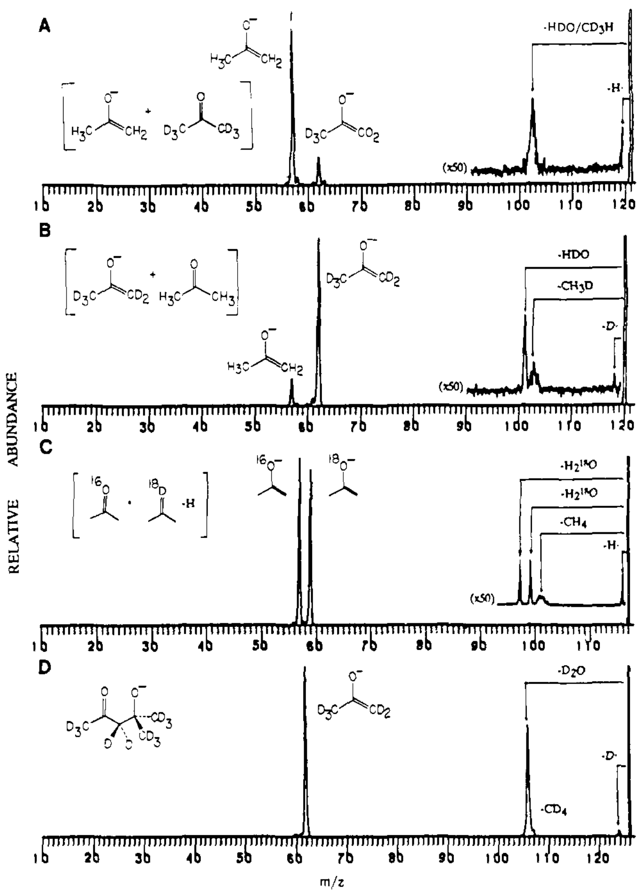
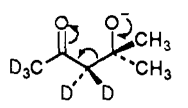
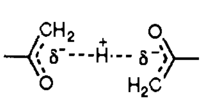


Figure 2. CA Mass spectrum of (A) the adduct(s) formed in the $CH_2{=}CMeO^-/CD_3COCD_3$ system, (B) the adduct(s) formed in the $CD_2{=}CCD_3O^-/MeCOMe$ system, (C) the adducts formed in the $MeC^{16}OMe/MeC^{18}OMe$ system, and (D) deprotonated 4-hydroxy-4-(methyl-d_3)-2-pentanone-*5,5,5*-d_3. Experimental conditions are given in the Experimental Section.



xiv



xv

The pattern for the losses of H•/D•, D_2O/HDO, and CD_4/CD_3H from the isotopically labeled adducts indicate that a fraction of the decomposing species have tetrahedral geometry.

In a similar fashion, the adducts, $C_6H_{11}{}^{18}O^{16}O^-$,[26] formed upon cross-condensations of ^{16}O- and ^{18}O-labeled acetones, fragment primarily to yield a 1:1 ratio of ^{16}O- and ^{18}O-acetone enolates, and to a lesser degree, by losses of $H_2{}^{16}O$ and $H_2{}^{18}O$ (also in a 1:1 ratio), CH_4 and H• (Figure 2C). The fragmentation behavior of the adducts formed in this system is also consistent with some fraction of the decomposing species being covalently bound.

The CA mass spectra of the model compounds: deprotonated 4-hydroxy-4-methyl-2-pentanone, 4-hydroxy-4-(methyl-d_3)-2-pentanone-*5,5,5*-d_3 and 4-hydroxy-4-methyl-2-pentanone-*1,1,1,3,3*-d_5 (Table II) show that the fragmentations of these compounds, which are models for the condensed-phase aldol, are directly analogous to those described for the gas-phase adducts [e.g., 4-hydroxy-4-(methyl-d_3)-2-pentanone-*5,5,5*-d_3 fragments

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[25] This is a standard procedure used to indicate whether two decomposing ions have the same structure (and energy distribution). See: Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973; p 104.

[26] The $^{16}O^{18}O$ adduct was mass selected at a mass resolution of 25 000 (10% valley definition) to avoid any possible contribution of an $^{13}C^{13}C^{16}O^{16}O$ adduct to the CAD spectrum.

Table II. CA Mass Spectra of $[M - H^+]^-$ from Aldol Condensations of Acetone and β-Hydroxy Ketones

			loss [% abundance (kinetic energy release × 10^{-3} eV)[a]]				
figure	enolate	neutral	$H^\bullet/D^\bullet$	CH4/CD4	H_2O/D_2O	Me_2CO	$(CD_3)_2CO$
	CH_2CMeO^-	MeCOMe	1 (235.0)	1 (507.3)	9 (87.4)	100 (18.6)	
	$MeCOCH_2CMe_2O^-$[b]		2 (240.1)	4 (515.4)	68 (90.1)	100 (19.1)	
	$CD_2C(CD_3)O^-$	$(CD_3)_2CO$	2 (142.2)	*c*	45 (73.2)[c]		100 (19.3)
2D	$CD_3COCD_2C(CD_3)_2O^-$[b]		2 (135.8)	*c*	32 (71.7)[c]		100 (19.2)
2B	$CD_2C(CD_3)O^-$	MeCOMe	*d*	0.4 (560.0)[e]	1 (73.3)[f]	100 (18.7)	18 (18.2)
	$CD_3COCD_2CMe_2O^-$[b]		*d*		18 (76.0)[f]	100 (18.7)	25 (18.8)
2A	CH_2CMeO^-	$(CD_3)_2CO$	*g*	*h*	1 (120.1)[f,h]	17 (18.3)	100 (18.2)
	$MeCOCH_2C(CD_3)_2O^-$[b]		*g*	*h*	24 (130.3)[f,h]	5 (19.0)	100 (19.1)
2C	$C_6H_{11}{}^{18}O^{16}O^-$[i]		1 (237.0)	0.5 (575.0)	*j*	*k*	*k*

[a] Kinetic energy release = $(m_2{}^2eV)/16m_1m_3)(\Delta E/E)^2$, where V is the accelerating voltage, ΔE is the peak width at half-height, E_1 is the electric sector voltage of the daughter ion peak center, m_1 is the mass of the parent ion, m_2 is the mass of the daughter ion, and m_3 is the mass of the neutral fragment. [b] β-Hydroxy ketone model compound. [c] Composite peak corresponding to losses of CD_4 and D_2O. [d] Losses of both $H^\bullet$ and $D^\bullet$ are observed: loss of $H^\bullet$, 0.7 (308.3); loss of $D^\bullet$, 0.7 (211.7). Model compound: loss of $H^\bullet$, 2 (281.9); loss of $D^\bullet$, 1.5 (212.9). [e] In this case loss of MeD is observed. [f] In this case loss of HDO is observed. [g] Losses of both $H^\bullet$ and $D^\bullet$ are observed: loss of $H^\bullet$, 0.7 (364.7); loss of $D^\bullet$, 0.1 (84.6). Model compound: loss of $H^\bullet$, 3 (339.8); loss of $D^\bullet$, 1.5 (95.7). [h] Composite peak corresponding to losses of CD_3H and HDO. [i] In this case isotopically mixed adducts re formed upon cross-condensations of ^{16}H- and ^{18}O-labeled acetones. [j] Losses of both $H_2{}^{16}O$ and $H_2{}^{18}O$ are observed: loss of $H_2{}^{16}O$, 2 (91.2); loss of $H_2{}^{18}O$, 2 (91.2). [k] In this case both ^{16}O- and ^{18}O-enolates are observed: loss of $Me_2C^{16}O$, 100 (18.5); loss of $Me_2C^{18}O$, 100 (18.5).

by loss of neutral acetone-d_6 to give an ion of m/z 62 and by losses of D_2O and CD_4 indicated by the composite peak at m/z 106, and $D^\bullet$, Figure 2D]. As can be seen from the data contained in Table II, the kinetic energy releases for each given decomposition are, within experimental error, the same for each model and adduct. Thus, it is likely that the structures of the two ions [i.e., the $(M - H)^-$ ion of the β-hydroxy carbonyl model and the gas-phase adduct] that decompose by losing H_2O, CH_4, and $H^\bullet$, are the same.

The charge-reversal mass spectra[27] of the gas-phase adducts and the model compounds are also consistent with a *fraction* of each having a common structure. Charge-reversal spectra are obtained by removing two electrons from a negative ion in a collisional activation event. The major fraction of the adduct undergoing fragmentation upon charge stripping, however, is that species that yields an enolate cation (e.g., $CH_2{=}CMeO^+$ from the $CH_2CMeO^-/MeCOMe$ system). In addition, the charge reversal mass spectrum shows the characteristic fragmentation $MeCO^+ + CH_2$.[28] Apparently, that species is the proton-bound enolate.

A model for the proton-bound species (xvi; cf. xv) can be formed in a chemical ionization source by a Riveros reaction[29] between CD_3O^- and HCO_2Me (eq 7). The proton-bound species frag-

$$CD_3O^- + HCO_2Me \rightarrow \underset{\text{xvi}}{CD_3O^{\delta-}\cdots H^+\cdots{}^{\delta-}OMe} + CO \qquad (7)$$

ments upon CA to give a nearly equal mixture of both CD_3O^- and MeO^-. The charge-reversal mass spectrum of this model ion similarly corresponds to a nearly equal mixture of CD_3O^+ and MeO^+ ions.

Discussion

Theoretical studies point to stable adducts in some nucleophilic substitution reactions as either proton-bound enolate complexes or structures of tetrahedral geometry because both are stable and have comparable energies.[13] Collisional activation (CA) of each stabilized adduct will presumably give rise to a different CA mass spectrum. Thus, for the systems described in this paper, in which at least two of the possible adducts are likely to be of comparable energy, it is not unreasonable for the CA mass spectra to represent both species. Indeed, as can be seen from a comparison of the CA mass spectra of the aldol adducts formed in this study with appropriate model compounds, there is evidence that at least two structures are formed (viz, one of tetrahedral geometry and another that may be proton-bound).

The relative proportion of a species can be calculated from a composite CA spectrum by measuring the relative abundances of peaks corresponding to ions formed through fragmentation processes characteristic of that structure. The CA spectra of appropriate model compounds are then used as benchmarks for comparison. By using the losses of H_2 and H_2O as representative fragmentations of a structure of tetrahedral geometry, we calculate that only a small fraction of the adducts formed in the reactant systems are of tetrahedral geometry (<0.6% in each of the acetaldehyde and acetone systems).

A proton-bound structure is expected to fragment upon collisional activation to give equal amounts of each enolate species (e.g., $CD_3O^{\delta-}\cdots H^+\cdots{}^{\delta-}OMe$ yields CD_3O^- and MeO^-). Thus, we predict that the CA spectrum of an adduct formed in the acetone-d_5 enolate/acetone system would show a 1:1 ratio of d_5-enolate to h_5-enolate ions. We observe, however, a 6:1 ratio of d_5-enolate to h_5-enolate ions. The excess of d_5-enolate ions that are formed are attributed to fragmentation of a third form of the adduct, namely, an ion–dipole complex. Indeed, in the reverse system (i.e., h_5-enolate/acetone-d_6), a 1:6 ratio of d_5-enolate to h_5-enolate products is formed, which also points to an ion–dipole complex that specifically loses the initial reactant enolate anion (i.e., h_5-enolate).

Moreover, the reactant systems are quite sensitive to perturbation of the source conditions (e.g., the ratio of loss of H_2O to loss of ketone could be varied by an order of magnitude by only raising the pressure of reactants in the source by 10%). Increasing the source pressure essentially "cools" the reactants by third-body collisional stabilization. Consequently, less excess energy is available to surmount energy barriers that lead to products. Thus, as the system cools, the concentration of the ion–dipole species (the first stable encounter complexes) will rise, and given a sufficient lifetime (ca. 10^{-5} s), be a more important contributor to the CA spectrum.

The metastable ion mass spectra of both aldol adducts and of the model compounds show that the only low-energy decomposition is the release of enolate ions (e.g., $CH_2{=}CMeO^-$ in the acetone system); dehydration or fragmentation by loss of methane is of higher energy and is not observed. Thus, there is only a small energy requirement for loss of neutral aldehyde (ketone), as would be expected of loosely bound specie, and there is a larger energy barrier for elimination of H_2O and CH_4 from the species of tetrahedral geometry.

Charge stripping by collision of a negative ion with an inert gas presumably requires considerably more energy than that required to effect fragmentation; thus, this process would be expected to sample even more stable species on a potential energy

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(27) Collision of a negative ion with a collision gas (e.g., He) can effect charge stripping leading to a decomposing positive ion. This produces a charge reversal spectrum. If two negative ions give identical charge reversal mass spectra, there is a probability that the original negative ions had the same structure. See: Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Howe, I.; Bowie, J. H.; Szulejko, J. E.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99.

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surface. A comparison of the charge reversal mass spectra of the adducts with those of the corresponding β-hydroxy carbonyl model compounds indicates that a small fraction of the positive species so produced is of tetrahedral geometry, and that the major fraction is a proton-bound enolate species. Little evidence for an ion–dipole species in the isotopically labeled acetone systems can be obtained from the charge reversal mass spectra. One explanation is that the cross section for charge stripping of the ion–dipole species is appreciably lower than that of either the tetrahedral or the proton-bound species, and that the favored process for ion–dipole complexes is to revert to starting materials. In other words, these loosely bound adducts never survive a charge-stripping collision. In general, loosely associated structures such as ion–dipole complexes are likely to be transparent to charge stripping.

In conclusion, species of tetrahedral geometry form to a small extent in base-initiated gas-phase aldol condensations of enolate negative ions with simple carbonyl compounds. The adducts of the aldol reactions and the corresponding deprotonated model compounds undergo fragmentation in a characteristic manner upon collisional activation. Nearly identical kinetic energy releases accompany the losses of $H^\bullet$, H_2, H_2O, and CH_4 from both adducts and appropriate aldol model compounds. The charge reversal spectra, like the kinetic energy release data, of both adducts and β-hydroxy carbonyl model compounds are consistent with formation of a small amount of a species of tetrahedral geometry. Most of the adducts, however, are loosely bound ion–dipole and proton-bound complexes.

We are at present continuing our investigations of the gas-phase condensation reactions of carbanions with simple carbonyl systems.

Experimental Section

Mass Spectrometry. CA mass spectra were measured with a Kratos MS-50 triple analyzer mass spectrometer of EBE design, which was described previously.[30] Ion–molecule reactions were performed in a commercially available (Kratos Scientific Instrumentation Mark IV) chemical ionization source: ion source temperature, 100 °C, accelerating voltage, 8 kV. Liquids were introduced through a commercially available (Kratos Scientific Instruments) reagent gas inlet system or through a custom fabricated all-glass heated inlet system held at 100 °C. Carbanions were generated by H^+ (D^+) abstraction by MeO^-. MeO^- was generated from methyl nitrite by dissociative secondary electron (at 70 eV) resonance capture.[20] The indicated source pressure of methyl nitrite was typically 5×10^{-6} Torr, and the pressure of each substrate was typically 2×10^{-5} Torr, corresponding to an approximate total pressure of 0.1 Torr. The pressure of helium in the second collision cell was sufficient to produce a decrease in the main beam signal of 50%.

Compounds. All unlabeled compounds are known and were prepared by a standard procedure.[4] Acetaldehyde-d_4 (d_4 = 99.9%) and acetone-d_6 (d_6 = 99.9%) were obtained from Aldrich Chemical Co., Inc., of Milwaukee, WI. 4-Hydroxy-4-(methyl-d_3)-2-pentanone-*5,5,5*-d_3, 4-hydroxy-4-methyl-2-pentanone-*1,1,1,3,3*-d_5 were prepared from acetone-d_6 and acetone by a standard procedure.[4] [^{18}O]Acetone (^{18}O, 20%) was prepared by the method of Bennet, Sinnott, and Wijisundera.[31]

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Characterization of Four C_4H_4 Molecules and Cations by Neutralization–Reionization Mass Spectrometry

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Abstract: The isomeric cations vinylacetylene ($\mathbf{a}^{\bullet+}$), butatriene ($\mathbf{b}^{\bullet+}$), methylenecyclopropene ($\mathbf{c}^{\bullet+}$), and cyclobutadiene ($\mathbf{d}^{\bullet+}$) can be distinguished by three methods: neutralization followed by collisionally activated dissociation (CAD) of the resulting ground-state neutrals ($^+$NCR$^+$ spectra); neutralization with an agent of ionization energy (6 eV) selected to produce excited C_4H_4 molecules that undergo characteristic dissociations ($^+$NR$^+$ spectra); and charge reversal to the unstable $C_4H_4^{\bullet-}$ anions ($^+$NR$^-$ spectra). Concomitant isomerization is minimized, in sharp contrast to that accompanying CAD of the cations themselves or their neutralization by sodium. Separate CAD of the neutral C_4H_4 isomers provides information on their unimolecular isomerization and dissociation reactions; conditions dissociating 28% of **a** dissociate 66% of **d**, producing from **a** and **d** respectively 28% and 8% of $C_4H_3^\bullet$, 38% and 19% of C_4H_2, and 14% and 59% of C_2H_2. Energy profiles are derived for both the neutral and the ionic isomers **a** and **d**. The $^+$NCR$^+$ and $^+$NR$^-$ spectra both show that 70-eV ionization of benzene yields $C_4H_4^{\bullet+}$ ions that are 30% $\mathbf{a}^{\bullet+}$, 0% $\mathbf{b}^{\bullet+}$, 70% $\mathbf{c}^{\bullet+}$, and 0% $\mathbf{d}^{\bullet+}$.

Isomeric characterization by dissociation of gaseous organic ions, especially hydrocarbon cations, can be seriously compromised because their isomerization often requires less energy than dissociation. Thus, mass spectra produced by electron ionization,[1] collisionally activated dissociation (CAD),[2] metastable ion (MI) dissociation,[3] and surface-induced dissociation,[4] are closely similar for isomeric ions such as $C_4H_4^{\bullet+}$,[5] $C_4H_6^{\bullet+}$,[1] $C_4H_8^{\bullet+}$,[6] and $C_4H_9^+$.[6a] For the corresponding neutrals, isomerization barriers are often

Table I. Thermochemical Data of C_4H_4 and $C_4H_4^{\bullet+}$ Isomers[a]

	IE, eV	$\Delta H_f°$(neutral), kJ mol^{-1}	$\Delta H_f°$(ion), kJ mol^{-1}
vinylacetylene (**a**)	9.58	305	1229
butatriene (**b**)	9.15	349	1232
methylenecyclopropene (**c**)	8.28[b,c]	410[d]	1209[e]
cyclobutadiene (**d**)	8.02[b,f]	464[g]	1238[d]

[a] Reference 8. [b] Reference 5c. [c] Also 8.15 eV (adiabatic): ref 11f. [d] $\Delta H_f°$(neutral) = $\Delta H_f°$(ion) − IE. [e] Also 1178 kJ mol^{-1}: ref 11f. [f] Also 8.10 eV: Kreile, J.; Münzel, N.; Schweig, A.; Specht, H. *Chem. Phys. Lett.* **1986**, *24*, 140–146. [g] Based on $\Delta H_f°$(**c**) and the theoretically calculated energy difference between **c** and **d** from ref 10c.

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