nucleophiles, we can predicate the strength of the hydrogen bond from the electron orbital occupancy of the remote nitrogen. For those proteins studied by ESEEM, we suggest that the histidine ligands of Cu(II) sites in stellacyanin and dopamine β-hydroxylase form strong hydrogen bonds, while for galactose oxidase, amine oxidase, and phenylalanine hydroxylase a much weaker or no hydrogen bond is present.

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Reaction of Anions with Activated Olefins in the Gas Phase. A Flowing Afterglow–Selected Ion Flow Tube Study

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Abstract: Reactions of anions with acrylonitrile, acrolein, methyl vinyl ketone, and methyl acrylate at room temperature under SIFT conditions are described. Stabilized carbanions such as benzyl anion, cyanomethyl anion, cyclohexadienide, acetone enolate, and nitromethyl anion add to activated carbon–carbon double bonds in a process that is competitive with other modes of reaction. With acrylonitrile and methyl acrylate, addition is in a 1,4 or Michael fashion, while with acrolein and methyl vinyl ketone, 1,2 addition competes with 1,4 addition. Hydroxide, methoxide, fluoride, and cyanide do not add to activated olefins by either mode (see Tables I–IV). A mechanism is proposed for hydride transfer from cyclohexadienide to activated olefins.

Reaction of anions with neutral organic molecules in the gas phase gives rise to a wide variety of products, including those that can be ascribed to the processes of proton transfer,[1] elimination,[2] substitution,[3] and attack at the carbon of carbonyl groups.[4] Using activated olefins such as acrylonitrile (**1**), acrolein (**2**), methyl vinyl ketone (**3**), and methyl acrylate (**4**) presents the opportunity for

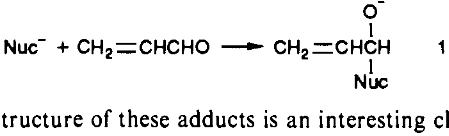
$$\underset{\mathbf{1}}{CH_2{=}CHCN} \quad \underset{\mathbf{2}}{CH_2{=}CHCHO} \quad \underset{\mathbf{3}}{CH_2{=}CHCOCH_3} \quad \underset{\mathbf{4}}{CH_2{=}CHCOOCH_3}$$

1,4 addition to carbon–carbon double bonds. A reaction of this type is of interest because it represents the gas-phase equivalent of a 1,4 or Michael addition. The work described shows that certain anions add to activated double bonds in the gas phase in a process that is competitive with other modes of reaction.

The tandem flowing afterglow–selected ion flow tube technique[5] was used to examine the reactivity pattern of **1–4** toward a range of anionic nucleophiles including the following: hydroxide, methoxide, benzyl anion, cyanomethyl anion, cyclohexadienide, fluoride, acetone enolate, nitromethyl anion, and cyanide. In many instances, peaks were prominent in the product mass spectrum indicating combination of olefin and anion to make a species that might be a cluster or a 1,4 or 1,2 adduct (eqs 1–3). Identifying

$$\mathrm{Nuc^- + CH_2{=}CHCHO \rightarrow [Nuc{\cdot}CH_2{=}CHCHO]^-} \qquad \text{cluster} \quad (1)$$

$$\mathrm{Nuc^- + CH_2{=}CHCHO \rightarrow Nuc\text{-}CH_2C^-HCHO} \qquad \text{1,4 adduct} \quad (2)$$



$$\mathrm{Nuc^- + CH_2{=}CHCHO \longrightarrow CH_2{=}CH\overset{O^-}{\underset{Nuc}{CH}}} \qquad \text{1,2 adduct} \quad (3)$$

the structure of these adducts is an interesting challenge, since mass spectrometry alone cannot give the structure of an observed ion. There were also peaks in the mass spectrum for deprotonation, the elimination of cyanide from acrylonitrile, and the cleavage of acrylate from methyl acrylate, along with other side reactions discussed under Results.

The main goal of these experiments was to look for addition of anions to carbon–carbon double bonds. Finding an addition peak in the product mass spectrum with the correct m/z ratio was the first step. Reaction with various deuterated reagents or butyl nitrite was then used to probe the structure of the adducts and determine if they were clusters, 1,4 adducts or 1,2 adducts.

Each type of product has characteristic reactions that allow the structure of the anion to be probed. For example, since clusters are held together by ion–dipole forces, interacting a cluster with a reagent such as water, acetone, or the perdeuterated neutral

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analogue of the nucleophile can result in an exchange of neutral species within the cluster to give a new peak in the mass spectrum for anion clustered with the reagent. The carbanion produced by a 1,4 addition typically contains an exchangeable proton attached to the negative carbon, which can be diagnostic for a 1,4 adduct. In contrast, a 1,2 adduct represents an alkoxide ion without an exchangeable proton. Experiments are described below that allow these features to be exploited and aid in the identification of addition products.

Hydrogen-deuterium exchange studies have been used successfully in many instances to elucidate the structure of carbanions.[6] In these experiments, an anion is added to an acidic deuterated reagent such as D_2O, MeOD, or EtOD to look for exchangeable protons. Several results are possible from such an experiment. If the proton affinity of the conjugate base of the deuterated reagent is much higher than the proton affinity of the basic site, there will be insufficient energy available from clustering to allow proton exchange with the probe reagent, and the signal in the mass spectrum will remain unaffected (provided the probe reagent does not cluster with the anion). When proton affinities are similar, deuterium exchange can occur, and an increase in m/z will be observed according to the number of exchangeable protons attached to the basic site. If the conjugate base of the reagent is much less basic than the basic site to be probed, deuterium can transfer from the probe reagent to the anion, but there will be little or no exchange, since the conjugate base of the probe reagent is too weak to abstract a proton before leaving the cluster. In this instance, the signal for the adduct in the mass spectrum is effectively attenuated and a new signal will appear for the anion of the probe reagent. If the anion to be probed is an alkoxide (e.g., 1,2 adduct), then protonation within the cluster occurs on oxygen. Since there is no hydrogen available for exchange, a deuterium exchange reaction will not be observed.[6a]

Whenever nonenolate carbanions such as succinonitrile anion or the 1,4 adducts of acrylonitrile are mixed with deuterated reagents, facile H-D exchange is observed.[6b] The same is true for 1,4 adducts of methyl acrylate. In contrast, the efficiency of deuterium exchange for enolate carbanions such as acetone enolate, propionaldehyde anion, and the 1,4 adducts of acrolein and methyl vinyl ketone is rather poor.[6a] For example, the addition products of acrolein were never observed to exchange with deuterated reagents even when there was independent evidence that 1,4 addition products to give enolate carbanions were present. Consequently, this test cannot be used to decide if an adduct to acrolein or methyl vinyl ketone has exchangeable protons. The failure of the H-D exchange test with enolates under flowing afterglow conditions is most likely due to excessive clustering of the enolate anion with the deuterated reagent so that H-D exchange is difficult to observe. Under ICR conditions this problem apparently does not arise.[6h]

A second reagent probe experiment is to use the perdeuterated neutral analogue of the nucleophile to exchange the protonated or deuterated nucleophile from a cluster. For example, mixing a methoxide cluster with CD_3OD gives rise to a new peak 3 amu higher in mass in which CH_3O^- is replaced by CD_3O^-. Treatment with methanol-d_4, acetone-d_6, and toluene-d_8 was used successfully in this series of experiments to differentiate between adducts and clusters.

An altogether different approach is to exploit the remarkably specific reactions of butyl nitrite toward carbanions, enolates, and alkoxides[7] Carbanions react with alkyl nitrites almost exclusively to exchange hydrogen for the NO group (nitrosation):

$$R\bar{C}HR' + BuONO \rightarrow [RCH(NO)R'{\cdot}BuO^-] \rightarrow R\bar{C}(NO)R' + BuOH \quad (4)$$

The initial step presumably involves nucleophilic attack by the carbanion on the nitroso nitrogen, generating a complex consisting of an alkoxide ion and a nitroso compound. Before decomposition of the complex, there is a deprotonation of the nitroso compound by the alkoxide to produce the corresponding nitroso carbanion (eq 4).

In those cases where the nitrosation takes place α to a carbonyl group, as is the case with enolates, the alkoxide may also react as a nucleophile in a reverse Claisen reaction (eq 5). If the

$$CH_3\bar{C}HCH{=}O + BuONO \rightarrow [CH_3CH(NO)CH{=}O{\cdot}BuO^-] \rightarrow CH_3\bar{C}HNO + BuOCH{=}O \quad (5)$$

nitrosation product contains no abstractable hydrogens, then the reaction proceeds exclusively by this pathway.

The major product from the reaction of alkyl nitrites with alkoxide ions (e.g., 1,2 adducts of acrolein or methyl vinyl ketone) is NO_2^-:

$$RO^- + BuONO \rightarrow NO_2^- + ROH + CH_3CH_2CH{=}CH_2 \quad (6)$$

Alkyl nitrites can react with other anions to form NO_2^-, either by an S_N2 or E2 reaction. NO_2^- is the major product from reaction of butyl nitrite with strongly basic alkoxides (eq 6) and a minor product with carbanions and enolates.

An alternative, in some instances, is to deprotonate neutral analogues of putative addition compounds and compare their exchange behavior with labeled reagents and their reaction with butyl nitrite.

Hydrogen-deuterium exchange, reagent switching reactions, the butyl nitrite test, and direct comparison with putative products are four ways to identify the structure of products. While one method may not give conclusive results, the combined use of all four techniques is a powerful means for making an unambiguous determination.

Experimental Section

Reactions of anions with olefins in the gas phase were studied by using the tandem flowing afterglow-selected ion flow tube (FA-SIFT) instrument.[8] In this technique, anions are generated in a short flow tube, similar in construction to a conventional flowing afterglow, by subjecting the appropriate gases to electron impact while being carried in a flow of helium at 0.2-0.4 Torr. The ions are then mass selected by a differentially pumped quadrupole mass filter for injection into the main flow tube. Since a single mass is selected for injection, the flow in the main tube is free of unwanted ions, neutrals, electrons, and stray photons. Neutral reactants such as labeled solvents for H-D exchange studies and butyl nitrite can then be mixed with the selected ion flow by introducing them into the main flow tube through a series of ports. The final product mixture is sampled through a small orifice at the end of the tube for analysis by a quadrupole mass spectrometer.

Hydroxide ion was generated by electron impact on a mixture of N_2O and CH_4. Fluoride was generated by electron impact on NF_3. Cyanide was generated by electron impact on BrCN. Methoxide and carbanions were generated by deprotonating the appropriate neutral precursor with hydroxide ion.

Reactions with deuterated reagents and butyl nitrite were performed by making the desired ion in the source flow tube and mass selecting it with the quadrupole mass filter for study in the main flow tube. Branching ratios were measured by extrapolating a plot of product distribution versus extent of reaction to zero time and then correcting for mass discrimination with a correction factor from a calibration plot of counting efficiency versus amu.[9]

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Table I. Summary of Reactants, Products, Branching Ratios, and Enthalpies of Reaction for Reaction of Acrylonitrile with Anions in the Gas Phase

anion	products	%[a]	type	$\Delta H°_{RXN}$[b]
OH^-	$CH_2{=}\bar{C}CN + H_2O$	100	m - 1	-20
MeO^-	$CH_2{=}\bar{C}CN + MeOH$	100	m - 1	-10
$PhCH_2^-$	$PhCH_2CH_2\bar{C}HCN$	75	1,4	-31.5
	$CH_2{=}\bar{C}CN + PhCH_3$	25	m - 1	-10
$^-CH_2CN$	$CH_2{=}\bar{C}CN + CH_3CN$	85	m - 1	-2
	$NCCH_2CH_2\bar{C}HCN$	15	1,4	-16
$C_6H_7^-$	$CH_2{=}CH_2 + C_6H_6 + {}^-CN$	100	*c*	-26.5
F^-	$CH_2{=}\bar{C}CN + HF$	55	m - 1	-0.5
	$CH_2{=}CHCN{\cdot}F^-$	45	cluster	*d*
$^-CH_2COCH_3$	$CH_3COCH_2CH_2\bar{C}HCN$	100	1,4	-15.5
$^-CH_2NO_2$	$H_2\overline{CCH_2C}HCN + NO_2^-$	75	*e*	-20
	$O_2NCH_2CH_2\bar{C}HCN$	25	1,4	-4
^-CN	$CH_2{=}CHCN{\cdot}{}^-CN$	100	cluster	*d*

[a] Branching ratios are corrected for mass discrimination. [b] Energies are in kcal/mol. [c] 1,4 addition, followed by hydride transfer. [d] -10 to -20 kcal/mol. [e] Methylene transfer.

Table II. Summary of Reactants, Products, Branching Ratios, and Enthalpies of Reaction for Reaction of Acrolein with Anions in the Gas Phase

anion	products	%[a]	type	$\Delta H°_{RXN}$[b]
OH^-	$CH_2{=}\bar{C}CHO + H_2O$	100	m - 1	-15
MeO^-	$CH_2{=}\bar{C}CHO + MeOH$	100	m - 1	-5
$PhCH_2^-$	$CH_2{=}CHC(O^-)(CH_2Ph)H$	100	1,2[c]	-16
	$PhCH_2CH_2\bar{C}HCHO$		1,4	-26
$^-CH_2CN$	$CH_2{=}CHC(O^-)(CH_2CN)H$	100	1,2[c]	-12
	$NCCH_2CH_2\bar{C}HCHO$		1,4	-15
$C_6H_7^-$	$CH_3\bar{C}HCHO + C_6H_6$	25	*d*	-34
	$CH_2{=}CHC(O^-)(C_6H_7)H$	55	1,2	+1
	m/z = 133, not identified	20		
F^-	$CH_2{=}CHCHO{\cdot}F^-$	100	cluster	*e*
$^-CH_2$-$COCH_3$	$CH_2{=}CHC(O^-)$-$(CH_2COCH_3)H$	100	1,2[c]	-12
	$CH_3COCH_3CH_2\bar{C}HCHO$		1,4	
$^-CH_2NO_2$	CH_2 transfer	>99	*f*	
	adduct, not identified	<1		
^-CN	$CH_2{=}CHCHO{\cdot}{}^-CN$	100	cluster	*e*

[a] Branching ratios are corrected for mass discrimination. [b] Energies are in kcal/mol. [c] Major product of addition. [d] 1,4 hydride transfer. [e] -10 to -20 kcal/mol. [f] Methylene transfer.

Table III. Summary of Reactants, Products, Branching Ratios, and Enthalpies of Reaction for Reaction of Methyl Vinyl Ketone with Anions in the Gas Phase

anion	products	%[a]	type	$\Delta H°_{RXN}$[b]
OH^-	$CH_2{=}CHC(O)CH_2^- + H_2O$	100	m - 1	-28
MeO^-	$CH_2{=}CHC(O)CH_2^- + MeOH$	100	m - 1	-18
$PhCH_2^-$	$PhCH_2CH_2\bar{C}HC(O)CH_3$	85	1,4[c]	-41
	$CH_2{=}CHC(O^-)(CH_2Ph)CH_3$		1,2	-18
	$CH_2{=}CHC(O)CH_2^- + PhCH_3$	15	m - 1	-18
$^-CH_2CN$	$CH_2{=}CHC(O)CH_2^- + CH_3CN$	55	m - 1	-10
	$CH_2{=}CHC(O^-)(CH_2CN)CH_3$	45	1,2[c]	-18
	$NCCH_2CH_2\bar{C}HC(O)CH_3$		1,4	-24
$C_6H_7^-$	$CH_2{=}CHC(O^-)(C_6H_7)CH_3$	80	1,2[c]	
	$C_6H_7CH_2\bar{C}HC(O)CH_3$		1,4	
	$CH_3\bar{C}HC(O)CH_3 + C_6H_6$	20	*d*	-41
F^-	$CH_2{=}CHC(O)CH_2^- + HF$	100	m - 1	-8.5
$^-CH_2$-$COCH_3$	$CH_3COCH_2CH_2\bar{C}HC(O)CH_3$	65	1,4[c]	-23
	$CH_2{=}CHC(O^-)(CH_2COCH_3)$-$CH_3$		1,2	-18
	$CH_2{=}CHC(O)CH_2^-$ + CH_3COCH_3	35	m - 1	-8
$^-CH_2NO_2$	CH_2 transfer	80	*e*	
	adduct not identified	20		-6
^-CN	$CH_2{=}CHC(O)CH_3{\cdot}{}^-CN$	100	cluster	*f*

[a] Branching ratios are corrected for mass discrimination. [b] Energies are in kcal/mol. [c] Major product of addition. [d] 1,4 hydride transfer. [e] Methylene transfer. [f] -10 to -20 kcal/mol.

Table IV. Summary of Reactants, Products, Branching Ratios, and Enthalpies of Reaction for Reaction of Methyl Acrylate with Anions in the Gas Phase

anion	products	%[a]	type	$\Delta H°_{RXN}$[b]
OH^-	$CH_2{=}\bar{C}COOMe + H_2O$	75	m - 1	-11
	$CH_2{=}CHCOO^- + MeOH$	25	$B_{AC}2$	-30.5
MeO^-	$CH_2{=}CHCOO^- + MeOMe$	40	S_N2	-26
	$CH_2{=}\bar{C}C(O)OCH_3 + MeOH$	30	m - 1	-1
	$CH_2{=}\bar{C}COOMe{\cdot}MeOH$	30	cluster	*c*
$PhCH_2^-$	$PhCH_2CH_2\bar{C}HCOOMe$	100	1,4	-14
$^-CH_2CN$	$NCCH_2CH_2\bar{C}HCOOMe$	100	1,4	-12
$C_6H_7^-$	$CH_2{=}CHC(O)C_6H_6^- + MeOH$	50	$B_{AC}2$	
	$C_6H_7CH_2\bar{C}HCOOMe$	40	1,4	
	$CH_3\bar{C}HCOOMe + C_6H_6$	10	*d*	-34
F^-	$CH_2{=}CHCOO^- + MeF$	100	S_N2	-8
$^-CH_2$-$COCH_3$	$CH_2{=}CHC(O)\bar{C}HCOCH_3$ + MeOH	100	$B_{AC}2$	-8.8
$^-CH_2NO_2$	$O_2NCH_2CH_2\bar{C}HCOOMe$	65	1,4	0
	CH_2 transfer	35	*e*	
^-CN	no reaction			

[a] Branching ratios are corrected for mass discrimination. [b] Energies are in kcal/mol. [c] -10 to -20 kcal/mol. [d] 1,2 addition followed by 1,4 hydride transfer. [e] Methylene transfer.

Enthalpies of reaction for anions reacting with olefins in the gas phase were calculated by using thermodynamic cycles. In some instances, the gas-phase enthalpy of formation of reactants and products was known, so the enthalpy of reaction could be calculated directly. All gas-phase acidities were obtained from the table by Lias et al.[10] Experimental gas-phase enthalpies of formation were chosen from the most recent compilations.[11] Where experimental values were unavailable, the group method of Pedley, Naylor, and Kirby[11d] was used to estimate the value of $\Delta H°_{RXN}$. A substitution method[12] was used for calculating enthalpies of formation for compounds with highly substituted tetrahedral centers.

Results

We were primarily interested in clustering and addition of anions to conjugated olefins. Other reactions were also observed. With sufficiently basic anions, deprotonation competes. With methyl acrylate, ester cleavage by either the $B_{AC}2$ or S_N2 route also takes place. A characteristic reaction of cyclohexadienide is hydride transfer. Nitromethyl anion gives methylene transfer as well as addition products. A complete summary of results is shown in Tables I–IV.

Hydroxide ($\Delta H°_{acid}(H_2O)$ = 391 kcal/mol, m/z = 17) and **methoxide** ($\Delta H°_{acid}(CH_3OH)$ = 381 kcal/mol, m/z = 31) react with the four olefins studied principally by proton transfer. With methyl acrylate, additional modes of reaction were observed. Methoxide reacts with methyl acrylate (MW = 86) to give an addition product at m/z 117. Treatment with CD_3OD shifts this peak to 120, as expected for a solvent switching reaction, while an ion at m/z 118 for H–D exchange on a 1,4 adduct is not observed. These results are those expected from clustering of the two reactants. Reaction of methyl acrylate with methoxide ion also generates some acrylate ion, as expected from an S_N2 reaction (eq 7).

$$MeO^- + CH_2{=}CHCOOMe \rightarrow CH_2{=}CHCOO^- + MeOMe \quad (7)$$

Acrylate ion (m/z = 71) is observed in the reaction of methyl acrylate with hydroxide ion as well. This is consistent with either an S_N2 or a $B_{AC}2$ mechanism. When $D^{18}O^-$ is used as the anion, there is a peak in the mass spectrum at m/z 73, showing that the labeled oxygen is incorporated into the acrylate, while the deu-

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[11] (a) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1). (b) Pedley, J. B.; Rylance, J. *Sussex-N. P. L. Computed Analyzed Thermochemical Data*; University of Sussex: Sussex, England, 1977. (c) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions*; U.S. Dept. of Commerce, National Bureau of Standards: Washington, DC, 1969. (d) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Themochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. (e) Bartmess, J. E.; Kiplinger, J. P. *J. Org. Chem.* **1986**, *51*, 2173.

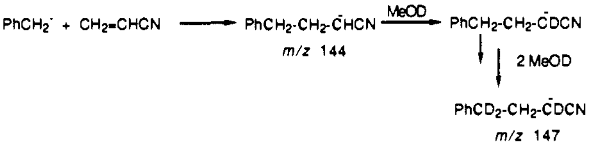
[12] Wiberg, K. B.; Squires, R. R. *J. Chem. Thermodyn.* **1979**, *11*, 773.

terium on oxygen leaves with the departing methanol (eq 8). This is consistent with hydroxide attack by the $B_{AC}2$ pathway.

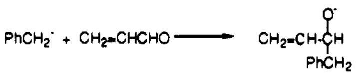
$$D^{18}O^- + CH_2{=}CHCOOMe \rightarrow CH_2{=}CHCO^{18}O^- + MeOD \tag{8}$$

Benzyl anion ($\Delta H°_{acid}$(toluene) = 381 kcal/mol, m/z = 91) reacts readily with all four olefins to give adducts. No exchange is observed when the adducts are allowed to react with toluene-d_8, suggesting that these ions are not simple clusters.

Acrylonitrile reacts with benzyl anion to give an addition product at m/z 144 (75%), as well as an ion at m/z 52 corresponding to deprotonation (25%). Reacting the m/z 144 ion with sufficient MeOD completely attenuates the 144 signal and gives a distribution of ions with m/z 145–147 corresponding to three deuterium exchanges, showing that there are three reasonably acidic sites in the adduct (eq 9). Reaction of the m/z 144 ion with butyl nitrite gives an ion at m/z 173 corresponding to nitrosation. This is the behavior expected from a 1,4 addition product in which a carbanion is formed.

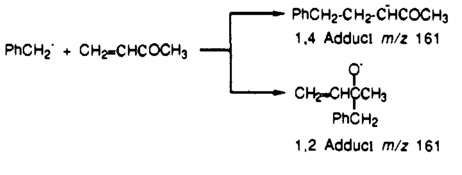

(9)

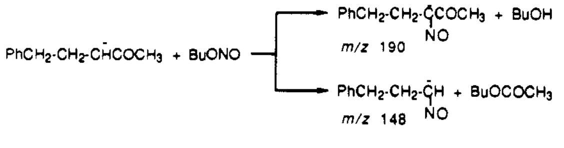
Benzyl anion reacts with acrolein to give an adduct at m/z 147 (100%). Reacting the m/z 147 ion with MeOD fails to give a deuterium exchange peak at m/z 148; instead, clustering is observed at m/z 180. Reacting the m/z 147 ion with butyl nitrite gives a large peak at m/z 46 (NO_2^-), a reaction characteristic of an alkoxide, but also a small peak at m/z 176 corresponding to nitrosation. These results are consistent with benzyl anion adding to acrolein primarily at the carbonyl carbon in a 1,2 fashion (eq 10) but also reacting to give a 1,4 adduct (eq 11).

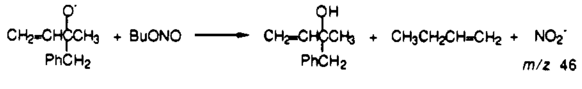

(10)

$$PhCH_2^- + CH_2{=}CHCHO \longrightarrow PhCH_2\text{-}CH_2\text{-}\bar{C}HCHO \tag{11}$$

Methyl vinyl ketone reacts with benzyl anion to give ions at m/z 161 for addition (85%) and at m/z 69 for deprotonation (15%). Treating the m/z 161 ion with MeOD or D_2O gives clustering without observable H–D exchange. Reacting the m/z 161 ion with butyl nitrite gives an ion at m/z 190 corresponding to nitrosation and also an ion at m/z 148 for a reverse Claisen reaction. The signal for m/z 46 (NO_2^-) was much smaller than was the case for butyl nitrite reacting with the benzyl anion adduct of acrolein. Evidently, the primary product is a 1,4 adduct with a smaller amount of 1,2 product (eqs 12–14).

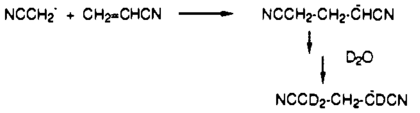

(12a)
(12b)


(13a)
(13b)

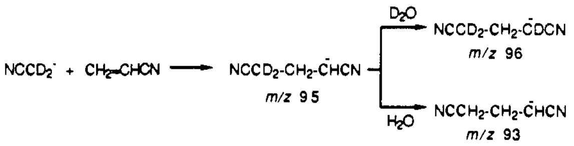

(14)

Benzyl anion reacts with methyl acrylate to give an adduct at m/z 177. Reacting the m/z 177 ion with MeOD gives a peak at m/z 178 for deuterium exchange. Reacting the m/z 177 ion with butyl nitrite gives an ion at m/z 206 for nitrosation of a carbanion. There is no signal at m/z 46 (NO_2^-) for an alkoxide reacting with butyl nitrite. The evidence indicates that the m/z 177 ion is a 1,4 adduct.

When **cyanomethyl anion** ($\Delta H°_{acid}(CH_3CN)$ = 373 kcal/mol, m/z = 40) is allowed to react with acrylonitrile, an ion at m/z 93 for addition (15%) is observed, although the major ionic product results from deprotonation (85%). By use of the SIFT, it was possible to inject the m/z 93 ion cleanly into the main flow tube for study. Reacting this ion with D_2O gives three deuterium exchanges consistent with the symmetry of the 1,4 adduct (eq 15).


(15)

In a variation of this experiment, acrylonitrile was allowed to react with deuterated cyanomethyl anion to give the addition product at m/z 95. Mixing the m/z 95 ion with D_2O generates a new ion at m/z 96. Mixing the m/z 95 ion with H_2O gives an ion at m/z 93. This is the behavior to be expected if the m/z 95 ion is a 1,4 adduct with one hydrogen attached to the basic site but two deuteriums available for exchange at an alternate basic site of the same acidity (eq 16).


(16a)
(16b)

Cyanomethyl anion reacts with acrolein to give only an adduct at m/z 96. Mixing with MeOD fails to give deuterium exchange. Reacting the m/z 96 ion with butyl nitrite gives primarily m/z 46 (NO_2^-) for an alkoxide reaction. An ion at m/z 125 for a carbanion exchanging hydrogen for NO (nitrosation) is almost nonexistent, so cyanomethyl anion adds to acrolein mostly in the 1,2 sense.

Cyanomethyl anion reacts with methyl vinyl ketone to give deprotonation (55%) as well as an addition product at m/z 110 (45%). Treating the m/z 110 ion with MeOD fails to give deuterium exchange. Reacting the m/z 110 ion with butyl nitrite gives an ion at m/z 139 for nitrosation and an ion at m/z 97 for the reverse Claisen reaction of an enolate carbanion. Significant amounts of NO_2^- for an alkoxide reacting with butyl nitrite is also observed. Apparently there are both 1,2 and 1,4 adducts present.

Cyanomethyl anion reacts with methyl acrylate to give only an addition product at m/z 126 (100%). The m/z 126 ion readily exchanges deuterium with MeOD. Reacting the m/z 126 ion with butyl nitrite gives a large signal at m/z 155 for nitrosation and also an ion at m/z 97 corresponding to a reverse Claisen product. These data are consistent with the m/z 126 ion being a 1,4 adduct.

A unique reaction of **cyclohexadienide** ($\Delta H°_{acid}(C_6H_8)$ = 373 kcal/mol, m/z = 79) is hydride transfer to give an M + 1 species.[13] This reaction competes with 1,2 and 1,4 addition.

Acrylonitrile and cyclohexadienide give mostly cyanide (>99%). Less than 1% hydride transfer or deprotonation is observed. Nevertheless, m/z 54, corresponding to the hydride-transfer adduct, can be isolated by using the SIFT and exchanges deuterium with EtOD, consistent with the m/z 54 ion being a 1,4 adduct (eq 17).

$$C_6H_7^- + CH_2{=}CHCN \rightarrow CH_3\bar{C}HCN + C_6H_6 \xrightarrow{EtOD} CH_3\bar{C}DCN \tag{17}$$

Acrolein reacts with cyclohexadienide to give a hydride transfer product at m/z 57 (25%), plus products at m/z 135 (55%) and 133 (20%). The m/z 133 ion is likely m/z 135 with loss of H_2. Reacting the hydride transfer ion at m/z 57 with MeOD fails to give deuterium exchange; instead, there is clustering to give a new ion at m/z 90. When propionaldehyde is deprotonated to give

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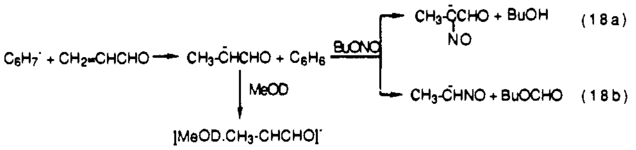
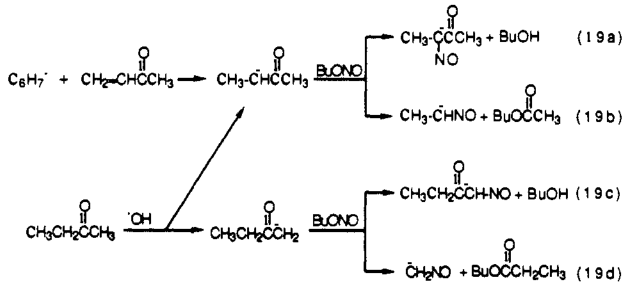
(13) DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920.

the putative 1,4 adduct and then mixed with MeOD, an identical result is obtained. Reacting the m/z 57 ion with butyl nitrite gives an ion at m/z 86 for nitrosation and also an ion at m/z 58 for the reverse Claisen reaction. NO_2^- from an alkoxide reacting with butyl nitrite is not observed. Reacting deprotonated propionaldehyde with butyl nitrite gives an identical result. Apparently, cyclohexadienide transfers hydride to acrolein to give a 1,4 adduct, which is identical with deprotonated propionaldehyde (eq 18).



Reacting the cyclohexadienide adduct of acrolein at m/z 135 with butyl nitrite gives a large amount of NO_2^- for an alkoxide reaction and a smaller amount of ion m/z 164 for nitrosation of a carbanion. This shows that m/z 135 is predominantly the 1,2 adduct with a smaller amount of 1,4 adduct.

Methyl vinyl ketone and cyclohexadienide give an ion at m/z 71 corresponding to hydride transfer (20%) as well as an addition product at m/z 149 (80%). Reacting the m/z 71 ion for hydride transfer with MeOD gives a new ion at m/z 72 for deuterium exchange, consistent with hydride addition in a 1,4 manner to give a deprotonated methyl ethyl ketone. Reacting the anion of methyl ethyl ketone (from reaction of OH^- with $CH_3CH_2COCH_3$) with MeOD gives the same result. In this instance, clustering of the anion with MeOD occurs too fast to observe complete exchange. Reacting the m/z 71 ion with butyl nitrite gives ions at m/z 100 for nitrosation and m/z 58 for the reverse Claisen reaction of an enolate carbanion. Reacting the anion of methyl ethyl ketone with butyl nitrite gives the same result, except for an additional ion at m/z 44 for a reverse Claisen reaction expelling $^-CH_2NO$. Since deprotonation of methyl ethyl ketone by hydroxide occurs on both sides of the carbonyl group, reaction with butyl nitrite by the reverse Claisen route gives two different elimination products. This demonstrates that the cyclohexadienide hydride transfer adduct with methyl vinyl ketone survives injection into the main tube without scrambling of the charged site, since only one reverse Claisen product is observed. The results with MeOD and butyl nitrite show that cyclohexadienide transfers hydride to methyl vinyl ketone in the 1,4 sense (eq 19).



The m/z 149 ion for addition of cyclohexadienide to methyl vinyl ketone reacts with butyl nitrite to give NO_2^- for an alkoxide attack and an ion at m/z 178 for nitrosation. Evidently, there are fair amounts of both 1,2 and 1,4 adducts. Estimating which is in greater proportion is difficult because of the possibility of differing reactivities of the different adducts toward butyl nitrite. Treating the m/z 149 ion with MeOD gives only clustering.

Methyl acrylate and cyclohexadienide give products at m/z 87 for hydride transfer (10%) and an addition peak at m/z 165 (40%). The major product is at m/z 133 (50%) for addition followed by loss of methanol, consistent with ester cleavage by the $B_{AC}2$ route. Reacting the hydride-transfer ion at m/z 87 with MeOD gives deuterium exchange. When deprotonated methyl propionate is mixed with MeOD, an identical result is found. Reacting the m/z 87 ion with butyl nitrite gives ions at m/z 116 for nitrosation and m/z 58 for the reverse Claisen reaction of an enolate carbanion. These results show that hydride transfer between cyclohexadienide and methyl acrylate occurs in a 1,4 sense.

The m/z 165 ion for cyclohexadienide addition to methyl acrylate exchanges one deuterium with MeOD. Reacting the m/z 165 ion with butyl nitrite gives ions at m/z 194 for nitrosation and m/z 135 for the reverse Claisen reaction of an enolate carbanion. Evidently, cyclohexadienide adds 1,4 to methyl acrylate.

Fluoride ($\Delta H^\circ_{acid}(HF) = 371.5$ kcal/mol, $m/z = 19$) reacts with olefins to give remarkably simple results. With acrylonitrile, deprotonation (55%) and an addition product at m/z 72 (45%) is observed. Treating the m/z 72 ion with MeOD fails to give deuterium exchange, but attenuates the signal for the m/z 72 ion with increasing MeOD pressure. Similarly, fluoride ion reacts with acrolein to give an addition product at m/z 75 (100%). Reacting the m/z 75 ion with MeOD or D_2O attenuates the signal for m/z 75 without exchanging deuterium. This kind of behavior is typical of clusters. Reacting the m/z 72 or 75 ion with MeOD switches acrylonitrile or acrolein out of the cluster to give a new cluster at m/z 52 corresponding to $MeOD{\cdot}F^-$. With methyl vinyl ketone, only proton abstraction is observed. With methyl acrylate, only a signal at m/z 71 for acrylate ion by an S_N2 reaction on methyl is found.

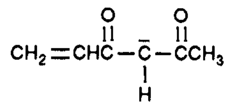
Acetone enolate ($\Delta H^\circ_{acid}(CH_3COCH_3) = 369$ kcal/mol, $m/z = 57$) adds to three of the olefins studied but not to methyl acrylate. Reacting adducts with acetone-d_6 fails to give new signals 5 or 6 amu higher in mass for exchange of anions, suggesting that these products must be adducts rather than clusters.

Acrylonitrile reacts with acetone enolate to give only an addition product at m/z 110. Reacting the m/z 110 ion with MeOD gives one deuterium exchange, consistent with 1,4 addition.

Acrolein reacts with acetone enolate to give only an addition peak at m/z 113. Treating the m/z 113 ion with MeOD does not give deuterium exchange. Reacting the m/z 113 ion with butyl nitrite gives m/z 142 for nitrosation of an enolate carbanion and also NO_2^- for an alkoxide reaction. Apparently, there are significant amounts of both 1,2 and 1,4 adducts.

Reaction of methyl vinyl ketone with acetone enolate gives an adduct at m/z 127 (65%) as well as some deprotonation (35%). Reacting the m/z 127 ion with MeOD gives a cluster at m/z 160. Reacting the m/z 127 ion with butyl nitrite gives ions at m/z 157 for nitrosation and m/z 114 for the reverse Claisen reaction of an enolate carbanion. There is also a small amount of NO_2^- at m/z 46 for reaction of an alkoxide, but the major product is the 1,4 adduct.

Methyl acrylate reacts with acetone enolate to give only a product at m/z 111, which is consistent with the stabilized enolate ion.



$$CH_2{=}CH\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{\bar{C}}}-\overset{O}{\overset{\|}{C}}CH_3$$

It can be understood as the product of a $B_{AC}2$ substitution with the departing methoxide ion deprotonating the strongly acidic $CH_2{=}CHCOCH_2COCH_3$. It is noteworthy that the m/z 111 ion does not react with butyl nitrite, presumably because the enolate is too weakly basic. A negative result in this instance, however, does not rule out the possibility of other isomers as products from this reaction.

A significant reaction of **nitromethyl anion** ($\Delta H^\circ_{acid}(CH_3NO_2) = 356$ kcal/mol, $m/z = 60$) with the four olefins studied is likely a methylene transfer to give a neutral product and NO_2^-. Since the methylene insertion products are neutral, they cannot be detected by a quadrupole mass spectrometer, and hence, we have no direct proof of their structure.

Acrylonitrile reacts with nitromethyl anion to give addition at m/z 113 (25%) plus methylene transfer (75%). The m/z 113 ion readily exchanges one proton with D_2O or MeOD, indicative of a 1,4 adduct. The hydrogens attached to carbon α to the nitro group in the 1,4 adduct are expected to be too acidic to exchange with D_2O or MeOD, so only one exchange is observed (eq 20).

$$CH_2{=}CHCN + {}^{-}CH_2NO_2 \rightarrow O_2NCH_2CH_2C^{-}HCN \xrightarrow{D_2O} O_2N\bar{C}HCH_2CHDCN \xrightarrow{D_2O} \text{no rxn} \quad (20)$$

Acrolein with nitromethyl anion gives almost 100% NO_2^-. The adduct peak at m/z 116 is very small. No experiments were done to determine the structure of the adduct. Methyl vinyl ketone reacts with nitromethyl anion to give an adduct at m/z 130 (20%), but mostly NO_2^- (80%) corresponding to methylene transfer. The m/z 130 ion fails to exchange deuterium with D_2O, MeOD, or DMSO-d_6. This is an inconclusive result because enolates show a weak propensity for H–D exchange in general.

Methyl acrylate reacts with nitromethyl anion to give addition at m/z 146 (65%) as well as methylene transfer (35%). Reacting the m/z 146 ion with MeOD gives one deuterium exchange, indicative of a 1,4 adduct.

Cyanide (ΔH°_{acid}(HCN) = 351 kcal/mol, m/z = 26) adds to acrylonitrile to give a product at m/z 79. The m/z 79 ion might be a cluster or a 1,4 adduct:

$$\underset{\text{cluster}}{{}^-\text{CN}\cdot\text{CH}_2{=}\text{CHCN}} \qquad \underset{\text{1,4 adduct}}{\text{NCCH}_2\text{C}^-\text{HCN}} \tag{21}$$

If the m/z 79 ion is a cluster, then hydrogen exchange with deuterated reagents will not occur, since there are no hydrogens attached to cyanide. The 1,4 adduct is identical with succinonitrile anion. A third alternative is that the m/z 79 ion is a cluster, but a proton has transferred from acrylonitrile to cyanide. This seems unlikely because the difference in acidity (20 kcal/mol) between acrylonitrile (ΔH°_{acid} = 371 kcal/mol) and HCN (ΔH°_{acid} = 351 kcal/mol) is too large to allow for proton exchange within the cluster with the available clustering energy (15–20 kcal/mol). When the m/z 79 ion is treated with D_2O or EtOD, no exchange is observed. When succinonitrile anion is mixed with EtOD, three exchanges are observed, consistent with the symmetry of the succinonitrile anion. Evidently, the species generated by cyanide reacting with acrylonitrile is not succinonitrile anion. The evidence indicates that m/z 79 is a cluster.

The enthalpy of reaction for cyanide adding in a 1,4 fashion to acrylonitrile is −1.4 kcal/mol. If an unfavorable adjustment of +6.9 to +10.8 kcal/mol[14] is made to account for the entropy of reaction at room temperature, then the overall free energy of reaction is positive.

The cyanide adducts of acrolein and methyl vinyl ketone also fail to exchange deuterium with D_2O or EtOD. This is the expected result if the adducts are clusters or if cyanide adds to the carbonyl group to give an alkoxide. The enthalpies of reaction for cyanide adding 1,2 to acrolein and methyl vinyl ketone are −2.4 and −6.1 kcal/mol, respectively. Including the contribution from entropy, the free energy of reactions are positive. Hence, the cyanide adducts of acrolein and methyl vinyl ketone must be clusters. Methyl acrylate does not react with cyanide.

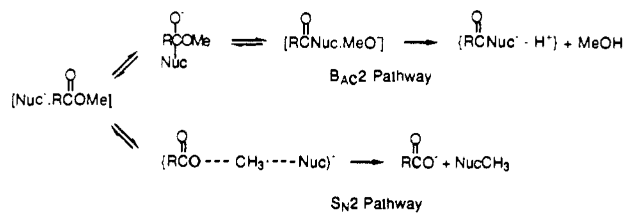
Discussion

A summary of reactants, products, branching ratios, and enthalpies of reaction for anions reacting with olefins in the gas phase at room temperature can be found in Tables I–IV. The results show that there are relatively few modes of reaction on the potential energy surfaces of these reactions: clustering, proton transfer, and 1,2 and 1,4 addition are the major ones. For methyl acrylate, these modes are in competition with cleavage of the ester by either the $B_{AC}2$ or S_N2 mechanism. Cyclohexadienide can transfer hydride to reduce the olefin and give benzene. Nitromethyl anion can transfer methylene to the olefin and give NO_2^-.

Stabilized carbanions such as benzyl anion, cyanomethyl anion, cyclohexadienide, acetone enolate, and nitromethyl anion add readily to double bonds in a 1,2 or 1,4 fashion to each of the four olefins studied. Hydroxide, methoxide, fluoride, and cyanide do not add by either route; instead, deprotonation and clustering is observed.

Acrolein shows a notable preference for 1,2 addition, with methyl vinyl ketone sharing this preference to a smaller extent. Acrylonitrile is constrained to add by the 1,4 route. With methyl acrylate, 1,2 addition is the first step in ester cleavage by the $B_{AC}2$ mechanism. Intermediates in this reaction are never observed, so only the 1,4 adduct is seen.

Scheme I



Scheme I shows the competitive mechanism for ester cleavage by addition/elimination ($B_{AC}2$) versus substitution (S_N2) pathways.[4a,b,15,16]

An important feature of the $B_{AC}2$ pathway is that the departing methoxide abstracts a proton before leaving the cluster in an exothermic step that drives the reaction to completion.[4c] If a proton is not available, then the alternate S_N2 pathway becomes competitive. The acidity of methyl acrylate (ΔH°_{acid} = 378–381 kcal/mol)[17] is low compared to saturated esters such as methyl acetate (ΔH°_{acid} = 372 kcal/mol) so that the departing methoxide must depend upon the entering nucleophile to supply an acidic proton. Fluoride, for example, attacks methyl acrylate to give entirely the S_N2 product. Hydroxide has an available proton for the leaving methoxide, and so the $B_{AC}2$ pathway is seen.

When methoxide is the nucleophile, a $B_{AC}2$ reaction in Scheme I that concludes with expulsion of methoxide is invisible, so that only the S_N2 reaction can be seen. Products from both the S_N2 and $B_{AC}2$ pathways have been observed under ICR conditions for the reaction of CD_3O^- with methyl acrylate,[15] without H–D exchange for the departing methoxide. Ester cleavage of methyl trifluoroacetate and methyl benzoate by CD_3O^- goes entirely by the S_N2 route.[16] The observation of S_N2 products in all three cases plus the absence of deuterium exchange in the case where the nucleophile is CD_3O^- shows that proton transfers from carbon are relatively slow compared to those from oxygen. Consequently, products from S_N2 attack are observed.

In principle, acetone enolate has the option of reacting with olefins via the charged oxygen to give O alkylation or deprotonation. However, comparing heats of formation of acetone enol (ΔH°_f = −38 kcal/mol)[18] with the keto form of acetone (ΔH°_f = −51.9 kcal/mol)[19] shows that the basicity of the oxygen (ΔH°_{acid} = 355 kcal/mol) must be 13.9 kcal/mol below that of the enolate carbon (ΔH°_{acid} = 369 kcal/mol). Hence, deprotonation of methyl vinyl ketone (ΔH°_{acid} = 363 kcal/mol) by the oxygen of acetone enolate is endothermic, and therefore, the observed reaction must be due to carbanion attack. Similar thermodynamic considerations suggest that adducts formed with acetone enolate are also the result of attack by carbon.[20]

Hydride transfer from cyclohexadienide gives exclusively 1,4 adducts for all four olefins. This finding contrasts with the observation that acrolein and methyl vinyl ketone, to a smaller extent, show a notable preference for forming 1,2 adducts with all of the other carbanions used in this study. A possible mechanism that accounts for this unusual specificity for 1,4 hydride transfer is to suppose that cyclohexadienide first adds *pseudo*axially to the olefin in the preferred 1,2 fashion. This places a hydrogen in position predisposed for transfer to the distal carbon of the vinyl

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[14] Values for ΔS°_{RXN} range between −23 and −36 cal/mol·deg for the change in entropy for a chemical reaction at 1 atm where the mole number decreases by 1. At room temperature this would give $-T\Delta S^\circ_{RXN}$ = +6.9–+10.8 kcal/mol. See: Johnson, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966; pp 306–307.

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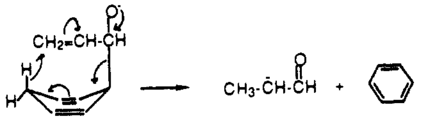
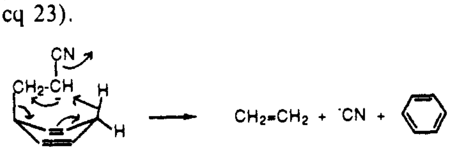
group. The result is an apparent 1,4 hydride transfer and benzene (eq 22).



(22)

Addition of cyclohexadienide to the carbonyl carbon in a *pseudo*equatorial position would place the hydrogens out of reach of the carbon–carbon double bond and would account for the observed stable 1,2 adducts with acrolein and methyl vinyl ketone. A 1,4 hydride transfer adduct was also observed with methyl acrylate. Application of this model to methyl acrylate implies that 1,2 addition of cyclohexadienide gives an intermediate with a lifetime long enough for hydride transfer to compete effectively with ester cleavage.

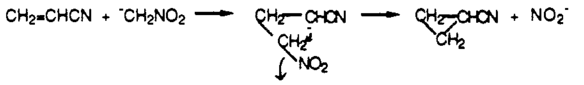
With acrylonitrile and cyclohexadienide, the major product is cyanide. Consistent with other carbanion reactions, cyclohexadienide must add to acrylonitrile in a 1,4 fashion. The structure of the 1,4 adduct shows that the anion is poised to expel cyanide by an internal rearrangement that gives ethylene and benzene (eq 23).



(23)

An E2 reaction between cyclohexadienide and acrylonitrile to give acetylene, H_2, benzene, and ^-CN is endothermic and therefore cannot occur under flowing afterglow conditions.

With nitromethyl anion, a major reaction is methylene transfer. It is tempting to speculate how methylene transfer might occur. At least for acrylonitrile, we can neglect the possibility of insertion into a carbon–oxygen double bond. Addition of nitromethyl anion in the 1,4 sense is an attractive possibility, as shown in the following tentative mechanism (eq 24):

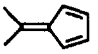


(24)

A 1,2 attack on acrolein or methyl vinyl ketone by nitromethyl anion would insert methylene into the carbonyl group to give an epoxide, but there is no way using our data to see if this actually occurs.

Structure–Reactivity Relationships. In a broad sense, the differences in observed reactivity with olefins between hydroxide, methoxide, and fluoride on the one hand and benzyl anion, cyanomethyl anion, cyclohexadienide, acetone enolate, and nitromethyl anion on the other conform to Pearson's hard and soft acid and base (HSAB) principle.[21] According to this principle, nucleophilic addition of a carbanion to an olefin would be counted as a soft base–soft acid interaction, which is highly favorable, while nucleophilic addition of fluoride, hydroxide, or alkoxide ion to an olefin would be a less favorable hard base–soft acid interaction. On the other hand, removal of a proton (hard acid) should be more favorable with hard bases (F^-, OH^-, MeO^-) and more difficult with soft bases (carbanions). This dichotomy is nicely illustrated when the reactivity pattern of a hard and a soft base of equal basicity are compared. A case in point is benzyl and methoxide ion, which both have ΔH°_{acid} = 381 kcal/mol for the conjugate acid. Methoxide ion reacts by deprotonation of the olefin or clustering, while benzyl anion forms adducts so easily that proton transfer is hardly observed in some instances. A similar situation prevails when comparing the equally basic fluoride and acetone enolate ions.

Table V. Reaction of Representative Anions with Acrylonitrile and 6,6-Dimethylfulvene[a]

no.	anion	% proton tranfser	ΔH°_{RXN}-(PT), kcal/mol	% 1,4 adduct	ΔH°_{RXN}-(ADD), kcal/mol
	$CH_2{=}CHCN$ (ΔH°_{acid} = 371 kcal/mol)				
1	OH^-	100	−20.0	0	−24.5
2	CH_2CN^-	85	−2.0	15	−16.0
3	$PhCH_2^-$	25	−10.0	75	−31.5
4	$CH_3COCH_2^-$	0	+2.0	100	−15.5
	 (ΔH°_{acid} = 354 kcal/mol)				
5	OH^-	100	−37	0	−41
6	CH_2CN^-	85	−19	15	−32
7	$PhCH_2^-$	51	−27	49	−39
8	$CH_3COCH_2^-$	99	−15	1	−27

[a] Reference 20.

A recent flowing afterglow study of the reaction of 6,6-dimethylfulvene with various anions in the gas phase showed similar competition between proton abstraction and nucleophilic addition as observed in the present work.[20] In general, localized anions such as hydroxide, alkoxide, trifluoromethoxide, and thiolates were shown to react exclusively by proton abstraction, while delocalized ions such as allyl and benzyl yielded mainly addition products; enolate ions showed a variety of behavior ranging from almost exclusive proton transfer to mainly addition. The authors[20] noted the good correlation with the HSAB principle for some of the anions, but pointed out an apparent breakdown of the principle in the reactions of localized carbanions and thiolate ions, as well as the difficulty with the principle in accounting for the wide variety of reactions of the enolate ions. They concluded that charge delocalization in the anion may be a better criterion than "softness" in favoring nucleophilic addition over proton transfer. It has been noted before that there is a kinetic barrier to proton transfer from one carbon to another in the gas phase, just as in solution, and that the barrier is greater to and from a charge-delocalized anion than to and from a charge-localized one.[22,23] Similar observations have been made for gas-phase H–D exchange rections, which are rare from one carbon to another.[23]

In order to develop a more detailed understanding of the factors that affect the competition between addition and proton transfer, we shall compare the reactivity patterns in the reactions of OH^-, CH_2CN^-, $PhCH_2^-$, and $CH_3COCH_2^-$ with the four olefins of this study as well as 6,6-dimethylfulvene. A necessary, but not sufficient condition for addition to be competitive with proton transfer is that the Gibbs free energy of the reaction is negative. Tables V and VI show that ΔH°_{RXN} of the reactions of the anions with the five olefins is substantially negative. Even if a positive contribution of 7–11 kcal/mol[14] to ΔG°_{RXN} by an entropy term is taken into account, ΔG°_{RXN} for most additions is still negative.

We first compare the reactions of the four anions with acrylonitrile and 6,6-dimethylfulvene. The percentage yield of the two competing reactions as well as the respective ΔH°_{RXN} values are summarized in Table V. There are striking similarities between the results of these two olefins. The differences in the enthalpies of reaction for a given anion [ΔH°_{RXN}(PT) − ΔH°_{RXN}(ADD)] are almost the same although all ΔH°_{RXN} values are substantially more negative for the 6,6-dimethylfulvene reactions. The relative yields of proton transfer versus addition product are nearly the same for the reaction of the substrates with OH^- and CH_2CN^-, and relatively similar with $PhCH_2^-$. Only with $CH_3COCH_2^-$ is there an almost complete reversal in relative yields (100% adduct with acrylonitrile, 99% proton transfer with 6,6-dimethylfulvene).

The dominance of the proton-transfer channel in the reaction of OH^- with either substrate is easily understood: even though

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(21) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533; *Science* **1966**, *151*, 172; *Chem. Br.* **1967**, *3*, 103. (b) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587, 643–648. (c) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827–1836. (d) Parr, R. G.; Pearson, R. G. *Ibid.* **1983**, *105*, 7512–7516. (e) Pearson, R. G. *J. Org. Chem.* **1989**, *54*, 1423–1430.

(22) For a recent review, see: Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187.

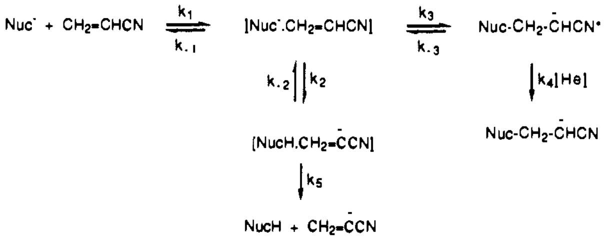
(23) Farneih, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891–7898.

Table VI. Reaction of Representative Anions with Acrolein, Methyl Vinyl Ketone, and Methyl Acrylate

no.	anion	% proton transfer	ΔH°_{RXN}(PT), kcal/mol	% addition	ΔH°_{RXN}(ADD), kcal/mol
		$CH_2{=}CHCH{=}O$ (ΔH°_{acid} = 376 kcal/mol)[c]			
1	OH^-	100	-15	0	-27 (1,2), -24 (1,4)
2	CH_2CN^-	0	+3	100[a]	-12 (1,2)
3	$PhCH_2^-$	0	-5	100[a]	-16 (1,2)
4	$CH_3COCH_2^-$	0	+7	100[a]	-12 (1,2)
		$CH_2{=}CHCOCH_3$ (ΔH°_{acid} = 363.3 kcal/mol)			
5	OH^-	100	-28	0	-34 (1,2); -31 (1,4)
6	CH_2CN^-	55	-10	45[a]	-18 (1,2); -24 (1,4)
7	$PhCH_2^-$	15	-18	85[b]	-18 (1,2); -41 (1,4)
8	$CH_3COCH_2^-$	35	-6	65[b]	-18 (1,2); -23 (1,4)
		$CH_2{=}CHCOOCH_3$ (ΔH_{acid} = 379.5 kcal/mol)[c]			
9	OH^-	75	-11	25 ($B_{AC}2$)	-30.5 ($B_{AC}2$)
10	CH_2CN^-	0	+7	100 (1,4)	-12 (1,4)
11	$PhCH_2^-$	0	-1	85 (1,4)	-14, (1,4)
12	$CH_3COCH_2^-$	0	+10	100 ($B_{AC}2$)	-9 ($B_{AC}2$)

[a] 1,2 adduct is major product. [b] 1,4 adduct is major product. [c] Reference 17.

Scheme II



ΔH_{RXN} for the addition mode is ~4.5 kcal/mol more negative than for the proton transfer, the negative entropy term will render ΔG°_{RXN} for the addition of 3.5–7.5 kcal/mol less negative than for proton transfer. Hence the larger thermodynamic driving force, coupled with an expected low barrier typical for proton transfers to charge localized anions,[22] should strongly favor proton transfer, as observed.

In the other examples, the thermodynamic driving force for the addition reaction is larger than for the proton transfer, even after the entropy factor is taken into account, and 1,4 addition is indeed favored in the reaction of acrylonitrile with $PhCH_2^-$ and $CH_3COCH_2^-$ but not in the reaction of acrylonitrile with CH_2CN^-, or in any of the reactions of 6,6-dimethylfulvene.

These results may be understood on the basis of Scheme II and the corresponding energy profile shown in Figure 1. This scheme is similar to one proposed by Moylan and Brauman[24] for the competition between proton transfer and Lewis acid–base complexation between an amine and a carbocation and the one used by Brickhouse and Squires.[20]

The first step in the scheme is the formation of an encounter complex between the olefin and the nucleophile that releases an estimated 15–20 kcal/mol of ion–dipole- and ion–ion-induced dipole energy.[25] This energy is available to overcome the reaction barriers of the proton transfer (k_2; E_{PT} in Figure 1) and in the addition process (k_3; E_{ADD} in Figure 1). The complex, $[NucH{\cdot}CH_2{=}CCN]^-$, which results from the proton transfer (k_2), rapidly decomposes (k_5), its energy being dissipated into relative translational energy, making the k_2 step essentially irreversible for exothermic proton transfers ($k_5 \gg k_{-2}$).

The 1,4 adduct that results from the k_3 step is in a high-energy state (symbolized by *) and may revert back to the initial encounter complex before its excess energy is dissipated by collisions with the carrier gas (k_4[He]).[26]

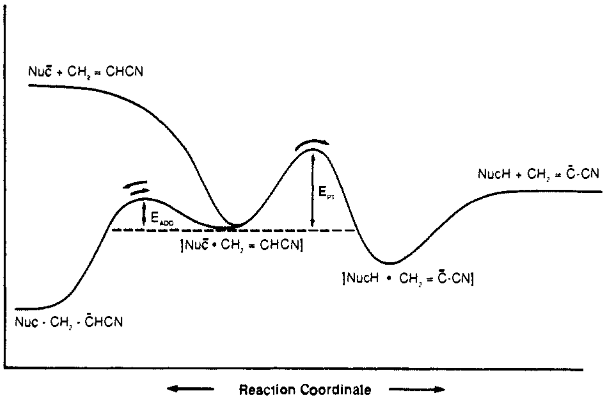


Figure 1. Schematic reaction coordinate–energy diagram for the reaction of acrylonitrile with anions such as $^-CH_2CN$ or $PhCH_2^-$.

If one treats $NucCH_2\bar{C}HCN^*$ and $[NucH{\cdot}CH_2{=}CCN]^-$ as steady states, the product ratio is given by eq 25

$$\frac{\text{ADD}}{\text{PT}} = \frac{k_3k_4[\text{He}]}{k_2(k_{-3} + k_4[\text{He}])}\frac{k_{-2} + k_5}{k_5} \tag{25}$$

which simplifies to eq 26 if $k_4[\text{He}] \gg k_{-3}$

$$\frac{\text{ADD}}{\text{PT}} = \frac{k_3}{k_2}\frac{k_{-2} + k_5}{k_5} \tag{26}$$

and further to eq 27 if $k_5 \gg k_{-2}$ (for $\Delta H^\circ_{RXN} \ll 0$).

$$\text{ADD/PT} = k_3/k_2 \tag{27}$$

We have not determined the product ratios as a function of helium pressure (which was held constant at 0.4 Torr). However, variation in helium pressure between 0.2 to 0.8 Torr did not affect product ratios in the reactions of 6,6-dimethylfulvene with anions,[20] suggesting that eqs 26 and 27 prevail. We shall assume this to be true in our system as well.

With reference to Scheme II and Figure 1, we may now understand the results in Table V as follows. (1) For nucleophiles with relatively localized negative charge the k_3/k_2 ratio appears to be <(≪)1, despite the larger exothermicity of the addition reaction, implying $E_{PT} < E_{ADD}$.[27] This is not only the case for OH^-, as discussed earlier, but also holds for CH_2CN^- (entries 2 and 6).

(2) For charge-*de*localized anions the increased E_{PT}[22,23,28] should lead to an increase in k_3/k_2 if delocalization does not affect E_{ADD} similarly; this probably accounts for the high yields of 1,4 adducts

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[24] Moylan, C. R.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 761.

[25] Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476.

[26] It should be noted that in situations where neither proton transfer nor addition is thermodynamically favorable, the initial encounter complex may be collisionally stabilized by He, leading to the observation of a cluster, e.g., in the reactions of the various olefins with CN^-.

[27] We are assuming that the activation entropies for the two reactions are similar.

[28] Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153.

with $PhCH_2^-$ (entries 3 and 7).

(3) In terms of charge delocalization, $CH_3COCH_2^-$ is probably between CH_2CN^- and $PhCH_2^-$. When $\Delta H^\circ_{RXN}(PT)$ is strongly negative, E_{PT} is low enough to render $E_{PT} \ll E_{ADD}$ and hence $k_3/k_2 \ll 1$.[27] This is exemplified in the reaction with 6,6-dimethylfulvene (entry 8). In the reaction of $CH_3COCH_2^-$ with acrylonitrile $\Delta H^\circ_{RXN}(PT)$ is slightly positive. This leads not only to an increased E_{PT} so that $E_{PT} > E_{ADD}$ and $k_3/k_2 >(\gg) 1$, but probably to significant reversibility of the proton transfer, i.e., $k_5 + k_{-2} >(\gg) k_5$ in eq 26, further enhancing the ADD/PT ratio.

The results with acrolein, methyl vinyl ketone, and methyl acrylate can be understood along similar lines although the presence of additional reaction channels such as 1,2 addition and the $B_{AC}2$ reaction are complicating features. The data are summarized in Table VI. We note the following points. (1) Proton transfer is again dominant for the reactions of OH^-, although with methyl acrylate (entry 9) the very strong exothermicity of the $B_{AC}2$ process appears to lower its barrier significantly to make it somewhat competitive with proton transfer. (2) Proton transfer is again strongly disfavored in the reactions of $PhCH_2^-$ and only somewhat competitive with addition modes when $\Delta H^\circ_{RXN}(PT)$ is strongly negative (entry 7). (3) With $CH_3COCH_2^-$ the yield of proton-transfer product in the reaction with methyl vinyl ketone (entry 8) is intermediate between the extremes of entries 4 and 8 in Table V, reflecting a ΔH°_{RXN} (−6 kcal/mol) that is intermediate between that of the reactions in Table V (+2 and −15 kcal/mol.

Conclusions

Our work shows that under flowing afterglow conditions 1,4 and 1,2 adducts of nucleophiles with electron-deficient olefins are relatively easily observed as long as competition from other reaction channels, especially proton transfer, is not too strong. Previous work by McDonald et al.[29] has shown that under flowing afterglow conditions cyclopentadienyl and phenylnitrene anion radicals react with **1**–**4** by 1,2 and 1,4 addition to give intermediates that react further to give fragmentation products. These results contrast with earlier unsuccessful attempts to observe adducts by the ICR technique. The main reason why adducts are more easily observed under flowing afterglow conditions can be attributed to the cooling effect of the helium carrier gas, which is able to carry away a good portion of the exothermicity of the reaction before the adduct can recross the barrier ($k_4[He] \gg k_{-3}$ in Scheme II).

By and large the reactivity patterns observed for the reaction of anions with acrylonitrile, acrolein, methyl vinyl ketone, and methyl acrylate can be understood by the HSAB principle, although a more detailed understanding requires an analysis of the mechanism and the energetics of the various steps involved in the competing reactions (Scheme II). With charge-localized anions (OH^-) proton transfer is by far the preferred reaction channel, provided that it is exothermic. With the strongly delocalized benzyl anion, addition is the preferred mode, especially when $\Delta H^\circ_{RXN}(PT)$ is not extremely negative, presumably because of the increased barrier for proton transfer. With the somewhat delocalized cyanomethyl and acetone enolate ions, addition and proton transfer are observed concurrently whenever both processes are exothermic.

Acknowledgment. This research was supported by Grants CHE-8617370 and CHE-8921739 (C.F.B.), and CHE-8815459 (C.H.D.) from the National Science Foundation.

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[29] (a) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498. (b) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6146–6147. (c) McDonald, R. N.; Chowdhury, A. K. *J. Phys. Chem.* **1982**, *86*, 3641–3645.