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Gas-Phase Brønsted versus Lewis Acid-Base Reactions of 6,6-Dimethylfulvene. A Sensitive Probe of the Electronic Structures of Organic Anions

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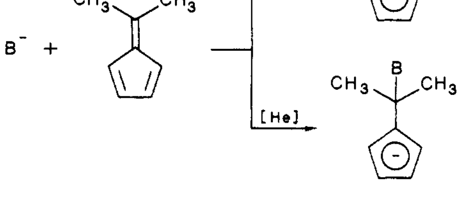
Abstract: The gas-phase reactions of a series of negative ions with 6,6-dimethylfulvene (DMFU) have been investigated in a flowing afterglow apparatus. Products are formed from competing Brønsted and Lewis acid-base reactions wherein the negative ion abstracts a proton from one of the acidic methyl groups, and/or adds to the exocyclic double bond to yield a substituted cyclopentadienide ion. Localized anions such as hydroxide, alkoxides, trifluoromethide, and thiolates react exclusively by proton abstraction, while delocalized ions such as allyl and benzyl yield mainly adduct with somewhat reduced efficiencies. The observed product distributions are independent of the total pressure in the reactor. Enolate ions show a wide variation in reactivity with DMFU: acyclic aldehyde and ketone enolates react exclusively by proton abstraction, while amide and ester enolates produce mainly adduct, despite their greater thermodynamic basicities. A pronounced ring-size effect is also found with cyclic ketone enolates wherein the larger ring ions such as cyclohexanone enolate show only proton transfer, whereas the small-ring ions such as cyclobutanone enolate show both addition and proton transfer. It is shown that yields for the Brønsted and Lewis acid-base reaction products are determined kinetically and that charge delocalization in the negative ion reactant substantially reduces its kinetic basicity. The results for the ambident enolate ions are shown to be largely determined by the proton affinity differences between the carbon and oxygen ends, i.e., the lower the proton affinity at oxygen, the greater the preference for adduct formation with DMFU through carbon. A detailed mechanism and energy profile is proposed for the DMFU reactions which is based on the results for over 30 different negative ions. Discussion of the relative nucleophilicities and kinetic basicities of these ions is also presented.

It was long believed that all exothermic gas-phase ion-molecule reactions would necessarily proceed rapidly with rates equal to the collision-limited values.[1] As the number of kinetic studies involving larger polyatomic reactants grew, it was quickly recognized that many exceptions to this generalization existed. Numerous investigations of slow, exothermic reactions involving organic ions and molecules have been carried out over the last two decades.[2] These studies provide many useful insights concerning the general shapes of potential energy surfaces and the salient dynamical features that account for this unexpected type of behavior. Gas-phase nucleophilic displacement reactions and the accompanying development of the double-well potential model is a particularly noteworthy example in this regard.[3]

Analysis of the branching ratios for gas-phase organic ion-molecule reactions with multiple product channels has also led to useful information about the topology of reaction energy surfaces, i.e., details about the relative magnitudes of the potential energy barriers that separate reactive intermediates. A commonly studied class of reaction of this type is that between negative ions and carbonyl compounds.[4] Debate continues as to the nature of the intermediates in these reactions and the relative magnitudes of the energy barriers, if any, involved in the proton transfer and nucleophilic addition channels which often compete. Significant issues are involved here which concern the intrinsic relationships between basicity and nucleophilicity of negative ions. Unfortunately, there are several drawbacks in working with carbonyl compounds as model substrates in competition studies of this type. Proton transfer tends to occur exclusively or dominate strongly when acidic α-hydrogens are present.[3b] Moreover, while nucleophilic acyl substitution ($B_{AC}2$) reactions are quite common with substrates such as esters and acyl chlorides in solution, they are often overwhelmed by competing elimination and S_N2 reactions in the gas phase.[5] Finally, nucleophilic addition reactions involving simple negative ions and most common carbonyl compounds are usually not observed at all in the gas phase because they are either thermodynamically unfavorable or the pressure regime of the experiments in which they might take place is too low to support termolecular addition reactions requiring collisional stabilization (e.g., ICR, 10^{-6}–10^{-7} Torr).[6] While nucleophilic additions to carbonyl compounds have been observed in a few instances in higher pressure experiments such as flowing afterglow (0.1-1.0 Torr),[4a,c] no carbonyl-containing substrates have been reported which exhibit reactivity with a wide range of negative ions. Thus, carbonyl compounds are not generally useful for investigating the microscopic competition between Brønsted and Lewis acid-base reactions (proton transfer and nucleophilic addition) within a single substrate.

With this background in mind, we sought an alternative type of neutral reagent for use in characterizing the relative nucleophilicities and kinetic basicities of gaseous anions. We have discovered that the cross-conjugated hydrocarbon, 6,6-dimethylfulvene (DMFU), is an ideal substrate for this purpose, since it cleanly undergoes both proton transfer and nucleophilic addition with an extraordinarily wide variety of gas-phase negative ions (eq 1). The cyclopentadienyl ring induces considerable



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polarization of the exocyclic double bond, producing electrophilicity and C–H acidity that is atypical of most hydrocarbons. More importantly, DMFU exhibits a broad range in its reactivity, as manifested in its reaction rates and the resulting product distributions. Changes in these measurable parameters indicate how intrinsic properties of anions such as size, geometry, and charge distribution affect their relative nucleophilicity and kinetic basicity.

The ability of DMFU to undergo both Brønsted and Lewis acid–base reactions in solution is well-documented in the literature.[7,8] It has been described as having carbonyl-like reactivity, comparable to its ketone analogue, acetone. Unlike most unsaturated hydrocarbons, it is readily reduced by $LiAlH_4$, producing an isopropyl-substituted cyclopentadienyl anion by nucleophilic addition of hydride to the 6-position.[9] DMFU is also subject to nucleophilic attack by methyllithium[10] and phenyllithium[11] reagents. DMFU is readily deprotonated by bases such as sodium amide,[10] triphenylmethylsodium[12] and lithium diisopropylamide,[13] much as acetone is converted to an enolate with such bases. Investigations of competing nucleophilic addition and proton-transfer reactions with DMFU in solution have been inconclusive. Hine and co-workers were able to confirm that DMFU undergoes H/D exchange by a deprotonation mechanism in alcohol/alkoxide solutions, but they could not completely rule out the participation of a nucleophilic addition–elimination route.[14] Electron transmission spectroscopy studies by Staley and Moore have shown that, in molecular orbital terms, DMFU is well suited as an electrophile.[15] The lowest unoccupied molecular orbital (LUMO) of DMFU lies near 0 eV, some 0.3 eV lower than the LUMO of acetone.[16] Thus, addition of anionic nucleophiles to DMFU can be expected to be kinetically favorable.

This paper presents a survey of negative ion reactions with DMFU in the gas phase that was carried out with the aim of understanding the factors controlling the competition between Brønsted and Lewis acid–base reactions during an ion-molecule encounter. In the course of these studies, an especially striking pattern emerged from the results with enolate ions. We discuss these results in terms of C versus O reactivity differences in ambident ions and propose a unified mechanism and energy profile for DMFU reactions based on the observed trends.

Experimental Section

All experiments were performed at 298 ± 2 K in a flowing afterglow apparatus that has been described in detail previously.[17] The branching ratio and rate measurements were carried out at 0.4 Torr total pressure with a helium flow rate of 190 STP cm^3/s and bulk flow velocity of 9400 cm/s. The initial CI reagents, NH_2^- and OH^-, were generated at the upstream ion source by electron impact on NH_3 and a CH_4/N_2O mixture, respectively. Unless otherwise noted, all of the anions described in this study were generated by deprotonation of the corresponding conjugate acids by NH_2^- or OH^-.

Certain of the parent acids (HA) such as ketones, aldehydes, alcohols, and thiols readily cluster with their conjugate base anions (A^-), forming homoconjugate cluster ions $A(HA)_n^-$. Since many of these clusters are reactive with DMFU, their presence can create difficulties in the product distribution measurements. These clusters were eliminated during branching ratio determinations by using low flow rates of the parent acid. The residual CI reagents, NH_2^- or OH^-, could be eliminated by rapid E2 reactions with phenetole to produce the relatively unreactive phenoxide ion (PA = 349.2 kcal/mol).[18] The NH_2^- ion ($EA(NH_2) = 0.74$ eV)[19] could also be removed by electron transfer to SF_6 (EA = 1.0 eV).[20] The desired conjugate base anions (A^-) react far more slowly with these added reagents.

Table I. Acidity Bracketing for 6,6-Dimethylfulvene

anion	PA[a] (kcal/mol)	k_{obsd} (cm^3/s)	eff[b]
$CF_3CH_2O^-$	361.8 ± 3.5	1.6×10^{-9}	1.1
$CH_3CH_2CH_2S^-$	354.2 ± 2.9	2.9×10^{-10}	0.18
$(CH_3)_2CHS^-$	353.4 ± 2.9	1.2×10^{-11}	0.008
$(CH_3)_3CS^-$	352.5 ± 2.9	9.6×10^{-12}	0.006
HS^-	351.2 ± 2.1	$<1 \times 10^{-12}$	<0.001

[a] Proton affinities taken from ref 18. [b] Efficiency = k_{obsd}/k_{ADO}, ref 24.

Kinetics were measured by the variable reaction distance technique.[21] Branching ratios were determined either from plots of the normalized product ion intensities versus the percentage of reactant ion conversion or from extrapolation of the normalized product yields to zero reaction time or zero DMFU flow rate.[22] To minimize mass discrimination, all branching ratio measurements were performed with a standard set of electrostatic lens potentials and with the lowest practical resolution setting at the mass spectrometer.

Dimethylfulvene and other liquid samples were obtained from commercial sources and were used without further purification. CH_3CH_2SD was prepared according to literature techniques.[23] All samples were subjected to several freeze–pump–thaw cycles just prior to use to remove dissolved gases. Gas purities were as follows: He (99.995%), CH_4 (99.0%), N_2O (99.0%), NH_3 (anhydrous, 99.5%), H_2S (99.5%), propene (99.0%), SF_6 (99.8%).

Results

The reactions of DMFU with over 30 different negative ions have been examined. In all cases, reaction occurs as shown in eq 1, with no other types of product ions appearing in the mass spectra. Moreover, neither the negative ion adducts nor the conjugate base carbanion of DMFU exhibit any secondary reactions with neutral DMFU, thereby making determination of the primary product branching ratios straightforward and reliable. In the following, we first present measurements of the gas-phase acidity of DMFU along with an evaluation of the product ion structures. The key observable parameters in the negative ion reactions with DMFU are the bimolecular rate coefficients (k_{obsd}), the calculated reaction efficiencies (eff = $k_{obsd}/k_{collision}$),[24] and the product branching ratios. Of all the negative ion properties considered, charge delocalization was found to exert the strongest influence on these parameters. Accordingly, we have organized the presentation of results into separate sections for localized and delocalized anions.

Gas-Phase Acidity and Product Ion Structures. The gas-phase acidity of DMFU (ΔH_{acid} (DMFU)) was determined by the bracketing technique by using localized anion bases with known proton affinities (PA).[18] As shown in Table I, DMFU transfers a proton to $CF_3CH_2O^-$ and *n*-PrS^- relatively rapidly, more slowly to *i*-PrS^- and *t*-BuS^-, and not at all to the weakest base in the series, HS^-. Proton-transfer reactions involving the conjugate base carbanion from DMFU and reference acids cannot be used to estimate DMFU acidity since protonation would undoubtedly

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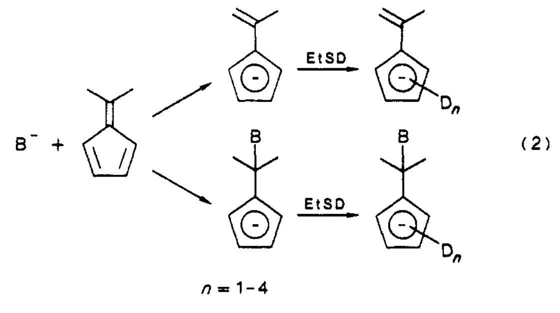
Table II. Reactions of Localized and Delocalized Anions with 6,6-Dimethylfulvene (DMFU)

B^-	PA[a]	k_{obsd}[b]	eff[c]	% proton transfer	% adduct	ΔH_{PT}[d]	ΔH_{add}[e]
NH_2^-	403.6	3.0	0.97	100	0	-50	-55
OH^-	390.7	2.4	0.86	100	0	-37	-41
CH_3O^-	380.6	2.8	1.4	100	0	-27	-36
CF_3^-	377.0	1.2	0.70	100	0	-23	-35
$CF_3CH_2O^-$	361.8	1.6	1.1	100	0	-8	-12
$CH_3CH_2CH_2S^-$	354.2	0.29	0.18	100	0	-0.2	-12
$(CH_3)_2CHS^-$	353.4	0.012	0.008	100	0	0.6	-11
$(CH_3)_3CS^-$	352.5	0.0096	0.006	100	0	1.5	-10
HS^-	351.2	<0.001	<0.001	0	0	2.8	-6
$CH_2{=}CHCH_2^-$	390.7	1.7	0.86	72	28	-37	-49
$PhCH_2^-$	380.8	0.94	0.63	51	49	-27	-39
$CH_3SOCH_2^-$	373.5	0.74	0.46	91	9	-20[f]	-34[f]
$NCCHCH_3^-$	375.0	1.6	0.92	66	34	-21[f]	-35[f]
$NCCH_2^-$	372.9	1.1	0.58	85	15	-19[f]	-32[f]
$MeOCOCH_2^-$	371.9	0.45	0.29	38	62	-18[f]	-31[f]
$CH_3COCH_2^-$	369.1	1.2	0.73	99	1	-15[f]	-27[f]
$(CH_3)_2CNO^-$	366.1	*g*	*g*	>99	<1	-12[f]	-24[f]
$OCHCH_2^-$	365.8	1.6	0.82	99	1	-12[f]	-24[f]
$PhNH^-$	366.4	1.0	0.69	97	3	-12	-23
$O_2NCH_2^-$	356.4	0.11	0.06	97	3	-2.4[f]	-18[f]

[a] Proton affinity in kcal/mol, ref 18. [b] Total rate coefficient in units of 10^{-9} cm^3/s. [c] eff = k_{obsd}/k_{ADO}, ref 24. [d] Enthalpy of proton transfer (kcal/mol). [e] Estimated enthalpy of addition to C6 position of DMFU (kcal/mol). [f] Estimated enthalpy of addition or proton transfer through carbon. [g] Rate not determined.

occur on the ring (C1–C5) rather than at the initial site of proton abstraction (C7) (vide infra). Despite this, the trend in the kinetic data listed in Table I is quite clear, and we have assigned ΔH_{acid}(DMFU) to be 354 ± 4 kcal/mol. It is interesting to note that while DMFU is formally a vinylog of cyclopentadiene, it possesses an identical acidity (ΔH_{acid}(cyclopentadiene) = 353.9 ± 2.9 kcal/mol).[18]

Certain anions form adducts with DMFU as well as producing proton transfer. The structures of the anionic proton transfer and addition products formed in the reaction of DMFU with methyl acetate enolate have been probed by using H/D exchange[25–27] (eq 2, B = $CH_3OCOCH_2^-$). These product ions are too weakly basic



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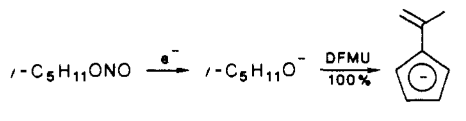
to undergo H/D exchange with D_2O, CH_3OD, and CF_3CH_2OD, but slow exchange is observed with EtSD. Both the proton-transfer product and the adduct undergo a maximum of four H/D exchanges with EtSD. The rate of exchange is low and approximately the same for the two anions, and the exchange patterns in the mass spectra appear essentially identical for similar EtSD flow rates. These results are consistent with H/D exchange exclusively on the cyclopentadienyl rings in both ions. This means that, as expected, reprotonation of the (M–H)⁻ ion to regenerate a fulvene structure does not occur. Furthermore, covalent bonding of the enolate anion nucleophile to the exocyclic double bond of DMFU, as opposed to ring addition, is required to account for the H/D exchange results.

Covalent bonding is also indicated by the absence of solvent switching. The anions produced by reaction of bare carbanions with DMFU do not undergo switching reactions with polar reagents such as CH_3CN and dimethyl sulfoxide (DMSO). In contrast, the cluster ions that can be formed by the termolecular association of deprotonated DMFU with reagents such as DMSO, CH_3CN, and certain alcohols[28] readily undergo solvent switching. We therefore assign covalently bonded structures as shown in eq 1 to all of the observed adducts. Condensed phase studies of DMFU also show that deprotonation occurs at the methyl groups and that nucleophilic addition occurs at the C6 site.[7]

Localized Anions. Localized anions are found to react with DMFU exclusively by proton transfer, as shown in the upper part of Table II. The reactions proceed at nearly unit efficiency over a wide range of reaction exothermicities. Only when the thermodynamic driving force for proton abstraction is small, as in the case of the thiolate ions, is an inefficient reaction observed. There is no visible size effect in the anion/DMFU reactions, in that OH^-, CH_3O^-, $CF_3CH_2O^-$, and i-$C_5H_{11}O^-$ anions all show essentially the same behavior with DMFU. The localized carbanion CF_3^- has shown a propensity for nucleophilic attack on certain carbonyl compounds in the gas phase,[4c] but it produces only proton transfer with DMFU. The CF_3^-/DMFU reaction efficiency of 0.70 is slightly lower than that observed for the oxyanions. Other localized carbanions such as HC_2^-, $C_6H_5^-$, and the fluorobenzene [M–H]⁻ anion also produce exclusive proton transfer.

Reactions with DMFU involving the alkoxides and thiolates can be complicated by the presence of homoconjugate clusters, $A(HA)_n^-$ when the alcohols and thiols are used as neutral precursors. It could be shown that the bare alkoxides react with DMFU only by proton transfer by generating the alkoxides in the absence of the parent alcohols. For example, electron impact on i-$C_5H_{11}ONO$ cleanly produces i-$C_5H_{11}O^-$ without formation of any cluster ions; on reaction with DMFU, no adduct is produced (eq 3).



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Delocalized Anions. As shown in the lower portion of Table II, delocalized anions exhibit a wide range of rates and product distributions in their reactions with DMFU. Delocalized carbanions exhibit a particularly wide range of reactivities. The strongly basic allyl and benzyl carbanions produce a considerable

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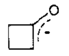
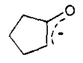
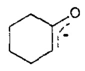
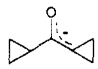
Table III. Reactions of Cyclic and Acyclic Enolate Ions with 6,6-Dimethylfulvene (DMFU)

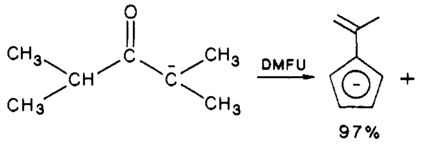
enolate	PA[a]	k_{obsd}[c]	eff[d]	% proton transfer	% adduct	ΔH_{pt}[e] C	ΔH_{pt}[e] O	ΔH_{add}[f] C	ΔH_{add}[f] O
$OCHCH_2^-$	365.8	1.6	0.82	99	1	−12	−2	−24	−12
$OCHCHCH_3^-$	365.3	1.4	0.82	99	1	−11	−3	−25	−14
$OCHC(CH_3)_2^-$	≃365[b]	1.6	0.98	99	1	−11	−5	−25	−15
$CH_3COCH_2^-$	369.1	1.2	0.73	98	2	−15	−1	−27	−12
$(CH_3)_2CHCOC(CH_3)_2^-$	366.8	*h*	*h*	97	3	−13	−1	−28	−15
$(CH_3)_3CCOCH_2^-$	368.1	1.7	1.1	94	1	−14	−2	−28	−12
$c\text{-}C_3H_5COCH_2^-$	368.9	*h*	*h*	94	6	−15	−2	−28	−12
$PhCOCH_2^-$	361.3	0.27	0.19	70	30	−7	7	−19	−4
$(CH_3)_2NCOCH_2^-$	374.9	0.93	0.56	63	37	−21	14	−36	1
$CH_3OCOCH_2^-$	371.9	0.46	0.29	38	62	−18	12	−31	1
$EtOCOCH_2^-$	≃372[b]	0.49	0.32	38	62	−18	12	−30	2
$i\text{-}PrOCOCH_2^-$	≃372[b]	0.38	0.26	43	57	−18	12	−30	2
$n\text{-}BuOCOCH_2^-$	≃372[b]	0.36	0.25	35	65	−18	12	−30	2
$EtOCOCHCH_3^-$	≃371[b]	1.2	0.82	8	92	−17	10	−31	0
$EtOCOCHCH_2CH_3^-$	≃371[b]	0.56	0.39	11	84	−17	10	−31	−2
$MeOCOC(CH_3)_2^-$	≃370[b]	0.84	0.57	18	82	−16	10	−31	−2
$FCOCH_2^-$	356.0	<0.01	<0.01	13	87	−2	29	−14	19
	367.2[g]	0.95	0.57	55	45	−13	6	−27	−5
	368.1[g]	1.5	0.96	81	19	−14	−2	−28	−13
	369.0[g]	1.1	0.76	97	3	−15	−5	−30	−15
	≃380[g]	1.2	0.81	37	63	−26	3	−39	−13

[a] Proton affinity through carbon (kcal/mol), ref 18. [b] Estimated values for substituted enolates based on established trends for analogous compounds. [c] Total observed rate coefficient in units of 10^{-9} cm^3/s. [d] eff = k_{obsd}/k_{ADO}, ref 24. [e] Estimated enthalpy of proton abstraction from DMFU through carbon (C) or oxygen (O) (kcal/mol). [f] Estimated enthalpy of addition to C6 position of DMFU through carbon or oxygen (kcal/mol). [g] Bracketed value, this work. [h] Rate not determined.

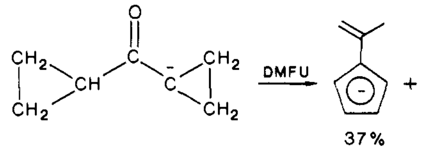
percentage of adduct and react with efficiencies comparable to those of localized anions with similar basicities. The dimsyl anion ($CH_3SOCH_2^-$) produces almost exclusive proton transfer with moderate efficiency, but CH_2CN^- and CH_3CHCN^- (which are of comparable basicity to the dimsyl anion) produce both adduct and proton transfer with somewhat greater efficiencies. The carbanions with strongly resonance delocalizing substituents,[29] $CH_3COCH_2^-$ and $O_2NCH_2^-$, produce almost exclusive proton transfer. The acetone enolate reaction is relatively rapid (eff = 0.73), but the nitromethane anion reaction is slow, presumably because of the low exothermicity for proton transfer (ca. −2 kcal/mol). Delocalized anions which contain heteroatoms such as anilide ($PhNH^-$) and acetone oximate (Me_2CNO^-) exhibit rapid rates and almost exclusive proton transfer.

Interestingly, we find that the reactivities of the two otherwise similar enolates derived from acetone and methyl acetate are quite different. The ester enolate is a stronger base than the ketone enolate, but it reacts less efficiently with DMFU, and adduct formation is the favored process. This unexpected behavior is general for a number of enolate/DMFU reactions, as is illustrated by the expanded series of results shown in Table III. Also shown in the table are the estimated enthalpies for addition and proton transfer through both the carbon and oxygen ends of these ambident ions.

In general, it appears that the nature of the substituent X at the carbonyl carbon of the enolate strongly affects reactivity. When X = –OR or –NR_2, reaction efficiencies are low, and adduct is formed. When X = –H or –R, efficiency is high, and proton transfer dominates. For the cyclic enolates, ring size strongly affects reactivity. Cyclobutanone enolate produces over 40% adduct while cyclohexanone enolate produces less than 5%. Here, the change in geometry as opposed to the change in molecular size appears to be the most important factor. For example, small acyclic anions such as acetaldehyde enolate react with the same high efficiency and dominance of proton transfer that is exhibited by the larger enolates such as pinacolone enolate. Furthermore, diisopropyl ketone enolate (PA = 366.8 kcal/mol)[18] reacts almost exclusively by proton transfer (eq 4), while dicyclopropyl ketone



(4)



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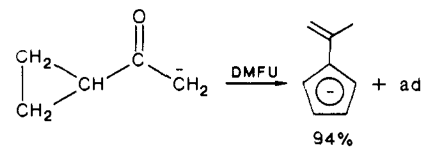

(6)

enolate (PA ≃ 380 kcal/mol)[30] with the same number of carbons but a significantly different geometry gives a high percentage of adduct (eq 5). The incorporation of the deprotonated α-carbon into a cyclopropyl ring appears to be responsible for the enhanced nucleophilic behavior of dicyclopropyl ketone enolate as well as its unusually high proton affinity. Methyl cyclopropyl ketone has a bracketed acidity of 369 kcal/mol and can be shown to undergo deprotonation only at the methyl group.[30] The resulting enolate ion produces only proton transfer with DMFU (eq 6). Thus, the

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(29) (a) Bordwell, F. G.; Imes, R. H.; Steiner, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 3905. (b) Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1216.

(30) Gas-phase acidities for carbonyl compounds not listed in ref 18 were determined from bracketing experiments involving proton-transfer reactions with standard acids and bases, or estimated by analogies with related compounds.

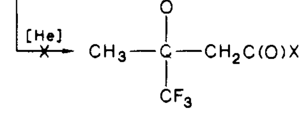
presence of the cyclopropyl group as a substituent on the carbonyl carbon of the enolate has little effect on reactivity.

Alkyl group substitution shows several types of effects. Alkyl substitution at the α-carbon of the aldehyde and ketone enolates shows little influence, i.e., CH_2CHO^-, CH_3CHCHO^-, and $(CH_3)_2CCHO^-$ all give essentially the same result. Similarly, increasing the size of the alkoxyl group in the ester enolates has little effect on reaction efficiencies or branching ratios. However, alkyl substitution at the α-carbon of ester enolates and nitrile carbanions has a pronounced effect. For example, the reaction of ethyl propionate enolate with DMFU is highly efficient and produces over 90% adduct, while the ethyl acetate enolate reaction is somewhat less efficient and produces 60% adduct. Also, cyanoethyl anion reacts more efficiently and with a greater percentage of adduct formation than the cyanomethyl anion.

The branching ratios for the anion/DMFU reactions are found to be independent of helium buffer gas pressure over a range of 0.200–0.800 Torr. Acetone and propanal enolates produce almost exclusive proton transfer at 0.400 Torr and yield no more than 3% adduct at 0.800 Torr. Anions producing a greater percentage of adduct at 0.400 Torr such as methyl acetate enolate and benzyl anion also show no significant change in product distribution from 0.200–0.800 Torr. The absence of any variation indicates that the termolecular addition channel is effectively saturated in this pressure regime.[31] The mechanistic implications of this finding are discussed in a later section.

Finally, proton transfer from a methyl group in DMFU is shown to be essentially irreversible by the complete absence of H/D exchange when deuteriated negative ions are used as the reactants. For instance, $CD_3COCD_2^-$, $MeOCOCD_2^-$, and deuteriated benzyl anion, $C_6H_5CD_2^-$, each react with DMFU to produce an $[M-H]^-$ ion in which no deuterium is incorporated. Moreover, at low conversions no signals corresponding to reactant anions with any lesser amount of deuterium than was originally present are observed, i.e., DMFU does not affect D/H exchange in the deuteriated ions. It has been shown previously that D/H exchange may accompany even highly exothermic proton-transfer reactions between OD^- and acidic hydrocarbons.[27,32] The absence of exchange with DMFU shows that multiple proton transfers do not occur during the course of the overall acid–base reaction.

Comparison with Other Neutral Substrates. The value of DMFU as a probe for examining competing nucleophilicity and basicity in a wide range of anions is revealed when its reactivity is compared with that of other neutral substrates. Typically, carbonyl compounds that are capable of adduct formation under FA conditions are weak acids which do not possess α hydrogens, such as pivaldehyde ($(CH_3)_3CCHO$). In contrast, carbonyl compounds that are as acidic as DMFU usually show exclusive proton transfer. For example, CF_3COCH_3 ($\Delta H_{acid} = 350.3 \pm 2.3$ kcal/mol)[18] does not produce stable adducts in reactions with a series of ketone and ester enolates (eq 7), despite the fact that



(7)

the $-CF_3$ group might otherwise be expected to strongly accelerate nucleophilic addition to the carbonyl (Table IV). McDonald and co-workers have reported that the negative ions CF_3^- and O_2^- can undergo competing Brønsted and Lewis acid–base reactions at 0.5 Torr with certain carbonyl substrates such as acetone and 2,3-butanedione.[4c,33] The proton-transfer channels for these particular reactions are not strongly exothermic (≤7 kcal/mol) and presumably not fast enough to totally overwhelm the nucleophilic addition channel.

Table IV. Reactions of Enolate Anions with 1,1,1-Trifluoroacetone

enolate	PA[a]	k_{obsd}[b]	eff[c]	% proton transfer	ΔH_{pt}[d]	ΔH_{add}[e]
$MeOCOCH_2^-$	371.9	1.1	0.77	100	−22	−26
$EtOCOCH_2^-$	≃372[f]	1.1	0.82	100	−22	−26
$CH_3COCH_2^-$	369.1	1.3	0.86	100	−19	−22
$OCHCH_2^-$	365.8	1.4	0.95	100	−16	−19

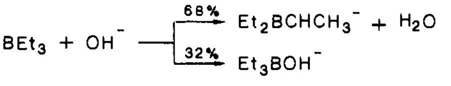
[a] Proton affinity (kcal/mol), ref 18. [b] Total observed rate coefficient in units of 10^{-9} cm^3/s. [c] eff = k_{obsd}/k_{ADO}, ref 24. [d] Enthalpy of proton transfer to carbon (kcal/mol). [e] Estimated enthalpy of addition through carbon (kcal/mol). [f] Estimated value.

Table V. Measured Efficiencies for Reactions of Acetone and Methyl Acetate Enolates

		reaction efficiency[a]	
	ΔH_{acid}	$CH_3COCH_2^-$	$CH_3OCOCH_2^-$
CH_3NO_2[b]	356.4	0.41	0.47
$(CH_3)_2CHSH$[b]	353.4	0.43	0.37
CH_3COCF_3[b]	350.3	0.86	0.77
CH_3Cl[c]		0.17	0.16
CH_3Br[c]		0.12	0.14
CO_2[b]		0.05	0.05
CS_2[d]		0.12	0.12

[a] eff. = k_{obsd}/k_{ADO}, ref 24. [b] Proton transfer. [c] Nucleophilic substitution. [d] Nucleophilic addition (0.400 Torr He).

A neutral substrate that is less acidic than DMFU and also shows competitive Brønsted and Lewis acid–base reactions in the gas phase is triethylborane ($\Delta H_{acid} = 367 \pm 3$ kcal/mol).[34] At 0.300 Torr, BEt_3 is found to react rapidly with hydroxide ion ($k_{obsd} = 1.7 \times 10^{-9}$ cm^3/s) to yield 68% proton transfer and 32% addition (eq 8). The total rate coefficient and reaction branching ratio



(8)

for reaction 8 are found to be independent of buffer gas pressure. The reaction of allyl anion with BEt_3 is found to produce adduct almost exclusively. As with DMFU, the delocalized anion shows a greater propensity for adduct formation with BEt_3. However, the low acidity of the borane restricts its utility as a probe reagent to a smaller group of anions, and, thus far, all enolate ions of any type reacted with it have produced only adduct.[34] BEt_3 does not exhibit the same broad range of reactivity shown by DMFU.

The DMFU reactions expose marked differences in the reactivity of acetone and methyl acetate enolates. In order to put this in perspective, we have characterized the kinetic behavior of these two ions in a series of related ion-molecule reactions. Shown in Table V are the measured efficiencies ($k_{obsd}/k_{collision}$) for selected proton-transfer, nucleophilic substitution, and nucleophilic addition reactions of $CH_3COCH_2^-$ and $CH_3OCOCH_2^-$. In each example, only one type of reaction is available to the ion-molecule pair, and any intrinsic differences in the reactivity of the two enolates toward these reactions should show up as differences in the efficiencies. However, within experimental uncertainty, the measured efficiencies for both enolates in each reaction are identical. Therefore, using kinetic criteria for ion-molecule reactions involving a single product channel, the ketone and ester enolates are indistinguishable. This shows that product branching ratios in general, and those with DMFU in particular, can be highly sensitive indicators of intrinsic reactivity differences among enolate ions.

Discussion

In discussing the Brønsted and Lewis acid–base reactions of organic anions, especially the enolates, it is important to consider hard–soft acid–base (HSAB) theory.[35] DMFU is a typical "soft"

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[31] Bohme, D. K.; Dunkin, D. B.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1969**, *51*, 863.

[32] Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565.

[33] McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123.

[34] Squires, R. R.; Workman, D. B.; Brickhouse, M. D., unpublished results.

Lewis acid. It has a low-energy LUMO, large orbital coefficient at the reactive C6 site, large size, and a high molecular polarizability. HSAB theory is capable of correlating some of the reactivity we have observed, i.e., the softer, charge-delocalized carbanions attack the soft C6 site more readily than the hard, charge-localized alkoxides. However, HSAB fails at several points. Certain bases usually classified as soft produce no adduct with DMFU, i.e., the thiolates and the localized carbanions. HSAB also does not adequately account for the wide range of enolate reactivities and the striking differences between aldehyde and ketone enolates versus ester and amide enolates. HSAB arguments about the relative reactivity of carbon and oxygen nucleophiles have often focused on solvent conditions, alkylation reagents, leaving group ability, and counterion effects.[35] Intrinsic properties of the enolate ions themselves have been considered less frequently. It has been known for some time that ester enolates form C-alkylation and C-acylation products under conditions that usually result in O-alkylation with ketone and aldehyde enolates.[36] Ester enolates will also silylate at carbon under conditions that produce O-silylation in ketone enolates.[37] However, the reasons for this behavior are not well understood. We find that the general variations in the reactivities of negative ions with DMFU in the gas phase are more properly understood in terms of charge delocalization, a component of HSAB theory, and the ways in which it may affect potential energy barriers to proton transfer and nucleophilic addition. Furthermore, it will be shown that the specific variations among the enolate ions can be readily accounted for on the basis of the keto–enol energy differences for the corresponding neutral carbonyl compounds.

Charge Delocalization Effects. Proton transfer often overwhelms nucleophilic addition and substitution processes in reactions between negative ions and carbonyl compounds. Grutzmacher has proposed that as a strong base such as NH_2^- approaches the carbonyl group of an acetate ester it will come into close proximity with the α hydrogens and that the initial stages of the proton transfer and nucleophilic addition reaction coordinates are similar.[38] However, since the transition state for an exothermic proton transfer is early compared to that for the obligatory rehybridization to a tetrahedral intermediate that accompanies addition, the proton transfer dominates. Brauman has also considered this phenomenon in terms of the potential energy barriers associated with the individual product channels.[3b] In the reaction of methoxide ion with acetyl fluoride, proton transfer ($\Delta H = -18$ kcal/mol) overwhelms the equally exothermic hydride transfer ($\Delta H = -20$ kcal/mol) and $B_{AC}2$ reactions ($\Delta H = -20$ kcal/mol).[3b] Brauman has proposed that nucleophilic displacement at a carbonyl center has an associated potential energy barrier, while proton transfer reactions often have little or no associated barriers.

In the case of the reactions between localized anions and DMFU, the nucleophilic addition pathway also appears to have a significant potential energy barrier. In all cases, adduct formation between localized anions and DMFU is exothermic (Table II), but only proton transfer is observed. Thus, the product distributions are clearly a result of kinetic control. The high efficiency of the reactions involving oxyanions suggests a small kinetic barrier to proton transfer, and this is certainly plausible for such exothermic reactions. However, the localized carbanion CF_3^- is nearly as basic as CH_3O^- but shows a lower reaction efficiency. It has been demonstrated previously that carbon-to-carbon proton transfer can be relatively slow,[39] and the CF_3^-/DMFU reaction appears to be a case in point. However, the barrier to proton transfer is evidently not large enough to make nucleophilic addition a competitive process.

Proton-transfer reactions have frequently been found to be considerably slower for delocalized anions, often to such an extent that nucleophilic addition and substitution processes may successfully compete. Depuy and co-workers have reported that delocalized carbanions show a greater propensity for nucleophilic acyl substitution with methyl formate than do localized carbanions.[6] The localized carbanions produce mainly Riveros-type α-elimination products through attack at the formyl hydrogen.[40] A comparable trend appears in the present work. Allyl and benzyl anions, despite their high basicity, both exhibit considerable adduct formation with DMFU. These species are known to be inefficient at deprotonating carbon acids.[39] Proton transfer requires temporary charge localization, resulting in loss of resonance stabilization and an increase in the energy of the transition state.[41] The higher energy barrier to proton transfer allows the strongly exothermic nucleophilic addition route to compete effectively. While charge delocalization can reduce the kinetic basicity of an anion, it does not necessarily weaken its intrinsic nucleophilicity. Brauman has reported a correlation between methyl cation affinity and empirically fitted potential energy barrier heights for nucleophilic substitutions at methyl centers.[42] The delocalized anions do not show consistently higher displacement barriers than do localized anions. While the analogy between substitution at a saturated carbon and addition to the polar double bond in DMFU is limited, our experimental results also indicate that delocalized anions such as allyl and benzyl are not necessarily intrinsically weak nucleophiles in addition reactions.

The less basic carbanions exhibit a range of reaction efficiencies and branching ratios that appear to be a function of the carbanion stabilizing substituent. The sulfoxy substituent stabilizes adjacent carbanions largely by induction, i.e., d_π–p_π conjugation does not appear to be important.[43] Accordingly, $CH_3SOCH_2^-$ bears an essentially localized charge and, like the other localized ions, produces almost exclusive proton transfer with DMFU. On the other hand, the nitro group is a strong π-acceptor, and in $CH_2NO_2^-$ the charge is localized mainly on the nitro oxygens.[44] It too produces mainly proton transfer with DMFU, albeit slowly. The low reaction exothermicity and obligatory carbon-to-carbon proton transfer are likely to be responsible for the low efficiency. Calculations have shown that both inductive and resonance charge withdrawal are important in the stabilization of adjacent carbanions by a cyano group. Hopkinson and Lien have reported that the α carbon in $NCCH_2^-$ bears the bulk of the negative charge, with only half as much being transferred to the cyano substituent.[45] This is consistent with our observation that $NCCH_2^-$ reacts by both proton transfer and adduct formation with DMFU. Unlike the simple ester enolates, the cyanocarbanions react with DMFU with moderate-to-high reaction efficiency, implying that their nucleophilicity with DMFU not only involves an increased barrier to proton transfer but also a reduced barrier to nucleophilic addition.

Enolate Ions and the Influence of C versus O Basicity. When the carbanion-stabilizing substituent is a carbonyl group, reactivity with DMFU varies markedly. First of all, it is important to emphasize that abstraction of a proton from DMFU by the amide enolate, all of the ester enolates, and certain of the small-ring ketone enolates is constrained by thermodynamics to occur only through carbon. In contrast, proton transfer from DMFU to either the carbon or the oxygen end of the aldehyde enolates and acyclic or larger ring ketone enolates is energetically feasible (Table III). For example, the experimentally determined keto–enol energy

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difference for acetaldehyde is 9.8 kcal/mol,[46] and the PA of the carbon in the corresponding enolate ion is 365.8 kcal/mol. Thus, the PA of the enolate oxygen is approximately 356 kcal/mol, rendering it just basic enough to abstract a proton from DMFU. For acetone, the measured keto–enol energy difference of 13.9 kcal/mol[46] combines with the carbon basicity of the enolate (369.1 kcal/mol) to yield a PA at oxygen of 355 kcal/mol. Within the uncertainties in these numbers, proton transfer to the oxygen in acetone enolate is therefore possible.

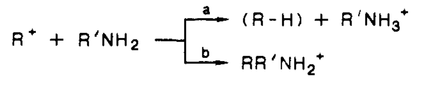
The keto–enol energy differences for all of the other compounds listed in Table III have not been determined experimentally. However, they can be reasonably estimated from Benson group-equivalents[47] and the recently evaluated parameter for an enolic oxygen.[46] The computed values for CH_3OCOCH_3 (30 kcal/mol) and Me_2NCOCH_3 (35 kcal/mol) are in reasonable agreement with recent ab initio calculations by Schwarz and co-workers.[48] Thus, keto–enol energy differences for esters and amides are 2–3 times larger than those for aldehydes and ketones. Accordingly, the oxygen proton affinities of the corresponding enolates are quite low (338–344 kcal/mol), and proton transfer from DMFU to oxygen cannot take place. Decreasing ring size in the cyclic ketones also results in increased keto–enol energy differences due to the increased strain energy of the small-ring enols. As a result, while proton transfer from DMFU to carbon is exothermic for all of the cyclic enolates, transfer to oxygen may only occur with cyclohexanone enolate and, perhaps, with cyclopentanone enolate.

It is also interesting to note the reactivity of the less basic ketone enolates. Acetophenone enolate has a carbon proton affinity PA(C) of 361.3 kcal/mol but an oxygen proton affinity PA(O) of 348 kcal/mol, a value less than ΔH_{acid} (DMFU). As in the case of the ester enolates and small-ring ketone enolates, adduct formation competes with proton transfer with this ion (Table III). The acetyl fluoride enolate, with a carbon proton affinity of 356.0 kcal/mol, is likely to have a very low oxygen proton affinity (PA(O) $\simeq$ 325.0 kcal/mol) based on its calculated keto–enol energy difference of 31 kcal/mol.[48] Accordingly, $FCOCH_2^-$ reacts very slowly by almost exclusive adduct formation. Only when proton transfer through the enolate oxygen is exothermic does proton transfer dominate in the enolate–DMFU reactions.

A similar set of conclusions applies to the enolate ion addition channels. Adduct formation through carbon is strongly exothermic for all of the enolates in Table III, but addition through oxygen may occur only with the aldehyde enolates, the acyclic and larger ring ketone enolates, and the α-branched ester enolates. It is noteworthy that these latter ions give significantly higher percentages of adduct than the unbranched ester enolates.

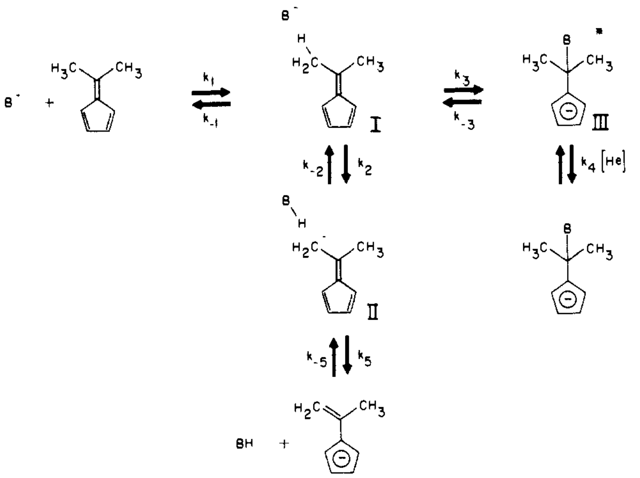
A clear trend for the enolate ions emerges from a consideration of these thermochemical data. While all enolates may undergo both Brønsted and Lewis acid–base reactions with DMFU through the carbon, only those ions that *cannot* proton abstract through oxygen show significant amounts of addition. The question now becomes the following: how can the *thermodynamic* basicity of the oxygen in an ambident enolate ion control the *kinetically* determined product branching ratios for the DMFU reactions? The origins of this influence can be discerned in the detailed mechanism for the DMFU reactions outlined in the next section.

Mechanistic Considerations. In formulating a unified mechanism and energy profile for the reactions of negative ions with DMFU, we have noted the close relationship of our system with the gas-phase reactions between carbocations and alkylamines that have been considered in great detail recently by several groups. These reactions also involve competing proton transfer and nucleophilic addition pathways (eq 9). Meot-Ner,[49] Moylan and Brauman,[50] and Ausloos and Lias[51] have each put forth different mechanisms to explain the observed pressure dependence and structural effects on the product distributions. Meot-Ner has proposed that the alkylamine and carbocation undergoing reaction initially form a relatively loosely associated cluster ion that can yield either proton transfer (eq 9a) or a highly energetic dialkylammonium ion. This latter species can undergo a four-center elimination of a neutral alkene or three-body collisional stabilization to produce an observable adduct (9b).[49] Moylan and Brauman have proposed a slightly different mechanism in which the initially formed intermediate is described as a hydrogen-bonded complex that can decompose over a relatively low-energy barrier to proton transfer through a loose transition state or over a higher barrier to addition through a tight transition state.[50] Four-center elimination to produce the proton-transfer product was deemed unlikely based on literature precedents and photodissociation experiments with certain of the dialkylammonium ions. Ausloos and Lias showed that the Moylan and Brauman experiments were complicated by the presence of certain amine impurities, and they formulated a modified version of Meot-Ner's mechanism for reaction 9.[51] They proposed that the initially formed intermediate may be either "hydrogen-bonded-like" or "condensation ion [adduct]-like" and that the branching ratio for the two channels is determined by the relative configuration of the reactants when they approach to within bonding distances of one another. Despite some differences, the above mechanisms each indicate that the Brønsted and Lewis acid–base reactions can (or must) ultimately arise from different intermediates, and all are consistent with the pressure independence of the product distributions that was observed at relatively high pressures.



$$R^+ + R'NH_2 \longrightarrow \begin{cases} \xrightarrow{a} (R-H) + R'NH_3^+ \\ \xrightarrow{b} RR'NH_2^+ \end{cases} \qquad (9)$$

Scheme I



Morton and co-workers have investigated the dynamics of carbocation–amine reactions by using neutral product collection techniques.[52] They examined the reactions of labeled 1-methylcyclopentyl cations with a variety of amine bases and found that base strength affects the distribution of isomeric proton-transfer products. This result, along with the absence of both primary isotope effects and H/D exchange, led to the conclusion that product fractionation occurs from an initially formed "orbiting intermediate" which may then decompose to the distinct hydrogen-bonded intermediates responsible for proton transfer. The orbiting intermediate can also collapse into a Lewis acid–base complex which does not participate in the proton-transfer reactions.

Scheme I summarizes our view of the anion/DMFU reaction mechanism with a kinetic model that incorporates many of the essential features of the above proposals for the carbocation/amine reactions. Figure 1 shows a corresponding energy profile that is consistent with our experimental results. The initially formed

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intermediate I is represented as an electrostatically bonded complex, possibly involving a hydrogen bond between the anion B^- and an acidic DMFU proton. I is flanked by two barriers, one leading to proton transfer (E_1) via formation of a second complex II and the other (E_2) leading to nucleophilic addition through the energy-rich adduct III. Barrier E_1 is analogous to the central barriers that characterize the usual double-well potential surfaces for slow proton-transfer reactions,[41] and it may have its origins in unfavorable charge localization requirements for the anionic base, or poor conjugation of the developing carbanion with the DMFU π system in the proton-transfer transition state. The addition barrier E_2 arises from the sacrifice of electrostatic or H-bonding energy in I that must accompany migration of the anion to the C6 addition site.

We have adopted a mechanism involving a single, primary intermediate (I) rather than two separate "proton transfer-like" and "adduct-like" intermediates such as those proposed by Ausloos and Lias for reaction 9.[51] It is difficult to see how the partitioning between these two intermediates during initial approach of the reagents through a loose transition state could vary so widely for the otherwise structurally similar ketone and ester enolates, yet the observed product distributions are quite different for these types of ions. On the other hand, it is likely that differences in the electronic structures of the reactant ions could exert an influence on the subsequent behavior of a more closely associated and specifically bonded complex such as I. Ab initio calculations have shown that hydrogen-bonded complexes formed from anionic nucleophiles such as OH^- or CH_3O^- and carbonyl compounds such as formaldehyde[53] or acetone[54] represent local minima on the potential energy surfaces and that a barrier must be surmounted before addition to the carbonyl can occur. Other types of ion-dipole bonding are also possible when hydrogen-bonding sites are not available. Han and Brauman recently demonstrated the existence of an interesting $[CF_3COCl{\cdot}Cl^-]$ cluster ion in which the two chlorines are chemically distinguishable.[55] Their conclusion that a barrier to formation of the tetrahedral addition complex also exists in this system has been corroborated by ab initio calculations reported by Jorgensen.[56]

In Scheme I the Bronsted and Lewis acid-base reaction channels ultimately stem from the distinct intermediates II and III, respectively. A direct connection between the excited intermediate adduct III and the proton-transfer pathway is not included in our mechanism since this would require a four-center elimination reaction, and Moylan and Brauman have provided convincing general arguments against the occurrence of these types of unimolecular reactions in a variety of other gas-phase ions.[50] Intermediates II and III are more likely connected through the initial complex I. The absence of significant H/D exchange in reactions of DMFU with deuteriated ions indicates that the interconversion of intermediates I and II is essentially irreversible, i.e., $k_5 \gg k_{-2}$. That is, once passage over the proton-transfer barrier E_1 occurs, the energy-rich (and loosely-bonded) complex II rapidly decomposes out the exit channel to products. Intermediate III is shown in Scheme I to be formed reversibly from I based on analogy with the amine–carbocation reactions described earlier. The most definitive evidence for this would be the observation of thermoneutral methyl exchange from a reaction between DMFU and CD_3^-. However, because of the present lack of a means to generate and react methyl anions in a flowing afterglow, such an experiment must remain hypothetical.

Application of steady-state approximations to the kinetic model outlined in Scheme I and solving for the ratio of adduct (ADD) to proton-transfer product (PT) gives the expression

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

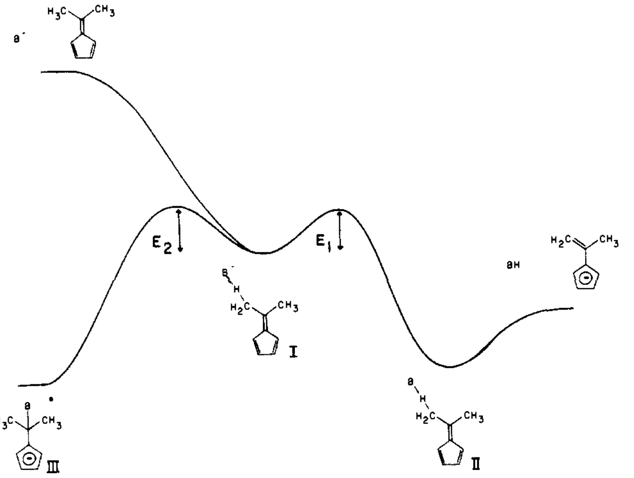

Figure 1. Energy profile for competing addition and proton-transfer reactions of DMFU.

Except for the last term, this expression is identical with the one derived by Moylan and Brauman for the cation/amine reactions.[50] This last term will drop out for moderately exothermic proton transfers where k_{-2} will be relatively small compared to k_5. In the high pressure limit the ADD/PT ratio will be constant and approximately equal to k_3/k_2. This is apparently the case for flowing afterglow conditions since the rates and product distributions of the anion–DMFU reactions are invariant with pressure in the range 0.200–0.800 Torr. At the low-pressure limit the ratio is equal to $k_3k_4[\mathrm{He}]/k_2k_{-3}$ and should therefore show linear pressure dependence.

The most important features in the potential energy diagram shown in Figure 1 are the two energy barriers E_1 and E_2. Although both barriers are lower than the total energy of the reactants, they can slow the overall reaction rate as well as the separate rates for each channel since passage over them may be impeded by a lower density of available microscopic states compared to the transition state leading back to reactants.[41,42] Thus, the reverse reaction is entropically favored and becomes dominant when the intermediate barriers increase, i.e., when the reactant anions are delocalized. As the relative heights of the barriers E_1 and E_2 change, the product distribution changes. The oxyanions are expected to have relatively low barriers to proton transfer, so that even though they can be strongly nucleophilic, addition does not compete (i.e., $E_1 < E_2$). The delocalized carbanions should have relatively higher barriers to proton transfer for the reasons given earlier, so reversion to reactants and nucleophilic addition becomes dominant ($E_1 > E_2$). That is, delocalized carbanions are nucleophiles by default.

The origins of the variations among the enolate ions and the apparent influence of the keto–enol energy differences for the corresponding carbonyl compounds are readily accounted for by the general mechanistic model outlined in Scheme I. Computational studies of enolates indicate that negative charge in the ion resides mainly on oxygen.[45a,57] Therefore, hydrogen bonding by an acidic DMFU proton to the oxygen end of the ambident enolate would be preferred kinetically for each ion listed in Table III. In terms of Scheme I, the initial intermediate formed in enolate/DMFU reactions probably has the structure (Ia) shown below which incorporates a ($O^-{\cdots}HC$) hydrogen bond. If complete proton transfer to oxygen is thermodynamically allowed, such as with most acyclic aldehyde and ketone enolates, then direct and rapid decomposition of Ia out the proton-transfer channel may occur. However, if the oxygen basicity in the enolate is low (i.e., the keto–enol energy difference for the neutral carbonyl compound is high) such as with the amide and ester enolates, then Ia must rearrange to another configuration in which proton transfer to carbon can take place (i.e., Ib). Moreover, once the rearranged

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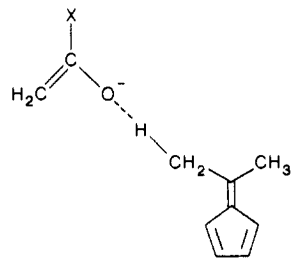
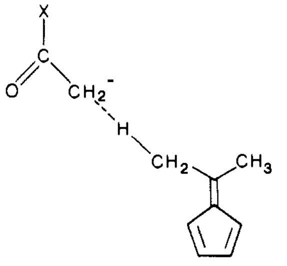


1a



1b

configuration is achieved, negative charge must localize on the α carbon for the proton transfer to proceed. These factors can act to raise the energy of the proton-transfer barrier E_1 for enolate ions with low oxygen basicities, and, as a result, addition (mainly through carbon) becomes competitive or even dominant. The implication here is that the proton transfers observed for all of the aldehyde enolates and acyclic or larger ring ketone enolates are occurring mainly through oxygen. Unfortunately, we cannot confirm this hypothesis directly since the neutral enol products cannot be detected directly in our experiments.

It is instructive to consider the differences in reactivity between DMFU and CH_3COCF_3 (eq 7) since their gas-phase acidities are similar and their structures are comparable. Trifluoroacetone does not yield an adduct with any type of enolate ion, despite the fact that addition to the carbonyl (through carbon) is estimated to be more exothermic than proton transfer for most enolates. This could imply the existence of an unusually high barrier to nucleophilic addition in CH_3COCF_3, but this is unlikely for several reasons. While the presence of barriers to carbonyl addition have been demonstrated experimentally,[3,55] computational studies have suggested that they are quite small when addition is exothermic.[53,54,56] Moreover, for certain dipole-aligned approach vectors of the anionic nucleophile and the carbonyl compound, no barrier at all is found in the calculations.[50] Thus, the absence of an observable adduct in the enolate ion/CH_3COCF_3 reactions is probably not due to a kinetic barrier preventing exothermic addition. Rather, it is more likely that it is due to facile reversion of the tetrahedral addition complex back to a hydrogen-bonded complex which readily undergoes proton transfer. That is, the tetrahedral adduct is not sufficiently long-lived for efficient collisional stabilization by the helium buffer gas. The analogous barrier separating the adduct III and the hydrogen-bonded intermediate I in the anion/DMFU reactions is likely to be much higher. When the adduct III forms, charge is extensively delocalized in the aromatic cyclopentadienyl ring, and the localization of charge that is required to reform intermediate I is energetically unfavorable. Accordingly, the adduct is relatively long-lived and undergoes efficient three-body stabilization.

Conclusions

6,6-Dimethylfulvene is a sensitive probe of the relative nucleophilicity and kinetic basicity of gas-phase anions. Charge delocalization appears to be the most important intrinsic property controlling anion reactivity. Localized anions react exclusively by proton transfer, while the behavior of delocalized anions is determined by the nature of the charge stabilizing substituent. Delocalized carbanions such as allyl, benzyl, and cyanomethyl anion react as both Brønsted and Lewis bases; certain resonance stabilized carbanions such as the aldehyde enolates and acyclic ketone enolates react only as Brønsted bases. Amide enolates, ester enolates, and small-ring ketone enolates show a greater tendency to act as Lewis bases. The observed reactivity patterns strongly suggest that the Brønsted and Lewis acid-base channels arise from kinetically distinct intermediates. The initially formed intermediate is proposed to be an electrostatically bonded ion-molecule complex that can either undergo proton transfer or rearrange to an excited adduct. Subtle changes in the electronic configurations of the reactant ions can affect the relative heights of the potential energy barriers for these two channels, and the reaction-branching ratios are kinetically determined by the microscopic partitioning of each system over these barriers. The differences observed for the enolates are attributed to the relative basicities of the oxygen and carbon ends of the ambident ions. The kinetically preferred intermediate involves a hydrogen bond between the DMFU proton and the enolate oxygen. Proton transfer either occurs directly, or, if energetically unfavorable, rearrangement of the intermediate occurs followed by both proton transfer and addition.

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Mechanistic Studies of Gas-Phase Negative Ion Unimolecular Decompositions. Alkoxide Anions

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Abstract: The unimolecular decompositions of 15 gas-phase alkoxide negative ions have been studied by infrared multiple photon photochemical activation in an ion cyclotron resonance spectrometer. Upon pulsed CO_2 laser irradiation, alkoxide anions undergo elimination of neutral molecules (e.g., alkanes RH) to yield enolate anions. The observed reactivity patterns and kinetic isotope effects further establish a stepwise decomposition mechanism involving initial heterolytic cleavage to an intermediate anion-ketone complex followed by proton transfer to give the ultimate products. A relative order of leaving group propensities $CF_3 > Ph > H > t\text{-Bu} > Me > i\text{-Pr} > Et$ was observed. The apparent anomalous reactivity order for the alkyl groups can be rationalized by invoking a change in mechanism to one involving an intermediate in which an electron is not bound specifically by the eliminated alkyl group for R = *t*-Bu, *i*-Pr, and Et: either a radical-ketone radical anion complex produced by homolytic cleavage or an anionic cluster. This order also leads to the conclusion that methane elimination from alkoxide anions proceeds via the pathway involving heterolytic cleavage. The results of this study have implications for bimolecular ion-molecule reaction dynamics, since the photochemically generated intermediates are also intermediates in bimolecular proton transfer reactions.

Infrared multiple photon (IRMP) photochemical studies of gas-phase ions trapped in an ion cyclotron resonance (ICR) spectrometer can provide insight into the mechanisms and dynamics of unimolecular ion decompositions.[1,2] This paper de-

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