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Dipole-Stabilized Carbanions in the Gas Phase

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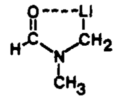
Abstract: The energetics, structures, and reactivities of several dipole-stabilized carbanions from formamides, aldehydes, and formamidines have been examined by ICR mass spectrometry and by MNDO calculations. Experimentally in the amides, only one of the alkyl groups on nitrogen appears to be deprotonated, but a stereochemical assignment cannot be made. The order of acidity is aldehyde > amide > ester based on the MO calculations, indicating that the external dipole moment of these carbon acids is not a good measure of acidity. The acidities follow the inductive ordering, based on σ_I constants.

The effect of adjacent substituents on the stability, structure, and reactivity of carbanions has been the object of considerable investigation. While it is well established that π-acceptor groups can stabilize carbanions appreciably,[1] the effect of π-donor groups is not so well understood. First-row heteroatom groups, such as OMe and F, which are π donors but σ acceptors, have variable and small effects on anion stability in both experiment[2] and in theory,[3] compared to π-acceptor groups, depending on the nature of the other groups attached to the anionic atom. Recently there has been considerable synthetic interest in lithiocarbon reagents apparently stabilized not by π-acceptor substituents, but by an adjacent heteroatom as the positive end of a dipole.[4] The observed stereochemistry of products from anions such as **1** is stated to be consistent with internal chelation of the lithium was the negative end of the dipole, as in **1**.[4,5] This is in contrast to molecular orbital calculations, which indicate that structure **2** is more stable than **1** in the absence of a counterion.[5] In order to provide some experimental evidence for the stereochemical preference of the free anion, as well as to assess the energetics of such species, we have undertaken a study of the reactivity of several such dipole-stabilized carbanions in the gas phase, using ion cyclotron resonance (ICR) mass spectrometry. Dipole-stabilized anions have previously been observed in the gas phase: 2,2-dimethylpropanal gives an M − 1 anion on reaction with hydroxide ion in an ICR spectrometer.[6] The fact that only eight of the nine remaining hydrogens in this anion undergo deuterium exchange with D_2O indicates that it is not the acyl anion from removal of the aldehydic proton, but rather the anion resulting from loss of a methyl hydrogen.[6] Aldehydes do not appear to be good precursors for dipole-stabilized carbanions in solution.[4] Most of the functional groups commonly used to generate such carbanions in solution, such as carboxamides and esters, have not been investigated in the gas phase, providing the impetus for this work.



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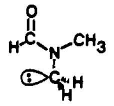

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Experimental Section

The apparatus and techniques used in this work have been previously described.[7] Mass spectra were taken in unquenched mode.[7d] Compounds **8a**, **8b**, and **8d** were kindly provided by Dr. A. I. Meyers and co-workers; *N-tert*-butyl-*N'*,*N'*-di-*n*-butylformamidine (**8c**) was synthesized by their method.[8] The amides were obtained commercially and purified by distillation, save for *N*,*N*-diethylformamide, which was synthesized by the method of ref 9, and 1,3,3-trimethyl-2-pyrrolidone, which was synthesized by the method of ref 10. $DCONMe_2$ was prepared from a (1:1:1) mixture of $(CH_3)_2NH{\cdot}HCl$, DCO_2Me, and Et_3N which was allowed to stir for 30 min. The crude mixture was injected onto a GLPC column and collected directly in the ICR sample tube as described in ref 7. ND_3 was obtained from Merck Isotopes. Compound **8d** was investigated with the vacuum system heated to 90 °C, since at room temperature the only ion signals seen for this were attributable to logical trace impurities more volatile than the compound of interest. Compound **8c** was investigated in a similar manner.

The negative ions used in this work were generated by electron impact on NH_3 (ND_3) to give NH_2^- (ND_2^-) at 6.2eV, H_2O (D_2O) to give HO^- (DO^-) at 6.3eV, and CH_3ONO to give CH_3O^- at 0.0 eV.

Results

Aldehydes. We have reexamined 2,2-dimethylpropanal in our ICR spectrometer and confirmed that it undergoes only eight exchanges with DO^-/D_2O. With ND_2^-/ND_3, we observe nine exchanges, indicating that the acyl anion is between NH_3 and H_2O in acidity. An M − 1 anion is observed for 2,2,4,4-tetramethyl-3-pentanone reacting with DO^-/D_2O. It exchanges at least nine hydrogens, but the signals in unquenched mode disappear into baseline noise at that point. More exchanges may be accessible, but the time window of the ICR method does not allow us to observe so many sequential reactions. The inference of acidity based on deuterium exchange is complicated by the possibility of endothermic exchanges taking place. This has been observed in the flowing afterglow, but not in the ICR spectrometer. For example, 2-phenylallyl anion undergoes eight exchanges with D_2O in the flowing afterglow,[11] but only the four expected from

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[1] Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, New York, 1973. Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965.

[2] (a) Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 4761–3. (b) Knunyants, I. L.; German, L. S.; Rozhkov, I. N. *Izv. Akad. Nauk SSR, Ser. Khim.* **1966**, 1062–5. (c) Hine, J.; Mahone, L. G.; Liotta, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 5911–20. (d) Lorand, J. P.; Urban, J.; Overs, J.; Ahmed, Q. A. *J. Org. Chem.* **1969**, *34*, 4176–8. (e) Streitwieser, A., Jr.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444–5. (f) Zoltewicz, J. A.; Grake, G.; Smith, C. L. *Ibid.* **1969**, *91*, 5501–5. (g) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1885–6.

[3] (a) Kollman, P.; McKelvey, J.; Gund, P. *J. Am. Chem. Soc.* **1975**, *97*, 1064–5. (b) Lehn, J.-M.; Wipff, G. *Ibid.* **1976**, *98*, 7498–7505. (c) Bernardi, F.; Bottoni, A.; Epiotis, N. D. *Ibid.* **1978**, *100*, 7205–9. (d) Burdon, J.; Davies, D. W.; del Conde, G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1205–7. (e) Hinde, A. L.; Pross, A.; Radom, L. *J. Comput. Chem.* **1980**, *1*, 118–28. (f) Hopkinson, A. C.; Lien, M. H. *Int. J. Quantum Chem.* **1980**, *18*, 1371–91. (g) Pross, A.; DeFrees, D. J.; Levi, B. A.; Pollack, S, K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693–9. (h) Liebman, J. F.; Politzer, P.; Rosen, D. C., "Chemical Applications of Atomic and Molecular Electrastatic Potentials"; Polizter, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981; pp. 295–308.

[4] Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275–316.

[5] Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108–10.

[6] Noest, A. J.; Nibbering, N.M.M. *J. Am. Chem. Soc.* **1980**, *102*, 6427–9.

[7] (a) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1970**, *41*, 555–8. (b) McIver, R. T., Jr. *Ibid.* **1978**, *49*, 111–8. (c) McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65–84. (d) Bartmess, J. E.; Caldwell, G. *Ibid.* **1981**, *41*, 125–34.

[8] Meyers, A. I.; Ten Hoeve, W. *J. Am. Chem. Soc.* **1980**, *102*, 7125–6.

[9] Robson, J. H.; Runhardt, J. *J. Am. Chem. Soc.* **1955**, *77*, 498–9.

[10] Gassman, P. G.; Fox, B. L. *J. Org. Chem.* **1966**, *31*, 982–3.

[11] Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.*, **1981**, *103*, 4256–8.

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Table I. Reactions of Some Carbonyl Compounds and Formamidines with Anionic Bases in an ICR Spectrometer[a]

acid	ND_2^-/ND_3		%	DO^-/D_2O		%	$MeO^-/MeOD$
$HCONMe_2$	72^-–75^-	M − 1 + d_n	30	35^-–38^-	$DO^-\cdots HOD$	28	n.r.
	91^-	addition	13	62^-–63^-	$DO\cdots HNMe_2$	35	
	100^-, 101^-	Claisen[b]	28	100^-	Claisen[b]	6	
	117^-	$(M + Me_2N^-)$	8	45^-–46^-	HCO_2^-	6	
$DCONMe_2$[c]	72^-	Me_2NCO^-	6	35^-–36^-	$HO^-\cdots HOH$	5	n.r.
	73^-	$HCON(Me)CH_2^-$	18	63^-	$HO^-\cdots HNMe_2$	6	
	92^-	addition	5	46^-	DCO_2^-	15	
	102^-	Claisen	2	102^-	Claisen	5	
	117^-	$(M + Me_2N^-)$	2				
$HCONEt_2$	72^-	$HCONEt^-$	85	72^-	$HCONEt^-$	87	72^- $HCONEt^-$ 100%
	45^-	HCO_2^-	8	45	HCO_2^-	7	
$HCON(n\text{-}Bu)_2$	100^-	$HCON\text{-}n\text{-}Bu^-$	7				
	91^-, 92^-						
	45^-	HCO_2^-					
3	98^-–99^-	M − 1	100				98^-–99^- M − 1 + d 100%
4	126^-	M − 1	33				
	127^-	M − 1 + d or 1^-	67				
8a	127^-–132^-	M − 1 + d_n	71	127^-–132^-	M − 1 + d_n	75	n.r.
	100^-	$HCONCMe_3^-$	4	73^-	Me_3CNH^-	9	
	73^-	Me_3CNH^-	9				
8b	155^-	M − 1	31	127^-	elim	38	127^- elim 100%
	127^-	elim or 1^-	69				
8c[d]	211^-	M − 1	66	155^-	elim	69	
	155^-	elim	19	100^-	$HCONCMe_3$	13	
	100^-	$HCONCMe_3$	15				
8d	100^-	$HCONCMe_3$	88	100^-	$HCONCMe_3$	96	100^- $HCONCMe_3$[d] 61% 215^- M − 1 + d 39%
Me_3CCHO	85^-–94^-	M − 1 + d_n	85	85^-–93^-	M − 1 + d_n	90	n.r.
$(Me_3C)_2CO$				141^-–150^-	M − 1 + d_n	90	

[a] Unquenched mode, ca. 10^{-6} torr of acid. The percentages are of total ion current; any percentage not shown is from ions in the background spectrum with the base alone. All spectra are at room temperature unless otherwise noted. [b] See text. [c] Nondeuterated bases used. [d] 90 °C vacuum system.

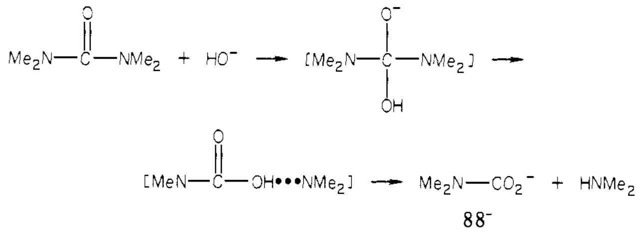
the allyl structure in the ICR.[12] It is our experience that in the ICR spectrometer the number of observed deuterium exchanges rapidly falls off with the increasing difference in acidity between the acid used as the deuterium source and the carbon acid being exchanged. The large number of exchanges observed here is consistent with this aldehyde being only 1 or 2 kcal/mol more acidic than the deuterium source, D_2O.

Formamides. These amides were chosen to reduce complications due to the presence of other acidic hydrogens in the molecule. Acetamides are known to be more acidic than methanol,[13] while benzamides, commonly used in solution,[4] likewise have ring hydrogens sufficiently acidic in the gas phase to complicate this work.[13] While the formyl hydrogens in formate esters are known to undergo the Riveros reaction 1 in the gas phase, involving

$$RO^- + HCO_2R' \rightarrow CO + ROH\cdots{}^-OR' \qquad (1)$$

decarbonylation and formation of a hydrogen-bonded species,[14] the resulting cluster ion can readily be identified by its ability to undergo solvent switching reactions,[15] as well as irreversible exchange of the solvent for CO_2. As given in Table I, *N*,*N*-dimethylformamide (DMF) yields an M − 1 anion as the major product on reaction with NH_2^-. If $DCONMe_2$ is used, both an M − 2 anion, from removal of the formyl deuteron, and an M − 1 anion, from loss of a methyl hydrogen, are observed in a 1:3 ratio upon reaction with NH_2^-. If the M − 1 anion from undeuterated DMF is reacted with ND_3, three deuterim exchanges are observed in addition to the original M − 1 signal. This is indicative of, but not conclusive evidence for, only one methyl group exchanging deuterium. The signal with three deuteriums is assigned to the multiply exchanged acyl anion. Small amounts of the Riveros reaction products, $Me_2N^-\cdots HNH_2$ and $HO^-\cdots HOH$ (from solvent switching of the first with trace H_2O in the vacuum system), are also observed, as well as an ion at mass 100^-. This latter ion undergoes a single exchange with ND_3 and is attributed to a Claisen-type condensation of the alkyl anion with DMF to give $HCON(Me)CH{=}CHO^-$ plus $HNMe_2$. There is precedent for such a reaction.[16]

Scheme I



If hydroxide or deuteroxide ions are used as the primary base, no products attributable to the M − 1 anions are seen, save for the cluster ions from the Riveros reaction. We observe $HO^-\cdots HOH$ and the deuterated analogue. This reaction of hydroxide with DMF to give $HO^-\cdots HNMe_2$ followed by rapid solvent switching with the high pressure of water needed to generate HO^- is the most efficient source we have found for the monosolvated hydroxide ion in our studies of such cluster ions.[17] All cluster ions inferred here have been checked by observation of solvent-switching reactions with methanol or other alcohols, and by reaction with CO_2 to form an ion that does not undergo further solvent switching. The lack of an M − 1 anion from the formamide on reaction with HO^- is unexpected since the amide has a larger dipole moment than the aldehyde, and thus the carbanion should be better stabilized.[18] The observed decarbonylation reaction may

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[12] Bartmess, J. E.; Burnham, R. *J. Org. Chem.*, submitted.

[13] (a) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9. (b) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046–66. (c) Bartmess, J. E.; McIver, R. T., Jr. "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 12.

[14] (a) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057–60. (b) Isolani, P. C.; Riveros, J. M. *Chem. Phys. Lett.* **1975**, *33*, 362–4. (c) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049–52.

[15] McIver, R. T., Jr.; Scott, J. A.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 2706–8.

[16] Bartmess, J. E.; Hays, R. L.; Caldwell, G. *J. Am. Chem. Soc.* **1982**, *103*, 1338-44.

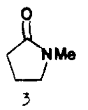
[17] Caldwell, G.; Bartmess J. E., paper in preparation.

[18] McClellan, A. L. "Table of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963.

be more kinetically favored than the deprotonation, however, and not necessarily reflect the thermochemistry involved. In an attempt to generate the M − 1 anion of an amide using hydroxide, free of the complications due to the Riveros reaction, tetramethylurea was reacted with HO^-. This affords only an ion of mass 88^-, which we envision as a carbamate arising by Scheme I. If reasonable values for the hydrogen bonding strength in the loose intermediates are used,[19] all steps in this scheme are exothermic.

N,N-Diethylformamide gives an ion of mass 72^- with all bases in Table I. The 72^- ion might arise from either a β-elimination reaction to give ethylene and a formamide anion or from an addition–elimination reaction at the carbonyl group to give Et_2N^-. The latter reaction should be endothermic for both HO^- and methoxide, and barely thermoneutral for NH_2^-, however, with more exothermic reaction channels available out of the complex such as in Scheme I. There is precedent for facile β-eliminations in the gas phase,[20] and such a reaction should be thermochemically favored for these products. A small amount of 45^- is observed in the reaction with NH_2^-; this is due to a small amount of water, and therefore, HO^- due to reaction with NH_2^-, being present in the vacuum system. An addition–elimination–deprotonation mechanism would give formate ion as 45^-. Examination of the analogous chemistry of *N,N*-di-*n*-butylformamide, where the formamide elimination product would be mass 100^- while the addition–elimination reaction at the carbonyl group should give mass 128^-, reveals that only mass 100^- is formed. The β-elimination reaction is favored kinetically over the pathway leading through the tetrahedral intermediate.

In order to examine the question of the stereochemistry of these dipole-stabilized anions, a system where the alkyl groups *E* and *Z* to the carbonyl oxygen can be distinguished mass spectrometrically must exist. The barrier to rotation about the C–N bond in amides is insufficient to enforce stereochemistry on a synthetic time scale, being typically 18–21 kcal/mole.[21] We have therefore attempted to utilize cyclic systems to distinguish between the two sites. *N*-Methylpyrrolidone (NMP, **3**) gives only an M − 1 anion on reaction with NH_2^- or CH_3O^-, which exchanges one proton with CH_3OD. This is consistent with the anion being a normal enolate, comparable in acidity to *N,N*-dimethylacetamide.[13] The dimethyl NMP (**4**), however, is unreactive with methoxide, but gives an M − 1 anion plus a signal one mass unit higher at 127^-, with ND_2^-/ND_3. The signal at 127^-, well in excess of the expected ^{13}C isotope abundance, may not be deuterium exchange, since it is also observed with NH_2^-/NH_3 as the primary base. This may be due to I^- since even trace amounts of alkyl iodides in the ICR spectrometer result in appreciable I^- signals owing to dissociative attachment of electrons, and methyl iodide was used in the synthesis of **4**. The M − 1 likewise could either be **5** or the products of elimination **6** or **7**. The lack of two exchanges rules out the *Z* dipole-stabilized carbanion; however, the elimination may be faster than the deprotonation as with the diethylformamide. This does not allow thermochemical limits to be placed on the stability of the carbanion. Unfortunately, any cyclic system that we can devise that locks the alkyl groups into the *E* and *Z* configuration and blocks β-elimination also rotates the most acidic hydrogen on the *E* carbon away from the preferred orientation beneath the carbonyl (see the section on MO calculations below). The experimental results are thus consistent with only one of the *E* or *Z* groups being more acidic than NH_3, but we cannot say unequivocally which is involved. It is evident that both the alkyl carbanion and the acyl anion in formamides are less basic than NH_2^-, but no lower limit can be put on them because of complications from side reactions.



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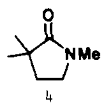

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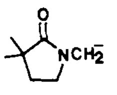

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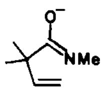

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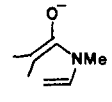

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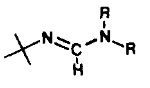
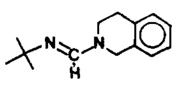
Formamidines. Compounds **8a-d** are used as solution-phase precursors to α-aza carbanions.[8] In the gas phase, their anionic chemistry is remarkably similar to the analogous formamides. The dimethyl compound **8a** is unreactive with methoxide, but gives an M − 1 anion with NH_2^- and HO^-. In this respect, it appears to be somewhat more acidic than DMF, lying between water and methanol in the gas-phase acidity scale.[13] Both D_2O and ND_3 react with the M − 1 anion to give up to five exchanges, indicating that the α-aza anion is forming (but not ruling out the anion from removal of the methine proton as well) and that both methyl groups must be exchanging deuterium. This may be due to conformational exchange of the methyls, since it would be expected that the barrier to rotation about the C–N single bond in **8** would be smaller than for the corresponding formamide, based on the electronegativity of the heteroatoms involved in the charge-separated resonance structure that contributes double-bond character to that bond.[22] The diethyl derivative **8b** gives a product corresponding to β-elimination product at 155^- with HO^-/H_2O, and no I^- signal. Only with the strongest base ND_2^- is an M − 1 anion seen. We interpret this last result to be from loss of the methine proton, since it is not seen with the weaker base hydroxide, which does give a dipole-stabilized anion with **8a**. Methoxide ion gives an M − 1 anion from **8d**, consistent with the presence of benzyl hydrogens in the molecule.[13]



8 a: R = Me
b: R = Et
c: R = n-Bu



8d

Esters. As noted above, formate esters undergo the Riveros reaction to form the monosolvated anions with a variety of bases from NH_2^- to alkoxides as weak as $CF_3CH_2O^-$.[14,17] There are occasionally small peaks in the mass spectrum which are of an M − 1 anion,[23] but the variety of reactions in which the ester functionality can participate in the gas phase is sufficiently large that the possibility of observing an unambiguous dipole-stabilized carbanion seems small to us.

Discussion

There are obvious parallels between the gas-phase chemistry of the carbanions investigated in this work and those observed in solution. In both phases, dipole stabilization of negative charge is relatively less effective than resonance delocalization, resulting in weaker acidity compared to carbon acids with good π-acceptor groups, such as ketones and nitriles. The polar effect of a β-aldehydic group is about equivalent in stabilizing effect to the resonance due to a vinyl group.[13]

There are also contrasts in the chemistry observed in the two phases. DMF in THF solution undergoes exclusive loss of the formyl proton on treatment with lithium diisopropylamide,[4] while both the methyl and formyl protons are lost to NH_2^- in the gas phase in a competitive fashion. Diethylcarboxamides in solution form the α-aza carbanions in a manner similar to that of the dimethylcarboxamides, while in the gas phase β-elimination is the sole process seen for the ethyl compound. This preference for elimination compared to deprotonation is the gas phase has also been observed for a variety of other systems, such as 1,3-dithianes

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(19) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139–43.

(20) (a) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 637–9, 3595–3602. (b) Sullivan, S. A.; Beauchamp, J. L. *Ibid.* **1976**, *98*, 1160–5. (c) Sullivan, S. A.; Beauchamp, J. L. *Ibid.* **1977**, *99*, 5017–22. (d) Clair, R. L.; McMahon, T. B. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 21–36. (e) DePuy, C. H.; Bierbaum, V. *J. Am. Chem. Soc.* **1981**, *103*, 5034–8. (f) vanDoorn, R.; Jennings, K. R. *Org. Mass Spectrom.* **1981**, *16*, 397–9.

(21) Gordon, A. J.; Ford, R. A. "Chemist's Companion"; Wiley: New York, 1972; p 119.

(22) Zielinski, T. J.; Peterson, M. R.; Csizmadia, I. G.; Rein, R. *J. Comput. Chem.* **1982**, *3*, 62–8.

(23) Dawson, J. H. J.; Nibbering, N. M. M. *Lect. Notes Chem.* **1978**, *7*, 148–183.

Table 11. Molecular Orbital Calculations on Alkyl and Acyl Acidities[a]

method	ref	$(CH_3)CCHO$	$(CH_3)_2NCHO$	CH_3OCHO	$HCOCH_3$	$HCONH_2$	HCO_2H
MNDO	*b*	*E* 401.1 *Z* 409.6	*E* 397.4 *Z* 404.6 377.8[e]	*E* 393.2 *Z* 398.2 370.7[e]			
4-31G//STO-3G	*c*		*E* 427.4 *Z* 436.3	*E* 420.9 *Z* 429.7			
4-31G*//4-31G	*b*				429.6	428.4	412.3
MNDO	*d*	389.6[e]	379.6[e]	372.1[e]	398.3	383.6	376.3
MP2/4-31+G//4-31+G	*d*				398.2	394.0	378.3
experimental		390 ± 5	<404				

[a] $\Delta H°_{acid}$ (MNDO) or $\Delta E°$ (ab initio), in kcal/mol. The acidic proton is in italics. *E* refers to a geometry as in 2; *Z* refers to a nonlithiated 1. For 8a, $\Delta H°_{acid}$(MNDO) = 398.2 for the *E* form, 407.8 for the *Z* form, and 383.1 for the methine proton. [b] This work; all geometric variables optimized. [c] Reference 5. [d] Reference 27. [e] The acidity is for the formyl proton.

and dithiolanes,[24] fluoralkanes,[19] and boronate esters.[24] We suspect that this is due to the entropic favorability of giving three rather than two products, while solvation reduces this effect in the condensed phase.

A major problem in determining the energetics of these species lies in the gaps in the gas-phase acidity scale. For quantitative equilibria, compounds of known acidity must be available every 1 to 2 kcal/mol. Relatively few such acidities are known in the region less acidic than methanol, and there are few primary anionic bases available by electron impact which can be used to bracket acidities between NH_3 and CH_3OH. In order to further analyze the reactivities observed, we have carried out molecular orbital calculations for the various acids and anions here, using the MNDO semiempirical method.[26] Other workers have used higher level ab initio calculations to examine stereochemical preferences in the dipole-stabilized anions from amides and esters, as well as the nature of the dipolar stabilization of the carbanion,[5] but have not included the aldehyde functionality. There has also been considerable activity in regard to calculations on the acyl anions which we observe either as stable species or infer as intermediates in the Riveros reaction. Our results and those of other are given in Table II. The calculations on the alkyl carbanions indicate that the order of acidity is aldehyde < amide < ester, with a range of less than 8 kcal/mol for the *E* isomers. The MNDO calculations agree in relative size with the ab initio ones,[5] but are ca. 10 kcal/mol less acidic in absolute value. The MNDO method has been shown to reliably predict the acidity of carbon acids giving delocalized anions, while giving acidities for localized anions 5 to 15 kcal/mol less acidic than observed.[26,27] Based on the relative acidities calculated by the MNDO metod for $(CH_3)_3CCHO$ and HCO_2CH_3 (acidic site in italics) as given in Table I, and the experimental observation that 2,2-dimethylpropanal is comparable in acidity to water, then HCO_2CH_3 should be slightly less acidic than methanol. We do not observe an $(M - H)^-$ signal for methyl formate reacting with methoxide ion, but that may be due to the Riveros reaction being a rapid, alternative channel. The calculated stereochemical preference is for the *E* anion being 7 to 11 kcal/mol more stable than the *Z* anion, by both molecular orbital methods. For the MNDO method the carbanions are pyramidal in both *E* and *Z* forms; however, the carbanion lone pair faces the carbonyl carbon in the favored *E* forms as expected for dipolar stabilization, but points away from the carbonyl oxygen in all *Z* forms. The calculated acidity order of aldehyde < amide < ester is surprising in light of the ordering of the dipole moments. It might be expected that the amide (μ_D = 3.82 D) would be more acidic than the aldehyde (μ_D = 2.6 D) and that more acidic than the ester (μ_D = 1.77 D).[18] The order given by the calculations follows the inductive order of $-OCOCH_3$ being more electron withdrawing than $-NHCOCH_3$, and that more so than $-CH_2CHO$.[28] In terms of the charges on the carbonyl oxygen and the atom next to the carbanionic site, the MNDO calculations indicate that in the anion the aldehyde actually has the most favorable dipole, with the ester and amide at about half that value. The change in charge density on these sites upon proton removal is perhaps a better measure of the relative dipolar effects on alkyl acidity; here the difference in charge is essentially the same for all three acids, with the most acidic ester having the least positive atom next to the carbanion. MNDO calculations predict a stereochemical preference for the *E* and *Z* sites in the formamidine **8a** similar to that for the amide, with the *E* site 9.6 kcal/mol more acidic than the *Z* site. The calculated acidities are again ca. 10 to 15 kcal/mol less acidic than observed experimentally. The calculations also predict that the methine hydrogen on the central carbon should be between water and methanol in acidity, while experimentally we infer that it is less acidic than water.

The acidities of these compounds can also be examined in terms of empirical correlations with other carbon acids. The acidities of the CH_3EWG species where EWG = electron-withdrawing group such as NO_2, CHO, etc., can be correlated with the dual substituent parameter equation

$$\Delta H°_{acid} = -38.8\sigma_I - 67.7\sigma_{R^-}{}^{(g)} + 409.7$$

where $\sigma_{R^-}{}^{(g)}$ is a gas-phase parameter for the π-acceptor ability of the EWG.[29] Using known values of σ_I for NHAc, CH_2CHO, and OAc,[28] and assuming that $\sigma_{R^-}{}^{(g)} = 0$ for these groups, based on the fact that the carbanion prefers a conformation without overlap to the π system in the MO calculations, we arrive at acidities of 406, 400, and 394 kcal/mol for the aldehyde, amide, and ester, respectively, using eq 2. These numbers are of the ordering given by the MNDO method, but underestimate the absolute values of the acidities by 15 to 20 kcal/mol, based on the experimental data for 2,2-dimethylpropanal. This difference is possibly due to the nature of the σ_I constants used. They represent a certain mixture of inductive (through-bond) and field (through-space) effects found in solution. In the gas phase and for these carbanions, the presence of the positive end of the dipole on the atom attached to the carbanion may result in a larger inductive component than is present in the systems used to define σ_I, resulting in eq 2 underestimating the stabilization. In addition, σ_I values are derived from a number of systems where an averaging occurs for the substituent-reactive site geometry due to different orientations and rotation in the defining systems, while for the calculations here, and presumably for the lowest energy gas-phase structure, a fairly specific geometry exists. It has been shown that reversing the direction of the substituent's dipole field with respect to the reactive site can reverse its apparent polar effect, such as with the pK_a's of the 8-substitued-9,10-ethanoanthracene-1-carboxylic acids.[30] The specific directional effects involved in

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(24) Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746-51.

(25) Bartmess, J. E.; Kiplinger, J. 30th Annual Conference on Mass Spectrometry and Allied Topics, June 6-11, 1982, Honolulu, Hawaii.

(26) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899-4917. Dewar, M. J. S.; Rzepa, H. S. *Ibid.* **1978**, *100*, 784-790. Program No. 353, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.

(27) Chandrasekhar, J.; Andrade, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609-12, 5612-4.

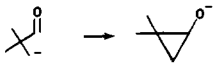
(28) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; p 98. We assume $\sigma_I(-NHCOCH_3) = \sigma_I(-NHCHO)$ and $\sigma_I(-OCOCH_3) = \sigma_I(-OCHO)$.

(29) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

anions such as **1** and **2** make the application of eq 2 only semiquantitative.

The calculations for the acyl anions show different relative acidities at the different levels. Both MNDO and the ab initio methods predict that a formyl ester should be more acidic than an aldehyde at the formyl site by about 20 kcal/mol. The absolute MNDO values, and the ab initio ones relative to methane,[27] indicate that the acyl anion from the aldehyde should be comparable in basicity to hydroxide ion, consistent with experiment, and that the formate ester should be 1 to 9 kcal/mol more acidic than methanol. This acidity for the ester is reasonable in terms of the proposed mechanism of the Riveros reaction involving a hydrogen-bonded acyl anion as an intermediate. The position of the formamide in this series differs, however; the ab initio results place it only 2 to 4 kcal/mol more acidic than the aldehyde, while MNDO indicates that it is 10 to 18 kcal/mol more acidic, or two-thirds of the way to the ester. While our experiments indicate that the formamide is more acidic than ammonia at the formyl site, we cannot place a comparable lower limit on its acidity because of the wide range over which bases can cause the Riveros reaction to occur.[14,17] Nevertheless, the fact that methoxide and other alkoxide bases up to 15 kcal/mol weaker than it can cause formate esters to undergo the Riveros reaction, while none of these are reactive in this fashion with the formamide, is indicative that the amide is considerably less acidic at the formyl site than the ester. This agrees with the ab initio calculations.

Schleyer and co-workers[27] have proposed that the alkyl carbanion observed on reaction of hydroxide ion with 2,2-dimethylpropanal may actually exist as the cyclopropoxide **9**, the cyclic form being more stable by 11 kcal/mole by both MNDO and 4-31+G calculations. Our estimates of $\Delta H_{f,298}$ for this isomerization, based on group additivity[31] for the neutral acids and reasonable estimates of their acidity, agree with the thermochemistry from the MO calculations. It is known from solution-phase experiments, however, that the base-catalyzed isomerization favors the opposite direction: trimethylcyclopropanol opens to pinacolone.[32] This may reflect the neutral stability where the acyclic form is more stable by ca. 16 kcal/mol since the reaction with the hydroxide catalyst is endothermic. Even if the isomerization of the anion does favor the cyclic form in the gas phase, the lack of solvent to dispose of excess energy will result in the more stable cyclic anion being formed in a vibrationally excited state and quickly reverting to the open isomer. Considering the number of deuterium exchanges seen and the limited time window of the ICR, a few hundred neutral collisions, then if the proton-transfer reaction is at all slower than the collision rate,[33] the anion must spend most of its time in the open form. There is no precedent for an alkoxide exchanging protons with D_2O.[34] Thus, the cyclic ion may lie on the reaction surface but is probably not an intermediate in the exchange reaction.



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Registry No. 3, 872-50-4; **4**, 5370-33-2; **8a**, 23314-06-9; **8b**, 84073-77-8; **8c**, 84073-78-9; **8d**, 81763-88-4; $HCONMe_2$, 68-12-2; $DCONMe_2$, 2914-27-4; $HCONEt_2$, 617-84-5; $HCON(n\text{-}Bu)_2$, 761-65-9; Me_3CCHO, 630-19-3; $(Me_3C)_2CO$, 815-24-7.

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(30) Golden, R.; Stock, L. M. *J. Am. Chem. Soc.* **1966**, *88* 5928–9. Golden, R.; Stock, L. M. *Ibid.* **1972**, *94*, 3080–88.

(31) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(32) DePuy, C. H.; Arney, W. C., Jr.; Gibson, D. H. *J. Am. Chem. Soc.* **1968**, *90*, 1830–40.

(33) Farneth, W. E.; Brauman, J. 1. *J. Am. Chem. Soc.* **1976**, *98*, 7891–8.

(34) Stewart, J. H.; Shapiro, R. H.; DePuy C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–3. DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *Ibid.* **1978**, *100*, 2921–2. Hunt, D. F.; Sethi, S. K. *Ibid.* **1980**, 6953–63.

Low-Pressure Oxidation Mechanism and Reactivity of Propylene on Ag(110) and Relation to Gas-Phase Acidity

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Abstract: The reaction of propylene with adsorbed oxygen atoms was examined on the Ag(110) surface by means of thermal desorption and surface titration experiments. The presence of oxygen was observed to enhance the adsorption of propylene at 140 K. Propylene reacted facilely with adsorbed oxygen at 140 K to produce H_2O and CO_2 which desorbed from the surface upon heating. Adsorbed carbon atoms were also deposited on the surface following thermal desorption of the volatile products. At 300 K the probability for the reaction of propylene with adsorbed oxygen atoms was two to three orders of magnitude less than at 140 K, suggesting the involvement of a weakly chemisorbed precursor state in the reaction. Surface titration experiments with acetic acid demonstrate that the reaction of propylene with oxygen reduces the number of Brønsted base sites on the surface by a factor of 2; these data were interpreted in terms of a mechanism by which propylene reacts irreversibly to form hydroxyl groups plus adsorbed carbon on the surface. A portion of the carbon is subsequently oxidized by oxygen atoms liberated by the disproportionation of adsorbed hydroxyl species. These results indicate that propylene is more reactive than ethylene toward adsorbed oxygen atoms; this observation is interpreted on the basis of relative hydrocarbon acidities in the gas phase.

Introduction

The heterogeneous selective oxidation of hydrocarbons is an area of immense industrial importance, and as such has received long and extensive study. Most of these processes are carried out over various composite metal oxides;[1,2] however, a few, such as the partial oxidation of ethylene over silver, utilize supported metal catalysts. While a number of questions remain to be answered about the properties of composite oxide systems, particularly with regard to the catalytic role of the various oxide components, the

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(1) D. J. Hucknall, "Selective Oxidation of Hydrocarbons", Academic Press, London, 1974.

(2) D. B. Dadyburjor, S. S. Jewur, and E. Ruckenstein, *Catal. Rev.-Sci. Eng.*, **19**, 293 (1979).

0002-7863/83/1505-0344$01.50/0