On the Dipole Stabilized Carbanions Derived from Methyl Formate and *N,N*-Dimethylformamide

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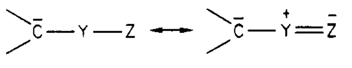
Proton abstraction from methyl formate and *N,N*-dimethylformamide in the gas phase has been investigated by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The competition between proton and deuteron abstraction from DCO_2CH_3 or HCO_2CD_3 with different reactant anions has been determined and it is concluded that the methyl group is less acidic in the gas phase than the formyl group. Proton abstraction from the methyl group in methyl formate is shown to lead to a primary carbanion. The ion derived by abstraction of the proton at the formyl position can best be described as a loose cluster of CH_3O^- and CO. Different amide ions and hydroxide ion react with $DCON(CH_3)_2$ through proton and deuteron abstraction. The ion formed by proton abstraction from $DCON(CH_3)_2$ reacts with various molecules according to a primary carbanion structure. This primary carbanion exchanges relatively fast two hydrogen atoms with ND_3. Exchange of a third hydrogen atom can be observed but occurs with a much lower rate. These results are discussed in terms of a difference in gas-phase acidity of the two methyl groups in *N,N*-dimethylformamide. The gas-phase acidity of the most acidic methyl group is placed qualitatively close to that of H_2O, whereas the formyl position is concluded to be somewhat more acidic. Deuteron abstraction from $DCON(CH_3)_2$ is concluded to result in a carbonyl anion with a rather weak carbonyl carbon-nitrogen bond.

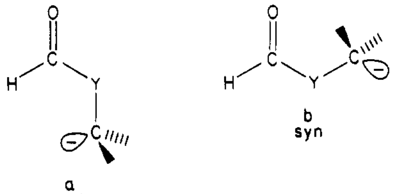
Introduction

Carbanions which bear an α-heteroatom are of theorectical interest and in the form of an organometallic compound of synthetic importance.[1] The formation of such an organometallic compound is known to be more facile when the heteroatom is bonded to a functional group capable of inducing a partial positive charge on the heteroatom.[2] This class of formal carbanions has been termed dipole stabilized (eq 1).[2] Recent ab initio calculations on formal dipole stabilized carbanions derived from methyl formate, *N*-methylformamide, and *N,N*-dimethylformamide indicate that the carbanions prefer the anti geometry over the syn geometry by approximately 37 kJ/mol.[3] Further, the calculations revealed that the carbanions are pyramidal with the lone pair in the plane of the functional group and oriented as shown. Lithiation of tertiary amides, however, has been shown to yield the syn form of the organometallic compound (eq 2).[3,4] This preference for syn metalation has been explained by a stabilization arising through chelation between the lithium atom and the oxygen atom of the amide function.[3]



(1)

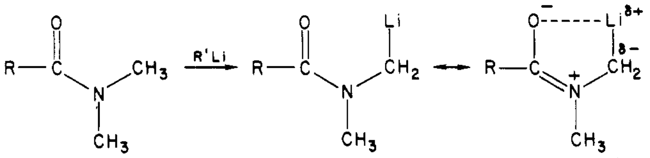
Y = NR, O, S
Z = N=O, C=O, C=S



a
anti

b
syn

Y = O, NH, NCH_3



(2)

In order to gain insight in the chemistry of formal dipole stabilized carbanions in the absence of counterion and solvent effects we have initiated a study of gas-phase reactions between anions and possible precursors of such species.[5] The present paper describes the results obtained for the cases of methyl formate and *N,N*-dimethylformamide. The general reactivity of methyl formate and *N,N*-dimethylformamide in gas-phase anion molecule reactions is described in a related paper.[6] Here the emphasis will be laid on the ions derived by proton abstraction from either a methyl or the formyl group. No report concerning the gas-phase chemistry of carbanions derived from methyl formate has appeared. Proton abstraction from *N,N*-dimethylformamide with NH_2^- as base has been examined recently with drift cell ion cyclotron resonance (ICR) mass spectrometry.[7] The present report, however, provides a more complete picture of the gas-phase chemistry of carbanions derived from *N,N*-dimethylformamide. The results have been obtained with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry.[8]

Experimental Section

Experiments were performed with a homemade Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.[9,10]

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[1] (a) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965. (b) Buncel, E. "Carbanions:Mechanistic and Isotopic Aspects"; Elsevier: Amsterdam, 1975. (c) Peterson, D. J. *Organomet. Chem. Rev. Sect. A* **1972**, *A7*, 295–358. (d) Cshwend, H. W.; Rodrigues, H. R. *Org. React.* (*N. Y.*) **1979**, *26*, 1–360.

[2] For a review see: Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275–316.

[3] Rondan, N. G.; Houk, K. N.; Beak, P.; Zajdel, W. J.; Chandresekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 4108–4110.

[4] (a) Schlecker, R.; Seebach, D.; Lubosch, W. *Helv. Chim. Acta* **1978**, *61*, 512–526. (b) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080–2082.

[5] For recent reviews on mechanistic aspects of gas-phase ion-molecule reactions see: (a) Nibbering, N. M. M. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 297–306. (b) Ingemann, S.; Kleingeld, J. C.; Nibbering, N. M. M. In "Ionic Processes in the Gas Phase"; Ferreira, A. M. Almoster, Ed.; Reidel: Dordrecht, 1984; pp 87–110. (c) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153. (d) DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science* (*Washington, D.C.*) **1982**, *218*, 955–960.

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[8] (a) Comisarow, M. B. In "Transform Techniques in Chemistry"; Griffiths, P. R., Ed.; Plenum Press: New York, 1978; Chapter 10, pp 257–284. (b) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A and the references cited therein.

[9] The essential hardware is described in Dawson, J. H. J. *Lect. Notes Chem.* **1982**, *31*, 331–364.

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The total pressure was kept normally around 10^{-4} Pa. The ratio of the partial pressures of methyl formate or *N,N*-dimethylformamide, NH_3, and HA (the conjugate acid of the anion of interest) was typically 1:1:1. The partial pressure of ND_3 used for studying hydrogen–deuterium exchange reactions was up to four times as high as the partial pressure of *N,N*-dimethylformamide. The pressures were measured on an ionization gauge placed in a side arm of the main pumping line.

General Procedure. The general operating procedure for the instrument has been described previously.[11,12] The NH_2^- ions were generated from NH_3 by dissociative resonance capture of electrons with a kinetic energy of 5 eV. This results also in the formation of H^- ions. In order to study unequivocally the reactions of NH_2^- with methyl formate or *N,N*-dimethylformamide the H^- ions formed were ejected from the cell by applying a radio frequency, RF, pulse with a frequency of 180 kHz to the trapping plates of the cell.[13] The pulse started simultaneously with the quench pulse and ended shortly after the electron beam pulse.[11] The majority of the other anions used were generated by exothermic proton transfer to NH_2^-. The hydroxide ions (OH^-, OD^-, and $^{18}OH^-$) were generated by forming first the oxygen anion radical from nitrous oxide (N_2O or $N_2{}^{18}O$, electron energy 1.2 eV) and then allowing this ion to react with a hydrocarbon (n-C_6H_{14} or c-C_6D_{12}) present at a partial pressure two times as high as that of the substrate. In order to observe the reactions between a given anion and methyl formate or *N,N*-dimethylformamide all other ions present were ejected from the cell by a RF pulse applied to the excitation plates. At the frequency corresponding to the cyclotron frequency of the reactant ion of interest the phase of this pulse was shifted 180 degrees. This causes a notch in the wave form of the ejection pulse at that frequency (see also Figure 2).[10b,14]

The relationship between a precursor ion and its product ions was established in all cases by ion ejection experiments. Ejection of a reactant ion was normally achieved with a RF pulse (amplitude 2.5–7.1 V_{p-p}, duration 20 ms) starting after the "notch ejection" pulse. Ejection of a product ion was carried out with a RF pulse (amplitude 0.16–0.88 V_{p-p}) starting after the "notch ejection" pulse and lasting till the start of the excitation pulse. Correction of the intensities was achieved in most cases with the use of the method described in ref 10a. A further correction was achieved by subsequently deconvoluting the peak height corrected absolute magnitude mode spectra by the method of Marshall and Roe.[15]

Materials. Most chemicals used were commercially available. The DCO_2CH_3 (~99% d_1) was purchased from Aldrich and $DCON(CH_3)_2$ (~99% d_1) from CEA. The ND_3 used (dissociative resonance capture of electrons by the sample resulted in 71% ND_2^-, 26% NHD^-, and 3% NH_2^- as determined with the FT-ICR instrument) was purchased from MSD isotopes. $N_2{}^{18}O$ has been described previously.[16] HCO_2CD_3 (~99% labeled with deuterium) was prepared by a standard ester synthesis and purified by preparative GC before use (fraktonitrile, temperature 30 °C).

Results

Methyl Formate. Anions react with methyl formate in the gas phase through proton abstraction, α-elimination, and $B_{AC}2$ and S_N2 substitution. The interplay between these processes is discussed in ref 6. Proton abstraction can occur from either the methyl or the formyl group. The competition between proton and deuteron abstraction from DCO_2CH_3 and HCO_2CD_3 with different reactant anions is given in Table I. The data in Table I have been obtained by following the relative abundances of the $[M-H]^-$ and $[M-D]^-$ ions from DCO_2CH_3 and HCO_2CD_3 as a function of reaction time and then extrapolating to zero reaction time.

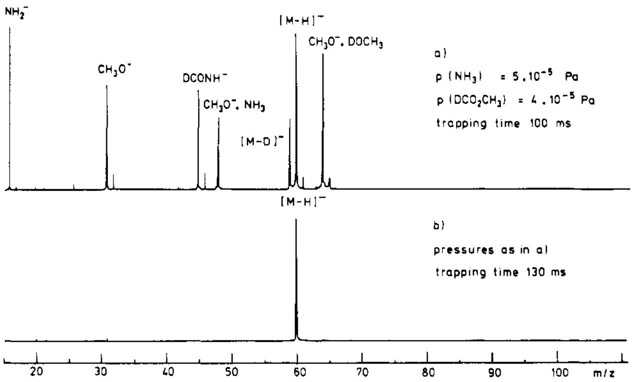

Figure 1. (a) Overall spectrum of the $NH_2^-/NH_3/DCO_2CH_3$ system. The trapping time is the time delay between the start of the electron beam pulse and the start of the excitation pulse. (b) Spectrum obtained after all ions have been ejected from the cell with the exception of the $[M-H]^-$ ion. The duration of the ejection pulse (see Experimental Section) was 30 ms; the amplitude was 5 V_{p-p}. Both spectra are plotted with the same gain. 1024 transients were accumulated in both cases. The experimental conditions were as follows: magnetic field strength, 1.4 tesla; electron energy, 5 eV; emission current, 800 nA; recording of *m/z* 12–300.

Table I. Initial Relative Abundances of the $[M-H]^-$ and $[M-D]^-$ Ions Formed in the Anion/DCO_2CH_3 or Anion/HCO_2CD_3 Systems

		DCO_2CH_3[b]		HCO_2CD_3[b]	
anion A^-	PA (A^-),[a] kJ/mol	$[M-D]^-$, %	$[M-H]^-$, %	$[M-H]^-$, %	$[M-D]^-$, %
NH_2^-	1689	78	22	89	11
$C_2H_5NH^-$	1671	93	7	98	2
$(CH_3)_2N^-$	1658	100		100	
$H^{18}O^-$[c]	1635	100			
$CH_3{}^{18}O^-$[d]	1587				

[a] Taken from ref 21; values for unlabeled ions. [b] Values corrected for the statistical preference for proton/deuteron abstraction from the methyl or the trideuteriomethyl group. [c] See Experimental Section. [d] Generated from $CH_3{}^{18}ONO$ (see: Noest, A. J.; Nibbering, N. M. M. *Adv. Mass Spectrom.* **1980**, *8A*, 227–237) by using electrons with a kinetic energy of 50 eV.

In the NH_2^-/DCO_2CH_3 system deuteron abstraction dominates over proton abstraction by a factor of four. In the NH_2^-/HCO_2CD_3 system proton abstraction is favored over deuteron abstraction by a factor of nine. These results indicate the occurrence of significant isotope effects in the reactions forming the $[M-H]^-$ and $[M-D]^-$ ions from DCO_2CH_3 and HCO_2CD_3. The variation observed in the relative abundances of the $[M-H]^-$ and $[M-D]^-$ ions (see ref 6) is caused by reactions of these ions with the molecules present in the system. In order to study selectively the chemistry of either the $[M-H]^-$ or the $[M-D]^-$ ion from DCO_2CH_3 all other ions present have to be ejected. In Figure 1a the overall spectrum of the $NH_2^-/NH_3/DCO_2CH_3$ system is given. Figure 1b displays the result from an experiment where all ions with the exception of the $[M-H]^-$ ions have been ejected. Only a minor decrease in the abundance of the $[M-H]^-$ ions is observed.

Increasing the reaction time results in the spectrum shown in Figure 2a. Figure 2b displays the spectrum obtained after the $[M-H]^-$ ions have been ejected from the cell. The results are summarized in Table II together with the equivalent ones obtained for the $NH_2^-/NH_3/DCO_2CH_3$

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[10] The essential software is described in the following: (a) Noest, A. J.; Kort, C. W. F. *Comput. Chem.* **1982**, *6*, 111–113, 115–119. (b) Noest, A. J.; Kort, C. W. F. *Comput. Chem.* **1983**, *7*, 81–86.

[11] Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 6520–6527.

[12] Kleingeld, J. C.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1982**, *17*, 136–139.

[13] Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1972**, *22*, 527–561.

[14] Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron* **1983**, *24*, 4193–4199.

[15] Marshall, A. G.; Roe, D. C. *J. Chem. Phys.* **1980**, *73*, 1581–1590.

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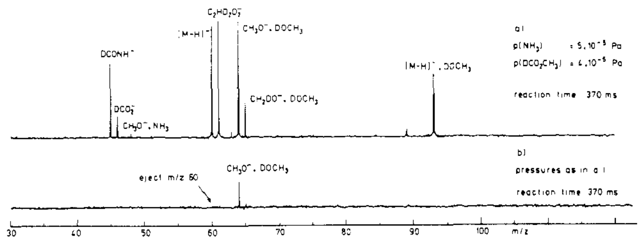


Figure 2. (a) Spectrum obtained after the $[M-H]^-$ ions have reacted with NH_3/DCO_2CH_3 for 370 ms. The reaction time is the time delay between the end of the ejection pulse and the start of the excitation pulse. 3600 transients accumulated. (b) Spectrum obtained after the $[M-H]^-$ ions have been ejected from the cell. The $CH_3O^-\cdot DOCH_3$ ions still observed are formed by a minor amount of H^- ions present in the system (see Experimental Section). 2500 transients accumulated. Both spectra are plotted with the same gain. Experimental conditions as given at Figure 1. Recording of *m/z* 25–300.

Table II. Product Ions Formed by Reaction of the $[M-H]^-$ and $[M-D]^-$ Ions from DCO_2CH_3 or HCO_2CD_3 with NH_3, DCO_2CH_3, or HCO_2CD_3

system	product ion[a]	*m/z*	yield, %
	DCO_2CH_3		
$[M-H]^{-b}$	$DCONH^-$	45	14
	DCO_2^-	46	4
	$CH_3O^-\cdot NH_3$	48	1
	$[M-H]^{-f}$	60	21
	$DCO\bar{C}HOD$	61	22
	$CH_3O^-\cdot DOCH_3$	64	17
	$CH_2DO^-\cdot DOCH_3$	65	8
	DCO_2CHCDO^-	89	2
	$DCOCH_2O^-\cdot DOCH_3$	93	11
$[M-D]^{-c}$	$CH_3O^-\cdot NH_3$	48	40
	$[M-D]^{-g}$	59	14
	$CH_3O^-\cdot DOCH_3$	64	46
	HCO_2CD_3		
$[M-D]^{-d}$	$HCONH^-$	44	20
	HCO_2^-	45	3
	$CD_3O^-\cdot NH_3$	51	2
	$HCO\bar{C}DOH$	60	9
	$[M-D]^{-f}$	61	23
	$CHD_2O^-\cdot HOCD_3$	68	17
	$CD_3O^-\cdot HOCD_3$	69	10
	HCO_2CDCHO^-	88	1
	$HCOCD_2O^-\cdot HOCD_3$	96	15
$[M-H]^{-e}$	$CD_3O^-\cdot NH_3$	51	29
	$[M-H]^{-g}$	61	8
	$CD_3O^-\cdot HOCD_3$	69	63

[a] See text. [b] Reaction time 370 ms; apparent conversion into products 78%. [c] Reaction time 75 ms; conversion into products 86%. [d] Reaction time 370 ms; apparent conversion into products 78%. [e] Reaction time 75 ms; conversion into products 92%. [f] These are the abundances of the formal $[M-H]^-$ ions (see text). [g] These are the abundances of the residual reactant ions.

system. In order to probe further the structure(s) of the $[M-H]^-$ and $[M-D]^-$ ions from DCO_2CH_3 or HCO_2CD_3 their reactions with C_6F_6 were investigated. The results are given in Table III. The relative abundances of the product ions listed in Table III are dependent to some extent on the partial pressures of the compounds used. However, to generate the necessary amount of the ion of interest only minor variation in the partial pressures appeared possible.

***N,N*-Dimethylformamide.** The different amide ions studied react with $DCON(CH_3)_2$ in the gas phase through proton and deuteron abstraction whereas the dominant reaction for hydroxide ions is α-elimination.[6]

Both the $[M-H]^-$ and $[M-D]^-$ ions are observed to react with the molecules present in the systems. The results in Table IV have been obtained by selectively studying the chemistry of the $[M-H]^-$ and $[M-D]^-$ ions formed in the NH_2^- system. These qualitative results indicate that the $[M-H]^-$ ions react slower with the molecules present than the $[M-D]^-$ ions.

Table III. Product Ions Formed by Reaction of the $[M-H]^-$ Ion from DCO_2CH_3 and the $[M-D]^-$ Ion from HCO_2CD_3 with C_6F_6

system	product ion	*m/z*	yield, %
	DCO_2CH_3		
$[M-H]^{-a}$	$C_6F_5^-$	167	69
	$C_8F_4HO_2^-$	205	14
	$C_8F_4DO_2^-$	206	10
	$C_8F_5HDO_2^-$	226	7
	HCO_2CD_3		
$[M-D]^{-a}$	$C_6F_5^-$	167	67
	$C_8F_4HO_2^-$	205	5
	$C_8F_4DO_2^-$	206	15
	$C_8F_5HDO_2^-$	226	8
	$C_8F_5D_2O_2^-$	227	5

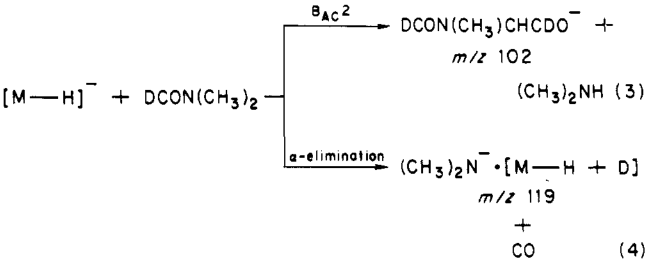
[a] Reaction time 370 ms.

Table IV. Product Ions Formed by Reaction of the $[M-H]^-$ and $[M-D]^-$ Ions from $DCON(CH_3)_2$ with NH_3, $DCON(CH_3)_2$, and H_2O (Present in Trace Amounts)

reactant ion	product ion[a]	*m/z*	yield, %
$[M-H]^{-b}$	$DCONH^-$	45	4
	$[M-D]^-$	72	7
	$HO^-\cdot M$	91	13
	$DO^-\cdot M$	92	15
	$DCON(CH_3)CHCDO^-$	102	25
	$(CH_3)_2N^-\cdot M$	118	30
	$(CH_3)_2N^-\cdot[M-H+D]$	119	6
$[M-D]^{-c}$	$HO^-\cdot HN(CH_3)_2$	62	2
	$HO^-\cdot M$	91	21
	$DO^-\cdot M$	92	10
	$(CH_3)_2N^-\cdot M$	118	67

[a] See text. [b] Reaction time 1470 ms; conversion into products 58%. [c] Reaction time 370 ms; conversion into products 74%.

The $[M-H]^-$ ions react with NH_3 under formation of a $DCONH^-$ ion. Reaction with $DCON(CH_3)_2$ forms the *m/z* 102 and 119 ions. Reaction with water (present in trace amounts) gives initially a *m/z* 63 ion.[6] The *m/z* 63 ion then transfers either an OH^- or an OD^- ion to $DCON(CH_3)_2$ yielding the *m/z* 91 and 92 ions (Table IV).[6] The $[M-D]^-$ ions react with $DCON(CH_3)_2$ by formal transfer of a $(CH_3)_2N^-$ ion. The *m/z* 62, 91, and 92 ions are formed by reaction with traces of water present (Table IV).



$$\underset{m/z\ 73}{[M-H]^-} + H_2O \longrightarrow \underset{m/z\ 63}{HO^-\cdot DN(CH_3)_2} + CO \qquad (5)$$

$$\underset{m/z\ 72}{[M-D]^-} + DCON(CH_3)_2 \rightarrow \underset{m/z\ 118}{(CH_3)_2N^-\cdot DCON(CH_3)_2} + CO \qquad (6)$$

When ND_3 is used hydrogen–deuterium exchange of the $[M-H]^-$ ions can be observed.[17,18] The result from an

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[17] (a) Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192. (b) Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565–2571.

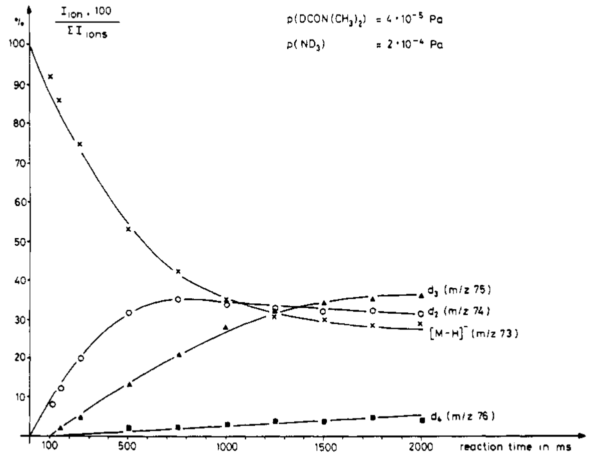

Figure 3. The hydrogen–deuterium exchange reaction between the [M–H]$^-$ ion from $DCON(CH_3)_2$ and ND_3 followed as a function of reaction time. The values have been corrected for ^{13}C contributions. Experimental conditions as given at Figure 1. Recording of m/z 12–300.

Table V. Product Ions Formed in the Reactions of the [M–H]$^-$ Ions from $DCON(CH_3)_2$ with CF_2O and N_2O

system	product ion[a]	m/z	% at reactn time 115 ms[b]	% at reactn time 865 ms[c]
CF_2O	$C_4H_3DNO_2^-$	99	95	30
	$C_5H_3FNO_3^-$	144	5	56
	$C_6H_2F_2NO_4^-$	190		14
N_2O	DCO_2^-	46		18
	$CDN_2O_2^-$	74		26
	$C_3H_3DN_3O^-$	99		56

[a] See text. [b] Conversion into products 37% at the pressures used. [c] Conversion into products 98% in the CF_2O system and 87% in the N_2O case. The partial pressure of N_2O was a factor of two higher than the partial pressure of $DCON(CH_3)_2$. Ions due to reaction of the [M–H]$^-$ ions with $DCON(CH_3)_2$ and traces of water are observed in this system. These ions have been omitted from the calculation of the conversion into products.

experiment in which the hydrogen–deuterium exchange process has been followed as a function of reaction time is shown in Figure 3. The ions in the m/z 73–76 region are likely to be only [M–H]$^-$ ions which have exchanged up to 3 hydrogen atoms for deuterium atoms. Of course, part of the [M–H]$^-$ ions might be converted to ions corresponding to the [M–D]$^-$ ions during the exchange process.[6] However, these ions will react relatively rapidly with $DCON(CH_3)_2$ as shown in eq 6.

The exchange process could not be followed accurately to longer times due to other reactions of the ions with the molecules present (Table IV). In this system the ion at m/z 102 (eq 3) is observed to incorporate 1 deuterium atom and the ions at m/z 118 and 119 (eq 4 and Table IV) 3 and 2 deuterium atoms. In order to gain more insight in the structure(s) of the [M–H]$^-$ ion from $DCON(CH_3)_2$ its reaction with CF_2O and N_2O have been studied. The results are given in Table V.

Discussion

Methyl Formate. Acidities. A direct quantitative determination of the thermochemical gas-phase acidity ($\Delta H°_{acid}$ (AH) = PA(A^-)) of the methyl and the formyl group in methyl formate is hampered by the occurrence of several reactions in competition with removal of a proton. The occurrence/nonoccurrence of proton/deuteron abstraction from DCO_2CH_3/HCO_2CD_3 can be used to some extent to place qualitatively the gas-phase acidity of the methyl and the formyl group. It should be stressed here that it is more correctly the heights of the local free energy barriers toward proton/deuteron abstraction relative to the heights of the local free energy barriers toward the other reactions which are compared qualitatively.[19] In other words, the kinetic acidity of the methyl and the formyl group is compared relative to the other reactions observed.[6] From the results in Table I it can be concluded that ions with lower proton affinity than $C_2H_5NH^-$ do not react with DCO_2CH_3 by proton abstraction. Similarly, no deuteron abstraction from HCO_2CD_3 is observed with weaker bases than $C_2H_5NH^-$. This agrees with the observation that NH_2^- reacts partly with $CH_3OCO_2CH_3$ by proton abstraction whereas $(CH_3)_2N^-$ does not react through this pathway.[20] These observations can be taken as an indication that the methyl group in methyl formate has a gas-phase acidity in between that of $C_2H_5NH_2$ and $(CH_3)_2NH$ (see Tables for values).[21] This can be contrasted with the fact that no [M–H]$^-$ ion from CH_3OCH_3 has been observed indicating that the gas-phase acidity of this compound should be sought in between those of CH_4 (1743 kJ/mol) and NH_3 (1689 kJ/mol). Based upon these considerations the substitution of a methyl group in CH_3OCH_3 by a formyl group increases the gas-phase acidity of the other methyl group by roughly 51 kJ/mol. This is not in disagreement with ab initio calculations which indicate a difference in gas-phase acidity of CH_3OCH_3 and HCO_2CH_3 of around 100 kJ/mol in favor of the methyl group in the latter compound.[3] From the results in Table I the gas-phase acidity of the formyl group can be expected to be between that of H_2O and CH_3OH. This should be compared with the acidity of H_2CO which is between that of NH_3 and $C_2H_5NH_2$ (see Table I for values).[22] The replacement of a hydrogen atom in H_2CO by a methoxy group enhances, therefore, the gas-phase acidity of the formyl group with roughly 70 kJ/mol. This can be contrasted with MNDO calculations which indicate that H_2CO is around 137 kJ/mol less acidic in the gas phase than the formyl position in methyl formate.[23]

Although we recognize that our estimates are very rough and may not correlate necessarily with the thermochemical acidities, it can be concluded that the methyl group is less acidic than the formyl group. In view of this, it could be expected that the [M–H]$^-$ ions abstract the deuteron from DCO_2CH_3. In the reactions of the [M–H]$^-$ ions with NH_3/DCO_2CH_3 ions are observed which could indicate that [M–D]$^-$ ions are being formed (see ions m/z 48 and 64 in Table II: these ions are also formed by reactions of the [M–D]$^-$ ions). However, it is not possible to conclude whether a direct deuteron abstraction or a conversion catalyzed by NH_3 occurs (see the second complex in eq 7) which could decompose into [M–D]$^-$ and NH_2D).

Ion Structures. A problem which can be associated with the determination of the stability/reactivity of ions in the gas phase is that isomerization to a mixture of structures may occur upon ion formation. A variety of

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(18) Ingemann, S.; Nibbering, N. M. M. *J. Org. Chem.* **1983**, *48*, 183–191.

(19) Local energy barriers toward proton-transfer reactions in the gas phase have been discussed: (a) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891–7898. (b) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906–2913.

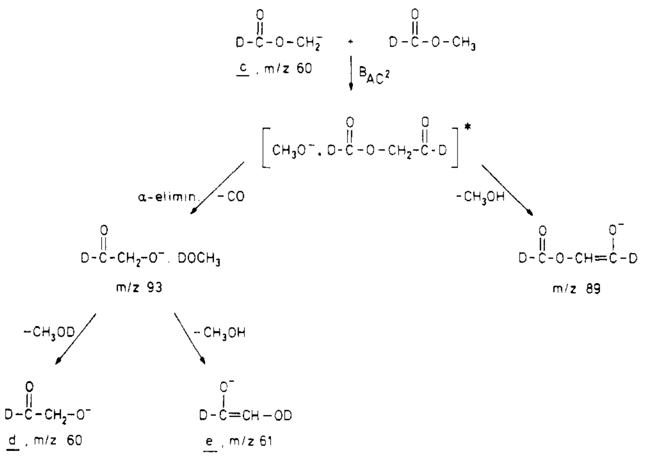
(20) Ingemann, S.; Nibbering, N. M. M., unpublished results.

(21) Values have been taken from Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11, pp 87–121.

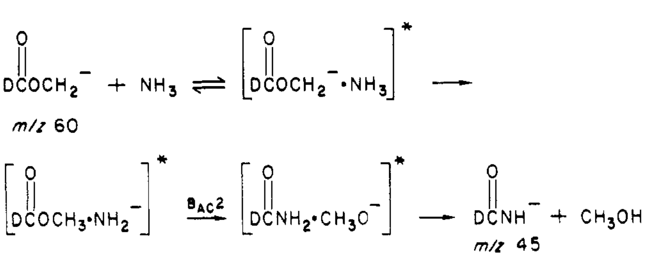
(22) Karpas, Z.; Klein, F. S. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 65–68.

(23) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612–5614.

Scheme I



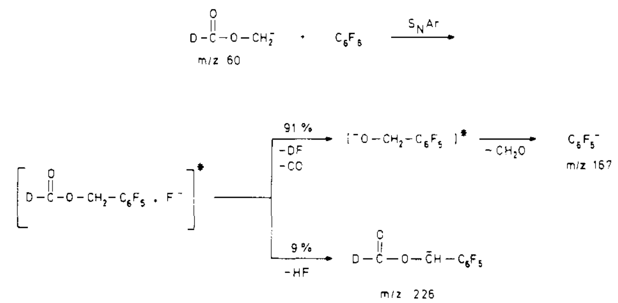
methods for the elucidation of structures of gaseous ions has been developed in the field of mass spectrometry during the last decades.[24] In ICR chemical reactivity, low kinetic energy CID, and photo/laser dissociation are at present possible means to gain insight into ion structures. We have applied the method of chemical reactivity to probe the structure(s) of the $[M-H]^-$ and $[M-D]^-$ ions from DCO_2CH_3 and HCO_2CD_3. The reactions which the $[M-H]^-$ ions from DCO_2CH_3 are observed to undergo with NH_3/DCO_2CH_3 (Table II, Figure 2) can all be explained upon the assumption that only the primary carbanion $DCO_2CH_2^-$ (ion c, see eq 9) is formed by proton abstraction. The geometry of the carbanion cannot be determined on the basis of the available data. Methyl formate prefers the syn geometry over the anti geometry by 16 kJ/mol[25] and the barrier toward rotation around the carbonyl carbon–oxygen bond has been measured to be 49.8 kJ/mol[26] by means of microwave spectroscopy. This barrier is probably too low to freeze the geometry of methyl formate at room temperature.[27] Further, the energy gained upon approach of an ion to methyl formate can be sufficiently large to facilitate rotation around the carbonyl carbon–oxygen bond. According to ab initio calculations the anti form of the carbanion c is more stable than the syn geometry.[3] In the following it is assumed that the observed carbanion has the anti geometry. Reaction of ion c with NH_3 can be classified as an indirect $B_{AC}2$.[18] When ND_3 is used instead



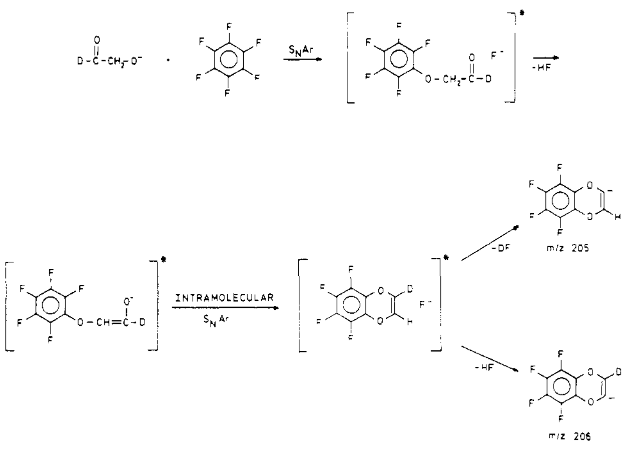
$$\underset{m/z\ 60}{\mathrm{D\overset{O}{\overset{\|}{C}}OCH_2^-}} + \mathrm{NH_3} \rightleftharpoons \left[\mathrm{D\overset{O}{\overset{\|}{C}}OCH_2^-\cdot NH_3}\right]^* \longrightarrow \left[\mathrm{D\overset{O}{\overset{\|}{C}}OCH_3\cdot NH_2^-}\right]^* \xrightarrow{B_{AC}2} \left[\mathrm{D\overset{O}{\overset{\|}{C}}NH_2\cdot CH_3O^-}\right]^* \longrightarrow \underset{m/z\ 45}{\mathrm{D\overset{O}{\overset{\|}{C}}NH^-}} + \mathrm{CH_3OH} \qquad (7)$$

of NH_3, no hydrogen–deuterium exchange reactions of the $[M-H]^-$ ion from DCO_2CH_3 are observed. Similarly, no exchange between $HCO_2CD_2^-$ and NH_3 is observed. This can be explained by the reaction back to the free carbanion being much slower than proton/deuteron abstraction from the formyl position and/or the indirect $B_{AC}2$ reaction.

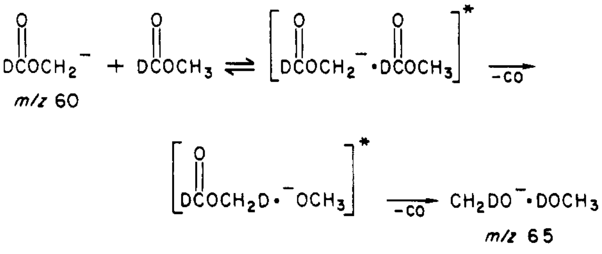
Scheme II



Scheme III



Reaction of ion c with DCO_2CH_3 proceeds through α-elimination (eq 8) and nucleophilic attack on the carbonyl group. Nucleophilic displacement of a methoxide ion by ion c results initially in the ion–molecule complex shown in Scheme I.



$$\underset{m/z\ 60}{\mathrm{D\overset{O}{\overset{\|}{C}}OCH_2^-}} + \mathrm{D\overset{O}{\overset{\|}{C}}OCH_3} \rightleftharpoons \left[\mathrm{D\overset{O}{\overset{\|}{C}}OCH_2^-\cdot D\overset{O}{\overset{\|}{C}}OCH_3}\right]^* \xrightarrow[-CO]{} \left[\mathrm{D\overset{O}{\overset{\|}{C}}OCH_2D\cdot{}^-OCH_3}\right]^* \xrightarrow[-CO]{} \underset{m/z\ 65}{\mathrm{CH_2DO^-\cdot DOCH_3}} \qquad (8)$$

The methoxide ion reattacks subsequently the formed molecule by proton abstraction or α-elimination. The latter reaction forms the *m/z* 93 ion which partly reacts further to give the *m/z* 60 or 61 ion. In principle the observed *m/z* 93 ion could also be a loose cluster of methoxide ion and methyl formate (eq 8). The ease of the reaction between the $[M-D]^-$ ion and DCO_2CH_3 (see eq 12, Table II and ref 6), which involves a similar complex, indicates that it will only be marginally stable with respect to CO loss.

The *m/z* 60 ion is the alkoxide ion from 2-hydroxyacetaldehyde and the *m/z* 61 ion the enolate ion of this compound (Scheme I). The former ion can react with DCO_2CH_3 by α-elimination yielding the *m/z* 93 ion which then reacts further to give back the reactant ion or the *m/z* 61 ion. Further evidence for the existence of ion c can be found in the reactions with C_6F_6 (Table III). Formation of the *m/z* 167 and 226 ions is rationalized in Scheme II.[28] Because DCO_2CH_3 is present in the system the ions listed

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[24] Levsen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie: New York, 1978; Chapter V, pp 209–305.

[25] Allinger, N. L.; Chang, S. H. M. *Tetrahedron* **1977**, *33*, 1561–1567.

[26] Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529–1536.

[27] The temperature in the FT-ICR instrument is not known but can be expected to be around 300 K.

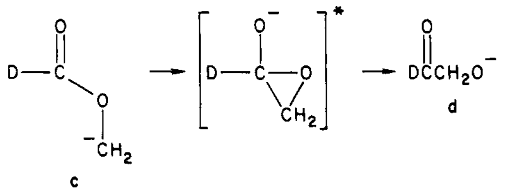
[28] The mechanism of this reaction type has been discussed in detail in previous articles. In general the reaction provides a good probe as to the reactivity and structure of some gas-phase anions; see ref 11, 18, and Ingemann, S.; Nibbering, N. M. M. *Nouv. J. Chim.* **1984**, *8*, 299–304.

Table VI. Estimates of Approximate Bond Dissociation Energies, BDE, and ΔH°_f of Ion-Molecule Clusters, $A^-\bullet B$

				values for B		
$A^-\cdot B$	BDE,[a] kJ/mol	ΔH°_f ($A^-\cdot B$),[a] kJ/mol	$10^{-8}r$,[b] cm	$10^{-25}\alpha$,[c] cm^3	$10^{-18}\mu_D$,[d] esu cm	van der Waals[e] diameter, 10^{-8} cm
$HO^-\cdot CO$	34	−288	2.6	19.5	0.112	3.16
$CH_3O^-\cdot CO$	23	−284	2.9			
$(CH_3)_2N^-\cdot CO$	18	−25	3.1			
$CH_3O^-\cdot NH_3$	73	−270	2.9	22.6	1.47	3.08
$CH_3O^-\cdot HOCH_3$	70	−421	3.2	32.6	1.70	3.76
$HO^-\cdot HN(CH_3)_2$	82	−244	3.0	56.5	1.03	4.08
$CH_3O^-\cdot H_2O$	85	−477	2.8	14.44	1.85	2.89
$HO^-\cdot H_2O$	111	−496	2.5			

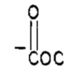
[a] ΔH°_f data of A^- and B from ref 30. [b] The distance used in the calculations is 0.85 of the sum of the van der Waals radii of AH and B. For the smaller ion–molecule clusters this reproduces experimentally determined values quite well (see note f). For the larger systems the interaction and the BDE is underestimated. This approach was chosen in order to avoid an overestimation of the ΔH°_f of interest (see text). [c] Taken from Hirschfeller, J. O.; Curtis, C. F.; Bird, R. B. "Molecular Theory of Gases and Liquids"; John Wiley and Sons: New York, 1966, or calculated from refractive index data. [d] Taken from "Handbook of Chemistry and Physics", 57th ed.; CRC Press: Cleveland, OH. [e] Calculated with van der Waals equation. [f] The experimentally determined value is 105 kJ/mol (Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445–476).

in Table II are formed to some extent. The *m/z* 205 and 206 ions (Table III) can be formed by reaction of ion d and possibly also ion e (Scheme I) with C_6F_6 (Scheme III, only shown for ion d). The complicating factor in studying the chemistry of ion c is that the isomeric ion d is formed. In Scheme I the formation of this ion d is rationalized by a bimolecular process between ion c and DCO_2CH_3. The formation of ion d could also be explained by postulating an intramolecular rearrangement of ion c. Based upon the present experiments a distinction between the various ways of forming ion d is not possible. However, several other carbanions react with methyl formate nearly exclusively through α-elimination and $B_{AC}2$,[6,29] so that the reactions in Scheme I do not seem to be unreasonable in forming ion d.



(9)

The possible structures of the $[M-D]^-$ ion are f and g. Ion f is a carbonyl anion and g is a "loose" complex of CH_3O^- and CO. Ab initio calculations have indicated that


$^-C(=O)OCH_3$

f

$CH_3O^-\cdot CO$

g

the energy required for loss of CO from a carbonyl anion is relatively low.[23] For example, the calculated energy required for dissociation of $^-CO_2H$ into CO and OH^- is 44 kJ/mol[23] (compare with Table VI). If the gas-phase acidity of the formyl group in methyl formate is placed at ~1611 kJ/mol, the energy required to dissociate the $[M-D]^-$ ion into CH_3O^- and CO becomes 14 kJ/mol (see "acidities").[30] Experimentally, the $[M-D]^-$ ion is observed to react with NH_3 or DCO_2CH_3 by transfer of a CH_3O^- ion (Table II).[6] The same reactions are observed in the other amide ion/amine systems and in the hydroxide ion/water system.[6] Although such a behavior is to be expected from ion g a strict distinction between this ion and ion f might not be possible. The main reason for this is that the $[M-D]^-$ ion is formed by an exothermic deuteron transfer and part of the excess internal energy will be retained in the ion. This can cause an initially formed ion f to convert into ion g. Further, the energy gained upon approach of ion f to a molecule might be sufficiently large to cause conversion into ion g. In principle, bond dissociation energies, BDE, of ion–molecule clusters can be obtained by MO calculations. This is beyond the scope of the present investigation. Rough approximations to BDE of ion–molecule clusters, however, can be obtained by estimating the pure long range electrostatic interaction, $V(r)$, between the species with the use of eq 10.[31,17] α is the gross molecular

$$V(r) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2} \tag{10}$$

polarizability of the molecule, μ_D is the dipole moment of the molecule, q is the charge of the ion, and r the distance between the two bodies. The results from such estimations are given in Table VI.

The energy required to dissociate ion g into CH_3O^- and CO is estimated to be ~23 kJ/mol with the use of eq 10. The ΔH°_f ($CH_3O^-\cdot CO$) becomes −284 kJ/mol and the gas-phase acidity of the formyl group is then estimated to be ~1602 kJ/mol (see "acidities"). On the assumption that ion g is formed, rough estimates of the ΔH°_r of the reactions between this ion and NH_3 or HCO_2CH_3, can be obtained. The ΔH°_f ($CH_3O^-\cdot HOCH_3$) given in Table VI

$$\underset{m/z\ 59}{CH_3O^-\cdot CO} + NH_3 \rightarrow \underset{m/z\ 48}{CH_3O^-\cdot NH_3} + CO \tag{11}$$

$$\Delta H^\circ_r = -51\ \text{kJ/mol}^{30}$$

$$\underset{m/z\ 59}{CH_3O^-\cdot CO} + HCO_2CH_3 \rightarrow \underset{m/z\ 63}{CH_3O^-\cdot HOCH_3} + 2CO \tag{12}$$

$$\Delta H^\circ_r = -8\ \text{kJ/mol}^{30}$$

has been used in order to avoid an over estimation of the ΔH°_r values. With the use of ΔH°_f ($CH_3O^-\cdot HOCH_3$) = −443 kJ/mol[32] eq 12 becomes exothermic with ΔH°_r = −30 kJ/mol. This reaction is also favored by an increase in entropy.

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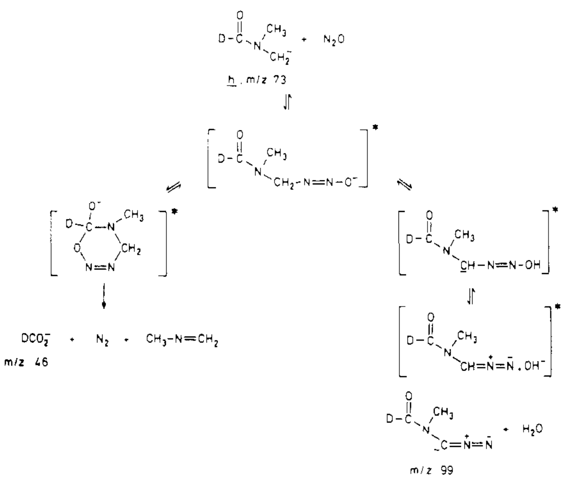
(29) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273–2281.

(30) ΔH°_f data have been taken from ref 21 and Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley (Interscience): New York, 1976.

(31) The same approach has been used to estimate the BDE of ion-molecule complexes involved in hydrogen–deuterium exchange reactions: (a) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641–3647. (b) Hunter, E. P.; Lias, S. G. *J. Phys. Chem.* **1982**, *86*, 2769–2775.

(32) ΔH°_f ($CH_3O^-\cdot HOCH_3$) = −443 kJ/mol obtained by using DE ($CH_3O^-\cdot HOCH_3$) = 91.6 kJ/mol, see: Jorgensen, W. L.; Ibrahim, M. *J. Comput. Chem.* **1981**, *2*, 7–11.

Scheme IV



Based upon these rough estimates the chemistry of the [M–D]$^-$ ion from DCO_2CH_3 becomes comprehensible in terms of the energetics of the reactions. All the observed reactions are exothermic and the most stable cluster ion, $CH_3O^-{\cdot}HOCH_3$, is the only ion observed after a reaction time of a few hundred ms.

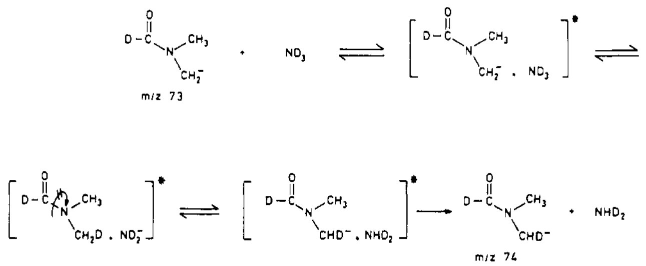
***N,N*-Dimethylformamide. Acidities.** The NH_2^- ion reacts with $DCON(CH_3)_2$ to give 93% [M–H]$^-$ and 7% [M–D]$^-$ ions whereas the weaker gas-phase base, $(CH_3)_2N^-$, gives 85% [M–H]$^-$ and 15% [M–D]$^-$ ions.[6] As discussed in the first paper hydroxide ions react with *N,N*-dimethylformamide in the FT-ICR partly by proton abstraction and in the SIFT exclusively by α-elimination.[6] As a probe to the acidity of the methyl groups in *N,N*-dimethylformamide the reactions of NH_2^- and hydroxide ions with *N,N,N′,N′*-tetramethylurea were investigated. The NH_2^- ion reacts with this compound to give ~40% [M–H]$^-$ and ~60% $C_3H_6NO^-$ ions.[33] The latter ion is formally the [M–H]$^-$ ion from *N,N*-dimethylformamide. Hydroxide ion reacts exclusively via the $B_{AC}2$ pathway.[7] The absence of a [M–H]$^-$ ion in this system indicates that the gas-phase acidity of the model compound is above that of H_2O.

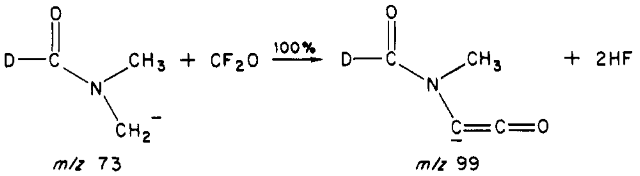
The combined results can mean that the gas-phase acidity of the most acidic methyl group in *N,N*-dimethylformamide is close to that of H_2O. The gas-phase acidity of $(CH_3)_3N$ is at present unknown but the value can be expected to be between those for NH_3 and CH_4. From these considerations it can be concluded that the substitution of a methyl in $(CH_3)_3N$ by a formyl group can increase the acidity with roughly 80 kJ/mol.

The observation that deuteron abstraction is somewhat more favored when anions with lower proton affinity is used could mean that the formyl group is more acidic than the methyl groups.[34] Based upon this it can be expected that the [M–H]$^-$ ion reacts with $DCON(CH_3)_2$ to give the [M–D]$^-$ ion. The formation of the [M–D]$^-$ ion in the reactions of the [M–H]$^-$ ion with $NH_3/DCON(CH_3)_2$, however, can also be explained by a conversion catalyzed by NH_3.[6]

Ion Structures. All the reactions which the [M–H]$^-$ ions are observed to undergo with various molecules point toward a carbanionic structure: $DCON(CH_3)CH_2^-$ (ion h). According to the previously mentioned ab initio calculations the anti form of ion h is more stable than the syn form by 25–37 kJ/mol.[3] No estimates of the height of the energy barrier toward rotation around the carbonyl carbon–nitrogen bond in the ion were given. If the most acidic methyl group has a gas-phase acidity close to that of H_2O both forms of ion h could be formed when NH_2^- is used as base. For simplicity, the anti geometry of the carbanion is drawn. The reactions of ion h with NH_3 and $DCON(CH_3)_2$ proceed analogous to those observed in the $DCO_2CH_2^-/NH_3/DCO_2CH_3$ system (see eq 3, 4, and 7 and Table IV). The reactions of primary carbanions with CF_2O and N_2O have been discussed previously.[35,16] In general these reactions provide a good probe as to the structure of carbanions in the gas phase. In the present case reaction with CF_2O proceeds exclusively through loss of 2HF molecules from the collision complex (Table V).[36] With N_2O three product ions are formed (Table V). The proposed mechanisms of the processes forming the *m/z* 99 and 46 ions are given in Scheme IV.

Scheme V





$$DCON(CH_3)CH_2^- + CF_2O \xrightarrow{100\%} DCON(CH_3)C^-{=}C{=}O + 2HF$$

$$\underset{m/z\ 73}{} \qquad \underset{m/z\ 99}{}$$

(13)

The reaction leading to the *m/z* 74 ion is less straightforward to rationalize. A possible mechanism is given in eq 14. The same result is obtained with the SIFT method.[6] Reaction between the [M–H]$^-$ ion from $HCON(CH_3)_2$ and N_2O results in 25% HCO_2^-, 35% $HCON_2O^-$, and 40% $HCON(CH_3)^-C{=}N^+{=}N^-$. The ratio between these ions is observed to be independent of the flow of N_2O.

$$\begin{aligned} \underset{m/z\ 73}{\text{ion h}} + N_2O &\rightarrow [DCON(CH_3)CH_2^-{\cdot}N_2O]^* \rightarrow \\ &[D\bar{C}O{\cdot}CH_3N{=}CH_2{\cdot}N_2O]^* \rightarrow \\ &[DCON{=}NO^-{\cdot}CH_3N{=}CH_2]^* \rightarrow \\ &\underset{m/z\ 74}{DCON_2O^-} + CH_3N{=}CH_2 \qquad (14) \end{aligned}$$

The result from the hydrogen–deuterium exchange reactions between the [M–H]$^-$ ion from $DCON(CH_3)_2$ and ND_3 (Figure 3) is interesting and important because two hydrogen atoms are relatively easily exchanged whereafter the process becomes much slower. The proposed mechanism of the exchange reaction is shown in Scheme V. The exchange process starts with formation of a complex of ion h and ND_3. Part of the energy gained upon approach is used to overcome the barrier toward overall endothermic deuteron transfer leading to the second complex in Scheme V. Rotation around the carbonyl carbon–nitrogen in

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[33] The [M–H]$^-$ ion from *N,N,N′,N′*-tetramethylurea exchanges 1 hydrogen atom with ND_3 and reacts with CF_2O through loss of 2 HF molecules from the collision complex.

[34] Lithiation of $HCON(CH_3)_2$ leads only to $LiCON(CH_3)_2$, see: Banhidia, B.; Schöllkopf, U. *Angew. Chem.* **1973**, *85*, 861–862.

[35] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800–5802.

[36] The *m/z* 99 ions react further with CF_2O to give the *m/z* 144 ions and DF. The *m/z* 190 ions observed arises through reaction between the *m/z* 144 ions and CF_2O (Table V).

N,N-dimethylformamide is hindered by a large barrier.[37] The results in Figure 3 can be explained upon the assumption that the energy within the second complex in Scheme V is too low to drastically increase the rate of this rotation. Further, proton abstraction must then be faster than internal rotation and must occur from the same methyl group as where the charge was located in the $[M-H]^-$ ion. This interpretation demands that the two methyl groups in *N,N*-dimethylformamide are nonidentical with respect to gas-phase acidity. However, it is not possible to conclude whether the syn or the anti methyl group is the most acidic. Considerations similar to those presented for the $[M-D]^-$ ion from DCO_2CH_3 apply to the $[M-D]^-$ ion from $DCON(CH_3)_2$. The latter ion transfers a $(CH_3)_2N^-$ ion to $DCON(CH_3)_2$ and H_2O (eq 6 and Table IV); no transfer of $(CH_3)_2N^-$ to NH_3 or the amines used occurs. If the gas-phase acidity of the formyl position is placed between that of H_2O and CH_3OH, the energy required to dissociate the $[M-D]^-$ ion into CO and $(CH_3)_2N^-$ becomes 110 kJ/mol.[38] In order for the reaction with H_2O to be exothermic (Table IV) the BDE of the $[M-D]^-$ ion has to be lower than 106 kJ/mol (calculated using ΔH_f $(HO^-\cdot HN(CH_3)_2)$ = −244 kJ/mol (Table VI)).

Ab initio calculations predict a larger dissociation energy for $^-CONH_2$ than for $^-CO_2H$.[23] The given considerations point toward a completely different BDE of the $[M-D]^-$ ion than the one obtained by assuming a "loose" ion–molecule structure of the ion (Table VI). This could mean that the ion is best described as a carbonyl anion with a rather weak carbonyl carbon–nitrogen bond.

Dipole Stabilization. The basic reason for carrying out these experiments was to prove that carbanions which might be dipole stabilized can be formed in the gas phase. The results obtained provide strong evidence that dipole stabilized carbanions can be formed from methyl formate and *N,N*-dimethylformamide in the gas phase. For both compounds the carbonyl group increases the gas phase acidity relative to that of CH_3OCH_3 and $(CH_3)_3N$, respectively. In other words, the carbonyl group stabilizes the primary carbanions generated from the two model compounds. It can here be mentioned that the methyl groups in 2,2-dimethylpropanal and 2-methyl-2-nitrosopropane have a gas-phase acidity between that of H_2O and CH_3OH.[39] The increased acidity of the methyl groups relative to that expected from 2,2-dimethylpropane (>1687 kJ/mol) has been explained by a through space interaction between the negative charge on the β-carbon and the dipole moment of the –CHO and –NO group. For the present carbanions the situation is more complex because of the resonance (see eq 1): the accompanying increase of charge separation will increase the dipole moment and tend to align it to the line connecting the heteroatoms. This in turn will lead to an increase in dipole stabilization. However, to gain real insight in the different factors affecting the stability of the carbanions derived from methyl formate and *N,N*-dimethylformamide a molecular orbital picture of the ions is needed.

Conclusions

Primary carbanions can be formed from methyl formate and *N,N*-dimethylformamide in the gas phase. These carbanions react according to their structure with various molecules. The results from hydrogen–deuterium exchange reactions between the primary carbanion from $DCON(CH_3)_2$ and ND_3 provide some experimental support that the two methyl groups are nonidentical with respect to their gas-phase acidity. The results indicate that the methyl group in methyl formate is less acidic than the most acidic methyl group in *N,N*-dimethylformamide. For both compounds the formyl position appears to be more acidic in the gas phase than the methyl groups. The ion formed by abstraction of the proton at the formyl position in methyl formate behaves chemically like a "loose" cluster of CH_3O^- and CO. The analogous ion derived from *N,N*-dimethylformamide can best be described as a carbonyl anion with a rather weak carbonyl carbon–nitrogen bond.

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Registry No. HCO_2CH_3, 107-31-3; DCO_2CH_3, 23731-38-6; HCO_2CD_3, 23731-39-7; $HCON(CH_3)_2$, 68-12-2; $DCON(CH_3)_2$, 2914-27-4; NH_2^-, 17655-31-1; $C_2H_5NH^-$, 54448-40-7; $H^{18}O^-$, 65553-37-9; $CH_3{}^{18}O^-$, 94203-51-7; CF_2O, 353-50-4; N_2O, 10024-97-2; HO^-, 14280-30-9; CH_3O^-, 3315-60-4; $(CH_3)_2N^-$, 34285-60-4; CO, 630-08-0; NH_3, 7664-41-7; $HOCH_3$, 67-56-1; $HN(CH_3)_2$, 124-40-3; H_2O, 7732-18-5.

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(37) The free energy barrier toward rotation around the carbonyl carbon–nitrogen bond in $HCON(CH_3)_2$ is at 401 K ΔG^{*} = 87.9 kJ/mol as determined by NMR on neat $HCON(CH_3)_2$, see: Rabinovitz, M.; Pines, A. *J. Am. Chem. Soc.* **1969**, *91*, 1585–1589 (note that the temperature of our system is assumed to be around 300 K). The barrier might be somewhat lower in the gas phase; see for the case of $CF_3CON(CH_3)_2$: Ross, B. D.; True, S. N.; Decker, D. L. *J. Phys. Chem.* **1983**, *87*, 89–94.

(38) $\Delta H°_f$ data from ref 21 and 31. $\Delta H°_f$ $(HCON(CH_3)_2)$ = −191.6 kJ/mol from Sanderson, R. T. "Chemical Bonds in Organic Chemistry"; Sun and Sand: Scottsdale, 1976.

(39) Noest, A. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1980**, *102*, 6427–6429.