Gas-Phase Reactions of Nucleophiles with Methyl Formate

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Abstract: Low-pressure gas-phase reactions of methyl formate and methyl pivalate with the nucleophiles NH_2^-, OH^-, and O^- have been examined via Fourier transform mass spectrometry. In contrast to a previous ion cyclotron resonance study of the reaction with NH_2^-, five anionic products are observed rather than the single product reported earlier. Reaction with hydroxide similarly yielded a greater variety of reaction products than previously found in any single study. With O^-, although product identities agree with those reported by other workers, significant differences in relative product abundances were found. Mechanistic details of these reactions were probed by isotopic labeling (^2H and ^{18}O) and ion ejection studies. Finally, superoxide anion ($O_2^-\cdot$) was found to be unreactive.

In solution, esters commonly react with nucleophiles by a $B_{AC}2$ mechanism in which a tetrahedral intermediate is formed, followed by cleavage of the acyl–oxygen bond.[1-3] A much different situation pertains in the gas phase, where the controlling factors are more complex and not as well understood.[4-11] For example, in an early mechanistic study of the gas-phase reactions of esters, Comisarow found that both methyl benzoate and methyl trifluoroacetate reacted with alkoxide ions by the S_N2 mechanism and found no evidence for a parallel competing $B_{AC}2$ process.[4] Similarly, Olmstead and Brauman reported gas-phase S_N2 reactions of trifluoroacetates and pivalate esters.[12] More recently, McDonald and Chowdhury have described a manifold of additional reaction channels for trifluoromethyl acetate ester reactions with the allyl anion, including both displacement and competitive carbonyl addition.[13] In other cases, such as reactions of alkyl formates with nucleophiles, a variety of reaction pathways, including $B_{AC}2$, S_N2, and proton abstraction exist. Of particular interest in the present context are the conflicting and often erroneous literature reports concerning the mechanistic course of reactions of NH_2^-, OH^-, and O^- with methyl formate. No doubt some of these discrepancies arise from the different experimental regimes employed. Accordingly, a single comparative study, using one instrument, might resolve some of the existing confusion and serve to unify previous theories. It seems likely that these nucleophiles might follow similar reaction patterns with methyl formate, since all of the proposed pathways are thermodynamically plausible. Of particular interest is the continuing controversy surrounding the detailed mechanism of the $B_{AC}2$ pathway in the gas-phase reactions of esters. From studies of ^{18}O-labeled methyl formate, Riveros and co-workers have recently concluded that the tetrahedral addition complex is a transition state rather than a stable intermediate.[14] On the other hand, McDonald and Chowdhury contend the adduct of F_3C^- with $(CF_3)_2C=O$, which they observe directly, is a true tetrahedral intermediate and that

the $B_{AC}2$ mechanism correctly describes the gas-phase reactions of anions with neutral carbonyl-containing compounds.[15] Although the present results do not resolve this particular issue, they substantially extend the completeness of information regarding the products of gas-phase reactions of common nucleophiles with methyl formate.

The reactions of OH^- with methyl formate exemplify the variety of mechanistic pathways available for such reactions of nucleophiles with esters. Use of oxygen-18-labeled hydroxide shows that three distinct reaction pathways exist for product formation (eq 1–3).[7,9,10] Reaction 1 presents the $B_{AC}2$ process, which DePuy
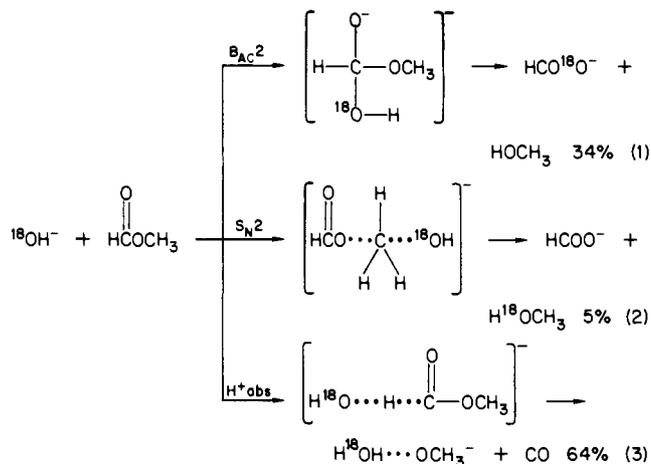
and co-workers have shown by flowing afterglow techniques to account for 34% of these three products.[10] Five percent arises via the S_N2 mechanism (eq 2) while proton abstraction, leading to formation of a solvated anion (eq 3), represents the dominant pathway (64%).

Formation of the clustered anionic species (eq 3) from alkyl formates resulting from reactions with a variety of nucleophiles, including CH_3O^-, HOO^-, and F^-,[7-10,16,17] is also of interest. The solvated ions are believed to form by abstraction of the acidic hydrogen followed by elimination of CO to produce the solvated ion (eq 4). This process is a convenient means of formation of

$$X^- + H-C(=O)-OR \rightarrow [X\cdots H\cdots C(=O)-OR]^- \rightarrow$$
$$XH\cdots OR^- + CO \quad (4)$$

$$X = OH^-, OOH^-, F^-, CH_3O^-, CH_3^-, CF_3^-, C_2H_5O^-, C_2H^-,$$
$$C_2^-, \text{etc.}$$

stable solvated ions even at low pressures (10^{-6} to 10^{-5} torr).

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Previous studies of ion–molecule reactions of the alkyl formates with various anions have been conducted by both flowing afterglow (FA)[10] and ion cyclotron resonance (ICR) mass spectrometry.[7-9,16-19] In the study we report here, Fourier transform mass spectrometry (FTMS)[20] using a trapped-ion cell[21] was employed. FTMS experiments are conducted at lower pressures (10^{-7} torr) than FA (0.1–0.5 torr) and conventional ICR (10^{-6} to 10^{-5} torr). Use of the low-pressure regime permits observation of reactions in the absence of clustering. The trapped-ion cell allows observation of products for reaction times varying from a few milliseconds to seconds rather than the much shorter reaction times allowed by FA or drift cell ICR. Measurement speed, resolution, and mass range are much enhanced over drift cell ICR.

Riveros and co-workers, in their ion cyclotron resonance studies of the reaction of NH_2^- with methyl formate, concluded that amide reacted with methyl formate to produce only one anionic product, methoxide.[7,8] They attributed the mechanistic origin of this ion to the proton abstraction pathway, which initially would yield a solvated anion, that in turn could dissociate to give methoxide, ammonia, and carbon monoxide. These workers rejected the possibility of formation of methoxide via the $B_{Ac}2$ mechanism, even though it is 22.2 kcal/mol exothermic while the proposed pathway is 15.5 kcal/mol exothermic. It appears that this conclusion derives, in part, from their failure to observe the expected product, $H_2NH\cdots OCH_3^-$. Based upon limited experimental evidence, these workers generalized that formate esters would yield methoxide as the observed product if the exothermicity of the reaction was greater than the bond energy of the product cluster. Therefore, they concluded that the sought-for cluster must have had very low bond energy. In the present FTMS study, amide was found to yield a number of ionic products in addition to methoxide, *including the cluster product judged too unstable for observation by Riveros and Isolani.*[8]

For reactions of the simple oxygen nucleophiles, O^- and OH^-, differences from previous reports of both ionic product identities and abundances[7-10,18,19] are also found in the present study. Reported product distributions for the reaction of OH^- vary with the type of instrument used.[7-10] The most complete work to date on the reaction of hydroxide with methyl formate is that of DePuy.[10] For O^-, products that were previously attributed to secondary reactions of OH^-[18,19] have been shown in the present study to be the direct result of reactions with O^-. An additional oxygen nucleophile, $O_2^-\cdot$, was also investigated but was found not to react with methyl formate under the experimental conditions.

Thus, methyl formate undergoes facile reactions with hydroxide, amide, and oxide under low-pressure FTMS conditions, and new products in addition to those previously reported are found. Related reactions of methyl pivalate were also investigated in the present study.

Experimental Section

A Nicolet Analytical Instruments FTMS-1000 Fourier transform mass spectrometer equipped with a 3.0 T superconductoring solenoid magnet and a 2.54 cm × 2.54 cm × 7.62 cm trapped ion cell was used. A potential of -1.0 V was applied to the trap plates to retain negative ions in the cell. Pressures were monitored with an uncalibrated Granville-Phillips ion gauge and controller (calibrated for N_2). The instrument was operated with a 2.63 MHz observation bandwidth from 464 kHz to 3.09 MHz (15–100 amu).

In a typical experimental sequence, negative ions were generated by a 100 ms beam of 5–6 eV electrons with filament emission currents of approximately 1–2 μA. Following the beam event, trapped electrons were ejected from the cell by application of 4.6 MHz radio frequency (rf) (the longitudinal oscillation frequency of electrons in a 7.62 cm long cell) with

an amplitude of 3 V peak to peak. The rf was applied to the rear trap plate for 500 μs.[22] The third event in the sequence was ejection of all ions formed by electron impact, except for the nucleophile of interest. Finally, after delay times ranging from a few milliseconds to several seconds to permit reactions to occur, the anionic products were observed. Confirmation of the identities of precursor ions for ionic reaction products was accomplished by ejection of suspected precursors with rf excitation at appropriate cyclotron resonance frequencies, prior to the reaction delay time and observation of the products. To ensure that pyrolysis product from hot surfaces were not contributing to the product distributions, the reactions were also conducted with the ion gauge off (off for 1 h prior to experiment). There was no variation in the observed product distribution.

NH_2^- or ND_2^- were formed by electron bombardment of NH_3 (Matheson, 99.99%) or ND_3 (Merck, 99%D) at -5.5 eV. Traces of water were present even though steps were taken to remove it.[23] The pressure of ammonia was typically 3.0×10^{-7} torr, while that of the ester was 2×10^{-8} torr.

$^{18}OH^-$ was generated by electron bombardment of $H_2^{18}O$ (Bio-Rad, 95% ^{18}O) with -5.0 eV electrons. For these measurements, the typical pressure of water was 3.0×10^{-7} torr, while that of the ester was 3×10^{-8} torr. $^{18}O^-$ and $^{18}O_2^-\cdot$ were produced from $^{18}O_2$ (Bio-Rad, 99.5% ^{18}O, 0.21% ^{17}O) using -6 eV electrons. A large yield of $^{18}O^-$ was obtained in this manner; however, the yield of $^{18}O_2^-\cdot$ was much lower.[24]

Unlabeled methyl formate and methyl pivalate were purchased from Aldrich, and methyl-d_3 formate was synthesized by distillation from a mixture of CD_3OD (Aldrich, 99.5%) and formic acid.

Results and Discussion

NH_2^-. The reaction of NH_2^- yields a variety of anion products (eq 5–9) differing from those found in ICR studies, in which the only anionic product reported was CH_3O^-.[7,8] Ions were observed

at m/z 31, 44, 48, 59, and 63, which correspond to the masses of CH_3O^-, $HCONH^-$, $H_2NHOCH_3^-$, $(M-1)^-$, and $CH_3OHOCH_3^-$.

Assistance in determining structural assignments for product ions and proposed mechanistic pathways was obtained from both double-resonance and isotopic labeling experiments. Double resonance shows that *both* $H_2NH\cdots OCH_3^-$ and CH_3O^- are precursors of $CH_3OH\cdots OCH_3^-$ (m/z 63). Ejection of CH_3O^- (m/z 31) continuously during the reaction period results in a decrease in the intensity of the ion at m/z 63. A similar decrease in intensity is observed when $H_2NH\cdots OCH_3^-$ (m/z 48) is ejected during the reaction period.

Identities of the ions at m/z 44 and 48 were confirmed by deuterium labeling studies in which ND_2^- and methyl-d_3 formate were used. With ND_2^- as reagent, the m/z 44 formamide anion peak shifts quantitatively to m/z 45 and the ammonia-solvated methoxide peak (m/z 48, eq 7) moves to m/z 50 (eq 10 and 11).

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(22) Studies in our laboratory indicate that pulses of a shorter duration; e.g., 100–200 μs, are ample for elimination of trapped electrons. See also: McIver, R. T., Jr.; Fukuda, E. K. *Lect. Notes in Chem.* **1982**, *31*, 164–182.

(23) The ammonia was passed through a drying tube when filling the sample bulb. The sample bulb was then frozen in liquid nitrogen and immersed in a dry ice-acetone bath during the experiment. The relative abundance of HO^- varied from 10–15% at 100-ms reaction time to 50% or more at longer reaction times. The intensity of HO^- is less than 1% of the NH_2^- when no reaction delay is used.

(24) A pulse at the cyclotron resonance frequency of O^- is applied for the duration of the beam event to eject O^-. Following the beam event, an ejection sweep over m/z 17 and 18 removes residual OH^- and O^- from the reaction.

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$$NO_2^- + HCOOCH_3 \longrightarrow \left[H-\overset{O}{\underset{NO_2}{C}}-OCH_3 \right]^- \longrightarrow \begin{array}{l} HCOND_2 + \\ CH_3O^- \quad (10) \\ m/z\ 31 \\ HCOND^- + \\ m/z\ 45 \\ CH_3OD \quad (11) \end{array}$$

When methyl-d_3 formate is used, deuterated anionic products with m/z 34, 44, 51, 62, and 69 are observed (eq 5–9).

Methoxide may result either via initial proton abstraction followed by rapid elimination of CO (eq 7) or by the $B_{AC}2$ mechanism. Both reactions are exothermic (see Table I). Previous ICR studies attributed the formation of methoxide exclusively to proton abstraction, rather than direct displacement (eq 5).[8] Isolani and Riveros calculated that the production of the solvated anion ($H_2NH\cdots OCH_3^-$) is exothermic. However, they did not observe it and explained its absence by stating that the reaction was more exothermic than the strength of the hydrogen bond, therefore yielding CH_3O^- as the exclusive product. The more exothermic $B_{AC}2$ process was discounted as a source of methoxide. Observation of three additional products, $HCONH^-$, $H_2NH\cdots OCH_3^-$, and $(M - 1)^-$, in our present FTMS study gives evidence that both the $B_{AC}2$ and proton abstraction pathways occur (although this is not unequivocal evidence of a $B_{AC}2$ route to methoxide). $HCONH^-$ (eq 6) appears to result from a $B_{AC}2$ attack at the carbonyl carbon followed by cleavage of the acyl-oxygen bond with either concerted loss of methanol or abstraction of the $HCO-NH_2$ proton by methoxide.[25] If dissociation of the collision complex occurs before proton transfer, CH_3O^- is the observed anionic product of this reaction. Products of initial proton abstraction from methyl formate include the M − 1 carbanion (eq 8) and the solvated anion (eq 7). In the present stuudy, an ion is observed at m/z 63 which, at long reaction times, becomes the major peak in the spectrum. This ion probably arises from the reaction of methoxide with neutral methyl formate to produce $CH_3OH\cdots OCH_3^-$ (eq 9).[16,17] This is evidenced both by double-resonance results and by the fact that at short reaction times CH_3O^- is the major product, while $CH_3OH\cdots OCH_3^-$ becomes the major anionic product after long reaction times (see Figure 1a).

To test this hypothesis methanol and methyl formate were introduced into the FTMS and methoxide was generated by electron impact. The only ionic reaction product observed was an ion at m/z 63 (presumably $CH_3O\cdots HOCH_3^-$). Use of methanol-d_4 or methyl-d_3 formate caused quantitative shifts of the m/z 63 ion to m/z 66. When methoxide was generated from methanol in the absence of methyl formate, no m/z 63 ion was formed. These reactions have previously been well characterized by Blair, Isolani, and Riveros.[17]

Consistent with double-resonance studies, $H_2NH\cdots OCH_3^-$ appears to undergo a secondary reaction. The associated ion initially represents 16% of the total product distribution but at longer times represents only 3%. $H_2NH\cdots OCH_3^-$ may undergo reaction with methyl formate to produce $CH_3O\cdots HOCH_3^-$. However, the basicity of the solvated anion will be lower than that of amide anion by the hydrogen bond strength, which we estimate to be greater than 24 kcal/mol.[26,27] Alternatively, the ion at m/z 63 may also be formed by a sovlent switching process in which $H_2NH\cdots OCH_3^-$ exchanges with CH_3OH to produce $CH_3O^-\cdots H-OCH_3$ and NH_3. This type of reaction is generally observed by ICR with solvated anions produced in a manner analogous to

Table I. Heats of Reaction (kcal/mol) for Some Ion–Molecule Reactions of Methyl Formate

reaction[a]	reaction type	ΔH_r° [a]
$^{18}OH^- + HCOOCH_3 \rightarrow HCO^{18}O^- + CH_3OH$	$B_{AC}2$	-44.0
$^{18}OH^- + HCOOCH_3 \rightarrow CH_3O^- + HCO^{18}OH$	$B_{AC}2$	-10.0
$^{18}O^- + HCOOCH_3 \rightarrow HCO^{18}O^- + CH_3O\cdot$	$B_{AC}2$	-57.0
$NH_2^- + HCOOCH_3 \rightarrow CH_3O^- + HCONH_2$	$B_{AC}2$	-22.2
$NH_2^- + HCOOCH_3 \rightarrow HCONH^- + CH_3OH$	$B_{AC}2$	b
$^{18}OH^- + HCOOCH_3 \rightarrow HCOO^- + CH_3^{18}OH$	S_N2	-44.0
$^{18}O^- + HCOOCH_3 \rightarrow HCOO^- + CH_3^{18}O\cdot$	S_N2	-57.0
$NH_2^- + HCOOCH_3 \rightarrow HCOO^- + CH_3NH_2$	S_N2	-59.7
$^{18}O^- + HCOOCH_3 \rightarrow CH_3O^- + {}^{18}OH\cdot + CO$	PA	+5.4
$^{18}OH^- + HCOOCH_3 \rightarrow H^{18}OH\cdots OCH_3^- + CO$	PA	~-15.0[c]
$^{18}OH^- + HCOOCH_3 \rightarrow CH_3O^- + H_2^{18}O + CO$	PA	-3.7
$NH_2^- + HCOOCH_3 \rightarrow CH_3O^- + NH_3 + CO$	PA	-15.1
$NH_2^- + HCOOCH_3 \rightarrow H_2NH\cdots OCH_3^- + CO$	PA	<-9.3[c]

[a] Gas-phase thermochemical data for the ions and neutral compounds were taken from the following sources: (1) $\Delta H_f^{\circ}(OH^-)$ = -32.8 kcal/mol, $\Delta H_f^{\circ}(O^-)$ = 25.2 kcal/mol, $\Delta H_f^{\circ}(HCONH_2)$ = -44.5 kcal/mol, $\Delta H_f^{\circ}(HCO_2CH_3)$ = -83.7 kcal/mol, $\Delta H_f^{\circ}(OH\cdot)$ = 9.3 kcal/mol, $\Delta H_f^{\circ}(CH_3NH_2)$ = -5.5 kcal/mol, $\Delta H_f^{\circ}(H_2O)$ = -57.8 kcal/mol, $\Delta H_f^{\circ}(CO)$ = -26.4 kcal/mol from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, No. 1. (2) $\Delta H_f^{\circ}(NH_3)$ = -11.0 kcal/mol, $\Delta H_f^{\circ}(NH_2^-)$ = 25.4 kcal/mol, $\Delta H_f^{\circ}(HCO_2H)$ = -90.5 kcal/mol, $\Delta H_f^{\circ}(HCO_2^-)$ = -112.5 kcal/mol, $\Delta H_f^{\circ}(CH_3OH)$ = -48.0 kcal/mol, $\Delta H_f^{\circ}(CH_3O^-)$ = -36.0 kcal/mol, from ref 35. $\Delta H_f^{\circ}(CH_3O\cdot)$ = -3 kcal/mol from ref 32. [b] Cannot be calculated because $\Delta H_f^{\circ}(HCONH^-)$ is not known. [c] From ref 8.

reaction 4.[28] The extent to which this reaction would occur is limited by the amount of CH_3OH. Only ions are retained in the cell for extended periods, and the neutrals are pumped out. Therefore, the only neutral in abundance is methyl formate, because it is continuously introduced.

An additional ion with m/z 45, $HCOO^-$, is also observed. This product may result from the S_N2 reaction pathway and/or the reaction of residual OH^-. When hydroxide is ejected during the entire reaction time, the intensity of $HCOO^-$ decreases, but it does not disappear entirely (Figure 2). When NH_2^- is ejected prior to the reaction delay time, all products disappear except for $HCOO^-$. These results support the contention that $HCOO^-$ may result both from reaction of methyl formate with NH_2^- and residual hydroxide. However, because it is impossible to completely eliminate hydroxide and because hydroxide regenerates at long reaction times, this is not unequivocal evidence for the S_N2 reaction of NH_2^-. The S_N2 reaction pathway is quite exothermic (Table I), but the energy barrier for this reaction is apparently so great compared to those for proton abstraction or $B_{AC}2$ reaction that it occurs to only a minor extent (for discussions of the energy barriers and $B_{AC}2$ and S_N2 gas-phase reaction pathways, see ref 12 and 29). This corresponds to the previous observations for reaction of methyl formate with hydroxide in which the $B_{AC}2$ and proton abstraction reactions occur preferentially and S_N2 products comprise only a minor portion of the total product distribution.[7–10]

For comparison, methyl pivalate was also examined. Riveros was unable to observe complex reactivity for NH_2^- reactions until he studied the alkyl pivalates.[7] Methyl pivalate lacks a formyl hydrogen, making the proton abstraction process (eq 4) impossible; therefore, the only pathway by which CH_3O^- can form is the $B_{AC}2$. Using conditions identical with those for the reaction of methyl formate with NH_2^-, the reaction of NH_2^- with $(CH_3)_3CCOCH_3$

(25) This was verified by allowing CH_3O^- (generated from CH_3OH) to react with $HCONH_2$ (Aldrich, 98%). An ion peak at m/z 44 was observed after a reaction time of 50 ms. This peak corresponding to m/z 44 (HCO-NH$^-$) increased in intensity as the reaction time was increased.

(26) This estimate is based on the measurement of Yamdagni and Kebarle [Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139–7143] for the hydrogen bond energy of HO$^-\cdots$HOH as 24 kcal/mol. NH$_2^-$ is a stonger base than HO$^-$ and would form a stronger hydrogen bond. See also: Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476.

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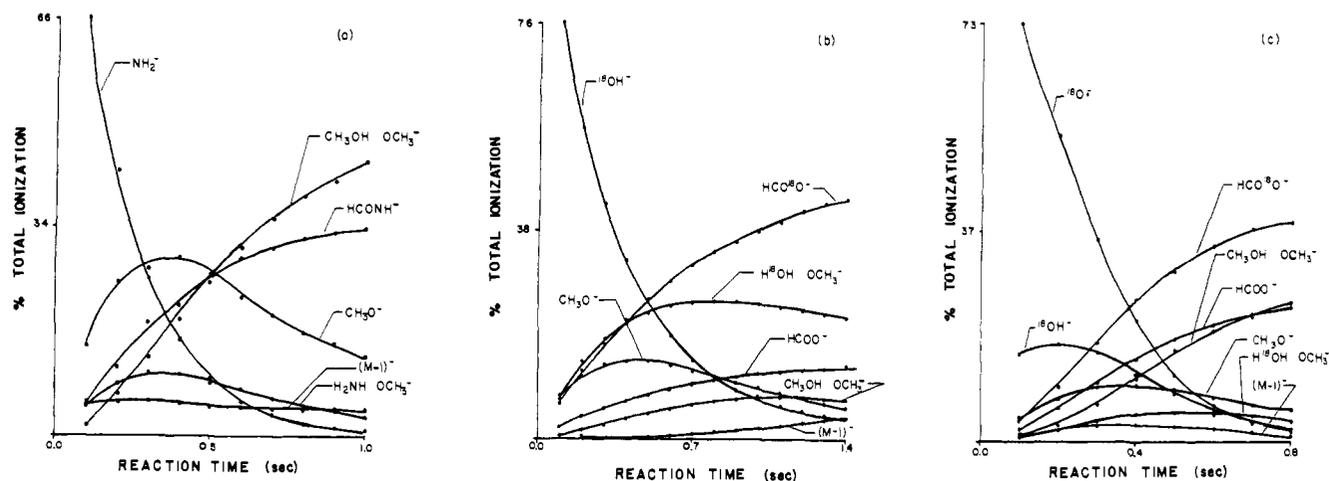**Figure 1.** Time-resolved mass spectral intensities for the reactions of (a) NH_2^- with methyl formate, (b) $^{18}OH^-$ with methyl formate, and (c) $^{18}O^-$ with methyl formate.
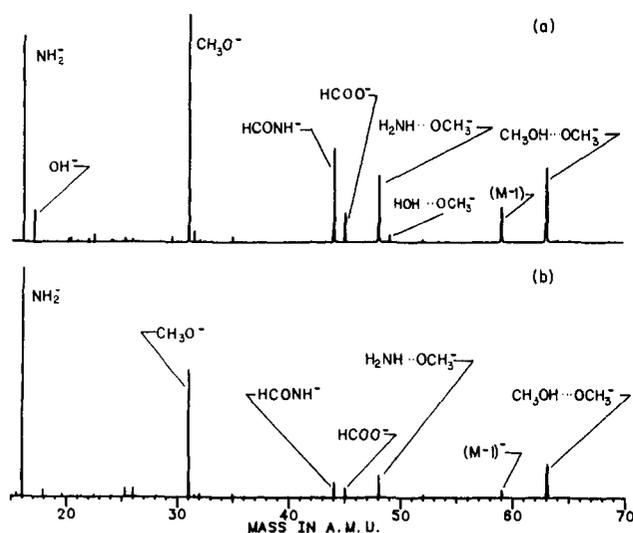

Figure 2. Fourier transform mass spectra of the reaction of NH_2^- and methyl formate (a) without ejection of residual OH^- during reaction time and (b) with ejection of OH^- during the entire reaction. These spectra were collected for a reaction time of 200 ms and are the average of 20 scans. The product intensities are lower because the cyclotron resonance frequency of OH^- is close to NH_2^-, and some NH_2^- is also ejected.

results in the array of products reported by Takashima and Riveros[7] (eq 12–15). In contrast with the slower methyl formate
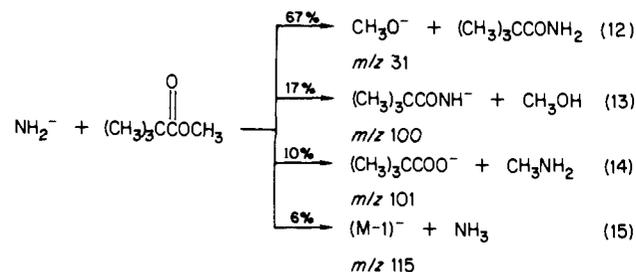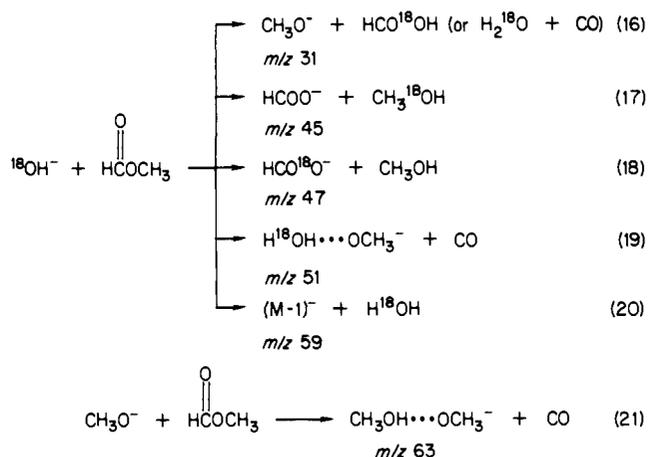

reaction in which unreacted NH_2^- is observed after 1 s, all NH_2^- reacts with excess $(CH_3)_3CCOOCH_3$ within a few hundred milliseconds. This may explain why in previous ICR studies[7,8] only one product was observed for te methyl formate system. In those studies, typical ion residence times were only 1–5 ms and possibly the reaction times were not long enough for formation of other products. As can be seen from Figure 1a, methoxide is the major product for NH_2^-/HCO_2CH_3. This indicates that the reaction which produces CH_3O^- proceeds faster than the other reactions.

Reactions 12 and 13 occur by the $B_{AC}2$ mechanism with formation of a tetrahedral intermediate while reaction 14 occurs by an S_N2 process. We have confirmed that the proton abstraction reaction (eq 15) (percentages indicated are for 100-ms reaction times), described as a questionable result by Riveros,[7] occurs to the extent of about 6% of the products.

OH^-. The product array reported in the literature for the reaction of hydroxide with methyl formate varies with the type of instrument used. Three major products are observed by Riveros and co-workers using ICR, $HOH\cdots OCH_3^-$, $HCOO^-$, and CH_3O^- (eq 1–3).[7] This experiment was later repeated using $^{18}OH^-$ and an additional product $HCO^{18}O^-$ observed.[9] Tanner, Mackay, and Bohme,[27] using flowing afterflow at a pressure of 0.3 torr, also found three products, $HCOO^-$, $HOH\cdots OCH_3^-$, and $CH_3OH\cdots O-CH_3^-$. They attributed the formation of $CH_3OH\cdots OCH_3^-$ to the reaction of $HOH\cdots OCH_3^-$ with methyl formate. DePuy and co-workers[10] using $^{18}OH^-$ observed $H^{18}OH\cdots OCH_3^-$, $HCOO^-$, $HCO^{18}O^-$, CH_3O^-, and $(M-1)^-$. In contrast with these previous results, in the present FTMS study all products are observed.

Because both the $B_{AC}2$ and S_N2 mechanistic pathways would produce $HCOO^-$, oxygen-18-labeled water was used to differentiate between the products arising from the competing mechanisms. Equations 16–21 summarize the reactions observed.[30] The S_N2

$$^{18}OH^- + \overset{O}{\underset{}{\overset{\|}{H C}}}OCH_3$$

$$\longrightarrow CH_3O^- + HCO^{18}OH \text{ (or } H_2^{18}O + CO) \quad (16)$$
$$m/z\ 31$$

$$\longrightarrow HCOO^- + CH_3^{18}OH \quad (17)$$
$$m/z\ 45$$

$$\longrightarrow HCO^{18}O^- + CH_3OH \quad (18)$$
$$m/z\ 47$$

$$\longrightarrow H^{18}OH\cdots OCH_3^- + CO \quad (19)$$
$$m/z\ 51$$

$$\longrightarrow (M-1)^- + H^{18}OH \quad (20)$$
$$m/z\ 59$$

$$CH_3O^- + \overset{O}{\underset{}{\overset{\|}{H C}}}OCH_3 \longrightarrow CH_3OH\cdots OCH_3^- + CO \quad (21)$$
$$m/z\ 63$$

process gives $HCOO^-$, while the $B_{AC}2$ process yields $HCO^{18}O^-$. As in the case of NH_2^-, CH_3O^- results from either the $B_{AC}2$ process (eq 16) or decomposition of the initial proton abstraction product (eq 19). The methoxide produced reacts with methyl formate to produce $CH_3OH\cdots OCH_3^-$ (eq 21). Reaction 20 represents the abstraction of a proton from methyl formate to produce CO_2CH_3. Reaction 21 is also the result of proton abstraction,

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(30) Neutral products are assumed.

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Figure 3. Fourier transform mass spectra demonstrating the effect of OH⁻ on the product distribution. (a) is the typical spectrum spectrum obtained when the major product ¹⁸OH⁻ is not ejected during a 150-ms reaction while (b) is the spectrum obtained when ¹⁸OH⁻ is ejected during the 150-ms reaction (207 scans).

but in this case CO is expelled and a solvated ion $CH_3OH\cdots OCH_3^-$ formed.[7-9,17]

Confirmation of the source of the m/z 63 product ion is obtained by double-resonance experiments. Ejection of CH_3O^- during the reaction period results in a decrease in the amount of $CH_3O-H\cdots OCH_3^-$ observed. It is seen from Figure 1b that as the reaction time increases the amount of CH_3O^- decreases while $CH_3OH\cdots OCH_3^-$ represents a larger percentage of the product distribution. Ejection of $HOH\cdots OCH_3^-$ as it is formed during the reaction also results in a decrease in the amount of $CH_3OH\cdots OCH_3^-$, indicating that the aquated ion is also a precursor of $CH_3OH\cdots OCH_3^-$. The pathway responsible for formation of $CH_3OH\cdots OCH_3$ from $HOH\cdots OCH_3^-$ is probably analogous to that for the $H_2NH\cdots O-CH_3^-$ reaction.

O⁻. The products of the reaction of O⁻ and methyl formate, as observed by Dawson and Nibbering, using ICR are OH⁻, (M – H)⁻, (M – H₂)⁻, and $HCOO^-$.[18,19] N_2O was used as their source of O⁻ at a total pressure of 3×10^{-5} torr. Under their conditions, OH⁻ reacted further with methyl formate to produce products as in reactions 16–21. The major product observed, $HCOO^-$, results from both the $B_{AC}2$ and S_N2 reaction pathways; therefore, ¹⁸O⁻ (from 71.5% $N_2{}^{18}O$) was used to distinguish between the two mechanisms. They found the $B_{AC}2/S_N2$ ratio to be 1.5.

The present FTMS studies produced product abundances which differ considerably from those observed by Dawson and Nibbering. (M – H)⁻ represents only a minor percentage of the total products, and the (M – H₂)⁻ peak is barely observable. In contrast, the published ICR spectra[18] show the intensities of the (M – H)⁻ and (M – H₂)⁻ ions to be almost equal, and each one has an abundance about one-half that of the major product $HCOO^-$. In our FTMS studies, abstraction of the formyl hydrogen resulting in the formation of hydroxide is the major process at 10^{-7} torr (eq 25). ¹⁸O-labeled hydroxide reacts further with methyl formate to produce $H^{18}OH\cdots OCH_3^-$ (m/z 51), $HCOO^-$ (m/z 45), and $HCO^{18}O^-$ (m/z 47). As the reaction time increases the amount of ¹⁸OH⁻ decreases and $HCO^{18}O^-$ becomes the major species (Figure 1c). If ¹⁸O hydroxide is ejected during the reaction time, the products of the ¹⁸OH⁻/HCOOCH₃ reaction can be eliminated. This results in a marked decrease in the intensities of $HCOO^-$ and $HCO^{18}O^-$ and the dominant ion becomes CH_3O^- (Figure 3b).

Ejection of ¹⁸OH⁻ during the entire reaction period resulted in the following product distribution (Figure 3b): CH_3O^-, 51% [from the sum of CH_3O^- 37%, and the secondary reaction (eq 22) $CH_3OH\cdots OCH_3^-$, 14%]; $HCOO^-$, 19% (S_N2), 25% $HCO^{18}O^-$ ($B_{AC}2$), and 5% (M – 1)⁻. Our ejection studies establish that CH_3O^- is the result of the reaction of O–/HCOOCH₃ and not only OH–/HCOOCH₃ (as suggested by Dawson and Nibber-

ing[18]). These ejection studies also demonstrate that in the absence of hydroxide, the ratio of the $B_{AC}2$-to-S_N2 pathways is 1.3 and that they constitute only a minor portion of the product distribution, while the competing pathways for proton and hydrogen abstraction dominate.

Methoxide may result from two possible mechanisms, $B_{AC}2$ substitution or proton abstraction. We rule out the $B_{AC}2$ process because in addition to methoxide, HCOO· would be produced. This is unlikely because the electron affinity of HCOO· is greater than that of H_3CO.[31] There is question as to whether or not HCOO· is stable,[32] decomposing to form H· and CO_2. The alternative is proton abstraction, which as seen from Table I is 5 kcal exothermic. Assigning formation of methoxide to this source would be consistent with the results observed for NH_2^- and OH⁻ in which proton abstraction is competitive with the $B_{AC}2$ and S_N2 reactions.

Reaction of ¹⁸O⁻ with methyl pivalate results in only two anionic products, with m/z 101 and 103. The product at m/z 101 is the result of the S_N2 reaction, $(CH_3)_3CCOO^-$ (eq 28). The product

at m/z 103 incorporates an ¹⁸O⁻, $(CH_3)_3CCO^{18}O^-$, and results from the $B_{AC}2$ mechanism (eq 27).

O₂⁻·. The superoxide radical anion was not observed to give any anionic products. O_2^-· has been shown to react in the gas phase with phenyl acetate via a $B_{AC}2$ mechanism in which the leaving group is phenoxide.[33] In the case of methyl formate, O_2^-· is not a strong enough nucleophile to displace CH_3O^-, a stronger gas-phase base. The gas-phase acidity of HO_2[34] is between that of phenol ($\Delta H_{acid}° = 349.8$ kcal/mol[35]) and acetic acid ($\Delta H_{acid}°$

(31) EA(CH₃O·) = 36.7 kcal/mol from: Janousek, B. K.; Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 6142–6148. EA(CH₃O·) = 36.2 kcal/mol from: Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1978**, *69*, 1826–1832. EA(HCOO·) = 81.4 kcal/mol from: Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 4050–4052.

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= 348.5 kcal/mol[35]), while the gas-phase acidities of formic acid and methanol are 345.2 kcal/mol[35] and 379.2 kcal/mol,[35] respectively. The order of basicity of the anions is $CH_3O^- > O_2^-\cdot > HCOO^-$. We considered it possible that the reaction would proceed via the S_N2 pathway because $HCOO^-$ might be a better leaving group than $O_2^-\cdot$. This was not observed. Apparently, $HCOO^-$, is not a good enough leaving group or the required reaction intermediate is unstable and the reaction does not proceed fast enough to be observed.

Conclusion

For reaction of NH_2^- with methyl formate, under the low-pressure conditions reported here, it has been established that two primary competitive pathways, the $B_{AC}2$ and proton abstraction reactions, exist. In contrast with previous ICR results, our FTMS study clearly contradicts the conclusion that methoxide results exclusively from a proton abstraction process. Direct observation of the NH_2^- solvated methoxide anion establishes that it has far greater stability than assumed by Isolani and Riveros. The present results with hydroxide generally confirm those of previous flowing afterglow and ICR studies. O^- reacts in a manner similar to that described earlier. However, this study establishes that product earlier attributed solely to the secondary reaction of OH^- are, in fact, derived from O^- reaction, as well. When OH^- is continually ejected, proton abstraction by O^- is dominant.

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Nonplanar Structures of the Singlet and Triplet Cyclopropenyl Anions. An ab Initio Study

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Abstract: Both the singlet and the triplet cyclopropenyl anions are found by ab initio MO theory to be strongly distorted from planarity. Discussions of these "antiaromatic" species which have assumed planarity are not realistic. Furthermore, the ground state is a $^1A'$ singlet (C_s) (not a triplet) with one hydrogen strongly out of plane and the other two hydrogens bent out of plane in opposite direction; a C_2 form is also lower in energy than either of the planar Jahn–Teller distorted (C_{2v}) forms. The triplet cyclopropenyl anion, about 15 kcal/mol less stable than the lowest singlet, also prefers nonplanar geometries in order to reduce electron repulsion. Triplets with C_{3v}, C_s, and C_2 symmetries are all over 10 kcal/mol more stable than the D_{3h} form. Open-chain $(CH)_3^-$ species also are low in energy, but ring opening is symmetry forbidden. The cyclopropenyl anion is indicated not to be stable toward spontaneous ejection of an electron in the gas phase.

The cyclopropenyl anion, $(CH)_3^-$, the smallest possible Hückel 4π electron system, is often regarded as the "antiaromatic" prototype.[1–3] Breslow's experimental pK_a estimate in solution emphasizes the thermodynamic instability of this species;[3a] no gas-phase studies have been reported and the "disquieting" question has been raised whether $(CH)_3^-$ can exist at all as an isolated entity.[4] Many prior theoretical investigations of the cyclopropenyl anions have assumed planarity of both singlet and triplet states, which we will show in the present paper to be incorrect. Simple Hückel theory assumes the trigonal (D_{3h}) planar form to be a ground-state triplet. Davidson and Borden[4] have discussed the Jahn–Teller distortions of the planar (C_{2v}) singlets which lead to quite unequal C–C bond lengths, but did not compute forms involving out-of-plane movements of the hydrogen atoms. A model study of the same group on the isoelectronic $(NH)_3^{2+}$ dications indicated that nonplanar forms might be important.[5]

Clark first pointed out that the "antiaromaticity" of the planar singlet cyclopropenyl anion could be relieved most effectively by the out-of-plane bending of one of the hydrogens,[6] but only limited geometry optimization was carried out at the ab initio level.

Similar results were obtained by Ha, Graf, and Günthard.[7] The fully optimized diffuse function-augmented study of Chandrasekhar et al.[8] indicated an inversion barrier ($C_s \rightarrow C_{2v}$) of 28.9 kcal/mol for the singlet cyclopropenyl anion at a correlated level (MP2/4-31+G//4-31+G), but triplet forms were not considered. All hydrogens were found to lie out of the carbon plane in the C_s singlet. Hess, Schaad, and Čársky found similar results at the MP2/6-31G* + diffuse p function level, but also did not compute the triplet.[9] In the most extensive prior computational study of $(CH)_3^-$ species (but with CNDO/2 semiempirical theory), Pancir and Zahradnik found a planar D_{3h} triplet ground state to lie

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‡ Bulgarian Academy of Sciences. We are saddened by the death of our colleague, Filip Fratev, on March 31, 1984.
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