(q, J = 7.5 Hz, 2, CH_2 of Et), 1.28 (t, J = 7.5 Hz, 3, CH_3 of Et), 0.97 (d, J = 7.0 Hz, 3, CH_3 on tertiary C with H), 1.23 (s, 3, CH_3 on tertiary C with $-NHCO_2Et$), 0.9–2.3 (m, 18, all H except NH, CH_2 of Et); secondary insertion product δ_{TMS} (CCl_4) 3.93 (q, J = 7.5 Hz, 2, CH_2 of Et), 1.11 (t, J = 7.5 Hz, CH_3 of Et), 0.87 (s, 6, CH_3's on tertiary C's), 1.95 (s, 1, H on C with $-NHCO_2Et$). The two methyl groups on each of the four secondary insertion products should each appear as a doublet. The singlet listed at δ 0.87 is the envelope of these closely spaced, unresolved doublets. The primary insertion product was not present in sufficient quantity for analysis and assignment was based on retention time and selectivity data.

The stereospecificty and selectivity were then calculated from the peak areas in the usual manner. The absolute yield was determined by using acetophenone as an external standard. Total moles of insertion product was then calculated from the area/mol for acetophenone using the calibration factor of 0.78 for the products relative to acetophenone. It was assumed that all the insertion products have the same detector sensitivity.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the California State University, Fullerton Foundation faculty research grant program.

Registry No.—*trans*-1,2-Dimethylcyclohexane, 6876-23-9; ethyl azidoformate, 817-87-8; dichloromethane, 75-09-2.

References and Notes

(1) J. S. McConaghy, Jr., and W. Lwowski, *J. Amer. Chem. Soc.*, **89**, 4450 (1967).
(2) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **89**, 3184 (1967).
(3) R. Belloli, R. H. Wollenberg, and J. P. Jaeger, *J. Org. Chem.*, **37**, 1857 (1972).
(4) D. S. Breslow and E. I. Edwards, *Tetrahedron Lett.*, 2041 (1972).
(5) G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Lett.*, 2037 (1972).
(6) For example, W. Lwowski and F. P. Woerner, *J. Amer. Chem. Soc.*, **87**, 5491 (1965).
(7) W. Lwowski, Ed., "Nitrenes," Interscience, New York, N. Y., 1970, p 203.
(8) Reference 7, p 201.
(9) J. M. Simson and W. Lwowski, *J. Amer. Chem. Soc.*, **91**, 5107 (1969).
(10) W. Lwowski and T. J. Maricich, *J. Amer. Chem. Soc.*, **87**, 3630 (1965).
(11) R. Gleiter and R. Hoffman, *Tetrahedron*, **24**, 5899 (1968).
(12) P. F. Alewood, P. M. Kazmaier, and A. Rauk, *J. Amer. Chem. Soc.*, **95**, 5466 (1973).
(13) W. Lwowski and J. S. McConaghy, Jr., *J. Amer. Chem. Soc.*, **87**, 5490 (1965).
(14) W. Lwowski and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **87**, 1947 (1965).

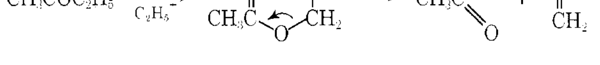
Studies in Chemical Ionization Mass Spectrometry. Mechanisms in Ester Spectra

Barbara L. Jelus, John Michnowicz, and Burnaby Munson*

Department of Chemistry, University of Delaware,
Newark, Delaware 19711

Received March 6, 1974.

We wish to report deuterium labeling experiments on the methane chemical ionization (CI) mass spectrum of ethyl acetate which were designed to establish some of the mechanisms previously postulated to explain the observed products.[1] In the partial CH_4 CI mass spectrum of ethyl acetate (Table I) the major decomposition product is the protonated acid. It was suggested that this ion could be formed in the following manner.[2]



(1)

Table I
CH_4CI Mass Spectra of Ethyl Acetates

m/e	100 I_i/Σ_i $-CH_2CH_3$[a]	$-CD_2CH_3$[b]	$-CD_2CD_3$[c]
61	44.8	45.0	2.3
62	1.1	4.6	30.4
63	0.7	1.0	1.2
87	0.4		
88	0.6		
89	44.8	3.3	0.3
90	2.3	1.0	2.4
91		38.8	0.1
92		1.8	0.4
93			2.6
94			49.4
95			3.2

[a] Registry no., 141-78-6. [b] Registry no., 51472-78-7. [c] Registry no., 51472-79-8.

An average CH_4 CI mass spectrum of $CH_3COOCD_2CH_3$ is also given in Table I. The major processes are the same for the deuterated and undeuterated species. It is apparent from Table I that reaction 1 is the dominant process, since very little deuterium is incorporated in the protonated acid ions.

From these and other data collected at different concentrations of ethyl acetate, repeller voltages of 0–2 V, source temperatures of 110–160°, and CH_4 pressures of 0.5–0.9 Torr, the average ratio of ionic abundances at m/e 62 and 61 was 0.109 ± 0.006. With the appropriate correction of ^{13}C, the ratio of abundances of species $(CH_3CO_2HD^+)/(CH_3CO_2H_2^+)$ is 0.086 ± 0.006. The specificity of the decomposition process is high, but not 100%: incorporation of the deuterium atom from the α carbon occurs about 8% of the time, and reaction 1 occurs about 92% of the time.

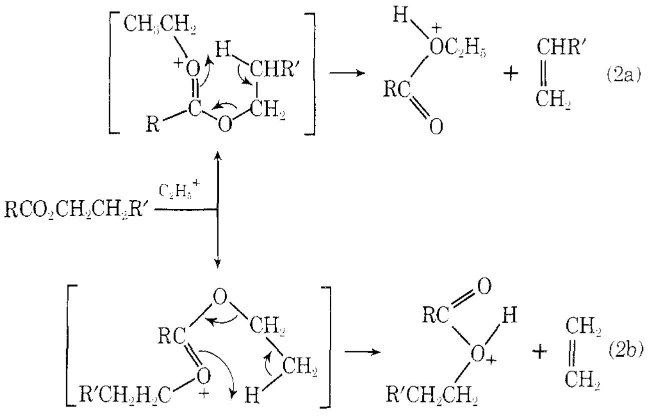
It is of interest to compare the rearrangement decomposition of protonated ethyl acetate in the CH_4 CI mass spectrum with the rearrangement decomposition of the moelcular ion of ethyl acetate in the electron ionization (EI) mass spectrum. The formation of CH_3COOH^+ from the molecular ion by the McLafferty rearrangement is the comparable process, involving the transfer of only one H (or D) atom. The observed ratio[3] for $(CH_3COOH^+)/(CH_3COOD^+)$ from the high-voltage EI spectrum of $CH_3COOCD_2CH_3$ was 0.7:0.3.

Appreciable scrambling occurs prior to decomposition of the radical molecular ions, $M\cdot^+$, produced by electron ionization. Little scrambling occurs prior to the decomposition of the even-electron $(M + H)^+$ ions produced in the methane CI spectra.

In the CH_4 CI spectra of alkyl esters, there were observed[1] ions of the type $RCOHOC_2H_5^+$. It was suggested that these "alkyl exchange" ions could be the result of the decomposition of an intermediate ethyl addition $(M + C_2H_5)^+$ ion (which is observed under some conditions in the CH_4 CI spectra of esters). This $(M + C_2H_5)^+$ ion can decompose in two ways (eq 2a and 2b).

Reactions 2a and 2b are, of course, indistinguishble for the unlabeled esters (R′ = H), but would give different products if the original alkyl group were propyl or higher (R′ = CH_3, . . .). Differentiable products will be produced if the original alkyl group of the ester is labeled, $CH_3COOCD_2CH_3$ and $CH_3COOCD_2CD_3$.

If the proposed mechanism is correct, the displacement reaction (2a) should give $CH_3CO_2HC_2H_5^+$ ions at m/e 89 in the spectrum of $CH_3CO_2CD_2CH_3$ and $CH_3CO_2DC_2H_5^+$ ions at m/e 90 in the spectrum of $CH_3CO_2CD_2CD_3$. Reaction 2b will give $(M + H)^+$ ions at m/e 91 and 94 for these two esters. Reaction 2b cannot be resolved from proton transfer from CH_5^+.



In the CH_4 CI spectrum of the α-dideuterioethyl ester, the abundance of the ion at m/e 89, although small, is significantly higher than the value for $(M - H)^+$ ions in the spectrum of the undeuterated ethyl acetate, m/e 87. This increase in abundance at m/e 89 in the spectrum of $CH_3CO_2CD_2CH_3$ is due to reaction 2a.

The ions expected from reaction 2a with $CH_3CO_2CD_2CD_3$ are observed at m/e 90 and the relative abundance, 2.4% in Table I, is consistent with the amount of reaction 2a observed for $CH_3CO_2CD_2CH_3$, 2.9%.

The difference in relative abundances of $(M + H)^+$ and protonated acid ions between the C_2D_5 ester and the other two esters can be attributed to a lower inlet temperature. It was necessary to use lower temperatures for the C_2D_5 ester than for the others to reduce surface-catalyzed exchange reactions, which were demonstrated by significant abundances of ions at m/e 89 and 61 from $CH_3COOC_2D_5$ and by the observation of changes in the abundances of these ions with temperature. A decrease in abundance of $(M + H)^+$ and an increase in abundance of $CH_3CO_2H_2^+$ with increasing temperature were observed previously[1] and were also noted in these studies.

In chemical ionization mass spectrometry, the reagent ions may also be labeled in order to study mechanisms. Such experiments have been reported with CD_4,[4] ND_3,[5] D_2O,[6] and C_4D_{10}.[7] We have obtained spectra with CD_4 of the three labeled ethyl acetates. These perdeuteriomethane spectra are not reported, however, because small amounts of partially deuterated methane and traces of water are present in the reagent and these impurities caused significant amounts of $(M + H)^+$ ions to be present in the spectra. In spite of this complication, several of the postulated[1] reactions can be confirmed.

In our CD_4 spectra, predominately $(M + D)^+$ ions are observed. This indicates that the protonated ethyl acetate obtains a hydrogen from the reactant ions. The observation of predominately $CH_3CO_2HD^+$ for $CH_3COOCH_2CH_3$ and $CH_3COOCD_2CH_3$ and of predominately $CH_3CO_2D_2^+$ for $CH_3COOCD_2CD_3$ indicates that one hydrogen of the protonated acid comes from the reactant ion and the other from the alkyl group as predicted by reaction 1. Small amounts of CH_3CO^+, m/e 43, are observed (~5%) in the CD_4 spectra of the ethyl acetates. This confirms the observations of CH_3CO^+ made under high resolution in CH_4 CI spectra. Reaction 2a is indicated by the formation of small amounts of $CH_3COHOC_2D_5^+$ ions, m/e 94, in the CD_4 spectra of $CH_3COOCH_2CH_3$ and $CH_3COOCD_2CH_3$.

Acknowledgments. The work was supported in part by a grant from the National Science Foundation, GP 20231. We are also grateful to Dr. Paul Kebarle for the gift of $CH_3COOCD_2CH_3$.

References and Notes

(1) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 4337 (1966).
(2) An equivalent mechanism can be written involving alkyl-oxygen protonation, which cannot be distinguished from 1.
(3) E. W. Godbole and P. Kebarle, *Trans. Faraday Soc.*, **58**, 1897 (1962).
(4) M. S. Wilson, I. Dzidic, and J. A. McCloskey, *Biochim. Biophys. Acta*, **240**, 623 (1971).
(5) D. F. Hunt, C. N. McEwen, and R. A. Upham, *Tetrahedron Lett.*, 4539 (1967).
(6) D. F. Hunt, C. N. McEwen, and R. A. Upham, *Anal. Chem.*, **44**, 1292 (1972).
(7) S. G. Lias, A. Viscomi, and F. H. Field, *J. Amer. Chem. Soc.*, **96**, 359 (1974).

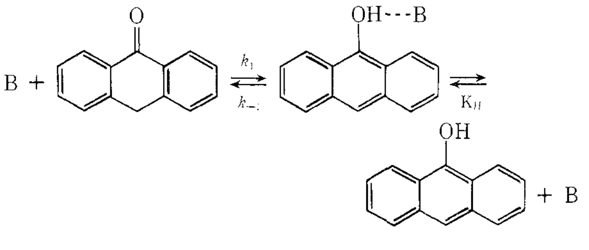
Communications

Proton Migration in an Aprotic Solvent Catalyzed by Very Weak Bases

Summary: Amides and other weak aqueous bases can in an aprotic solvent effectively catalyze an intramolecular migration of a proton from a carbon atom to a distant oxygen.

Sir: Association constants for complexation between p-fluorophenol and a wide variety of bases have provided a measure of base strength in CCl_4.[1] The logarithms of these constants (pK_{HB}'s) do not correlate with pK_a values in water.[2] This has been attributed to a relatively small degree of proton transfer (<30%) within the hydrogen-bonded complexes.[1-3] An alternate explanation for the lack of correlation, namely hydration effects on aqueous basicity, has been rejected.[3,4] The strongest support for the "extent of transfer" hypothesis comes from the observation that upfield F nmr shifts of hydrogen-bonded ion pairs, formed between organic bases and p-fluorobenzenesulfonic acid in CH_2Cl_2, parallel pK_a rather than pK_{HB}.[3]

We have found that extremely weak aqueous bases can assist proton removal from carbon acids in aprotic solvents. Thus, acetamide catalyzes the tautomerization of anthrone to anthranol in acetonitrile. The simplest mechanism for this reaction consistent with the kinetic data is given in eq 1.[5,6] Each of the following reaction variables was determined independently[7] for a variety of bases: k_1 (the rate of the base-catalyzed proton removal from the



(1)