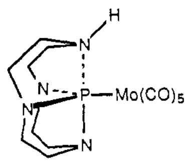
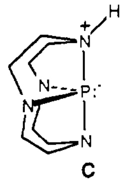
The X-ray structure of **2** shows that the cyclen ring does have the correct bite for a tbp geometry around phosphorus and indeed adopts that orientation via a P–N transannular interaction. This provides the first direct structural evidence for this often-suggested ability.[1-3,14] Moreover, in view of the geometry about phosphorus, the electronics of cyclenP might be best described as a zwitterionic phosphoranide[3d] ligand C.



2



C

Acknowledgment. We thank the Robert A. Welch Foundation for generous financial support. D.V.K. thanks Prof. Narayan S. Hosmane for helpful discussions. We thank Prof. Robert H. Neilson for obtaining the ^{13}C NMR spectrum of **4**.

Supplementary Material Available: Tables of summary of X-ray analysis, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates for **2** (6 pages); tables of observed and calculated structure factors for **2** (11 pages). Ordering information is given on any current masthead page.

---

(13) As an alternative explanation to that in ref 12, the ^{31}P chemical shift may not indicate any transannular interaction since $(Me_2N)_3PMo(CO)_5$ may not be a suitable comparison standard. The upfield position of **2** compared to $(Me_2N)_3PMo(CO)_5$ may be due simply to incorporation of the phosphorus into two five-membered rings. We thank a referee for pointing out this possibility.

(14) Richman, J. E.; Kubale, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 749.

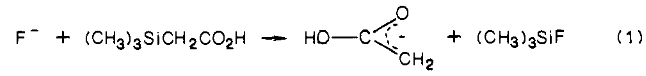
Gas-Phase Ion Chemistry of the Acetic Acid Enolate Anion $[CH_2CO_2H]^-$

Richard A. J. O'Hair,[1a,b] Scott Gronert,[1b]
Charles H. DePuy,[1b] and John H. Bowie*[,1c]

Department of Organic Chemistry
The University of Adelaide, Adelaide 5001
South Australia, Australia
Department of Chemistry and Biochemistry, University of
Colorado, Boulder, Colorado 80309-0215

Received November 14, 1988

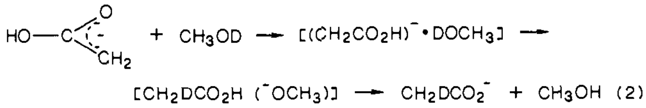
Deprotonation of acetic acid forms mainly the acetate anion $CH_3CO_2^-$ [$\Delta G^\circ_{acid}(CH_3CO_2H)$] = 341.5 kcal mol^{-1}].[2] The isomeric enolate ion $[CH_2CO_2H]^-$[3] has not been studied in the gas phase, although it is implicated in condensed phase reactions.[4] We wish to report that in our tandem flowing afterglow-selected ion flow tube (FA-SIFT),[5] the acetic acid enolate anion can readily be prepared by the reaction shown in eq 1.[6]



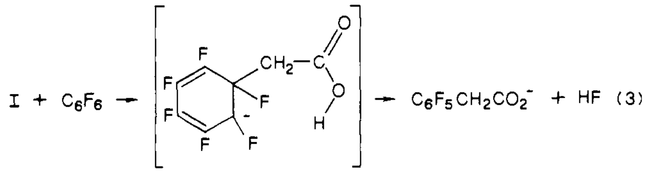
$$F^- + (CH_3)_3SiCH_2CO_2H \rightarrow HO{-}C(O)CH_2^- + (CH_3)_3SiF \quad (1)$$

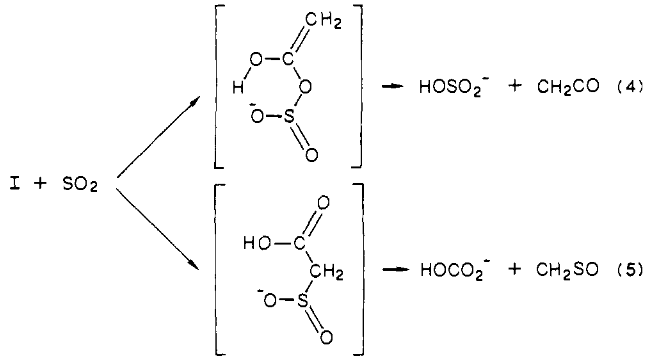
I

Enolate ion I deprotonates acetone [ΔG°_{acid} = 361.9 kcal mol^{-1}][7] but not methyl acetate [ΔG°_{acid} = 365.1 kcal mol^{-1}];[7] this brackets $\Delta G^\circ_{acid}(CH_3CO_2H)$ at 363 ± 3 kcal mol^{-1}. Ion I undergoes quite different reactions from that of its isomer the acetate anion II. For example, (i) I (*m/z* 59) reacts readily with CH_3OD to form *m/z* 60 (eq 2);[8] the acetate anion undergoes no deuterium incorporation under these conditions;[9] (ii) I undergoes the characteristic nucleophilic aromatic substitution with C_6F_6[10] shown in eq 3;[11] and (iii) I may act as an ambident nucleophile with SO_2 as shown in eq 4 and 5.[12]



$$HO{-}C(O)CH_2^- + CH_3OD \rightarrow [(CH_2CO_2H)^- \cdot DOCH_3] \rightarrow [CH_2DCO_2H\ (^-OCH_3)] \rightarrow CH_2DCO_2^- + CH_3OH \quad (2)$$





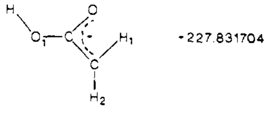
We have shown that thermalized ions I and II are discrete species with quite different reactivities. However, if enolate I is excited (for example, by collisional activation), will it convert to the more stable acetate anion by 1,3 proton transfer?[14] This

---

(1) (a) On leave at Boulder from the University of Adelaide. (b) Boulder. (c) Adelaide.

(2) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *58*, 56.

(3) (a) For early ab initio calculations, see: Wagner, H.-U.; Boche, G. *Z. Naturforsch.* **1982**, *37b*, 1339; *Helv. Chim. Acta* **1983**, *66*, 842. (b) Ab initio calculations on $[CH_2CO_2H]^-$ give the geometry (RHF/6-31+G*) and energy (MP2/6-31+G*//6-31+G*) indicated below (GAUSSIAN 82, Release H—Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; DeFrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. Carnegie Mellon University). Results are as follows (hartrees, Å, deg): HO_1 (0.048), O_1C (1.392), CO_2 (1.244), CC (1.374), CH_1 (1.075), CH_2 (1.075), HO_1C (103.68), O_1CC (114.94), O_2CC (130.68), CCH_2 (119.36), CCH_1 (120.96), planar.



-227.831704

(4) Angelo, M. B. *C. R. Acad. Sci. Paris, C* **1973**, 293. Nesmeyanov, A. N.; Surkov, B. A.; Sazonova, V. A.; Zaimovskaya, T. A. *Dokl. Akad. Nauk. SSSR* **1974**, *219*, 614.

(5) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1987**, *109*, 4412.

(6) (a) The generation of gas-phase anions from trimethylsilyl compounds is reported by the following: DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012. (b) The $(M - H^+)^-$ ion is also a product of the reaction between F^- and $Me_3SiCH_2CO_2H$ (branching ratio 0.10). (c) $Me_3SiCH_2CO_2H$ is a commercial product.

(7) Bartmess, J. E.; McIver, R. T. The Gas Phase Acidity Scale. In Gas Phase Ion Chemistry; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 99. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(8) (a) The ion $[(CH_2CO_2H)^- + CH_3OD]$ is also detected in this experiment. (b) Anion I undergoes slow incorporation (one deuterium) with D_2O at high D_2O flows.

(9) (a) The acetate ion is made by the reaction $F^- + (CH_3)_3SiOCOCH_3 \rightarrow CH_3CO_2^- + (CH_3)_3SiF$. (b) The only detectable product of the reaction between $CH_3CO_2^-$ and CH_3OD is $[CH_3CO_2^- + CH_3OD]$.

(10) For other nucleophilic aromatic substitution reactions of perfluorobenzenes, see: Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 6520.

(11) (a) The ion $[(CH_2CO_2H)^- + C_6F_6]$ is also noted: branching ratio $[(CH_2CO_2H)^- + C_6F_6]{:}C_6F_5CH_2CO_2^-$ = 1:2. (b) $CH_3CO_2^-$ reacts with C_6F_6 to give only $[CH_3CO_2^- + C_6F_6]$.

(12) (a) The ion $[(CH_2CO_2H)^- + SO_2]$ is also noted: branching ratio $[(CH_2CO_2H)^- + SO_2]{:}HOSO_2^-{:}HOCO_2^-$ = 4:4:1. (b) $CH_3CO_2^-$ reacts with SO_2 to give only $[CH_3CO_2^- + SO_2]$.

(13) Bowie, J. H.; Blumenthal, T. *J. Am. Chem. Soc.* **1975**, *97*, 2959. Szulejko, J. E.; Bowie, J. H.; Howe, I.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 99.

0002-7863/89/1511-3105$01.50/0

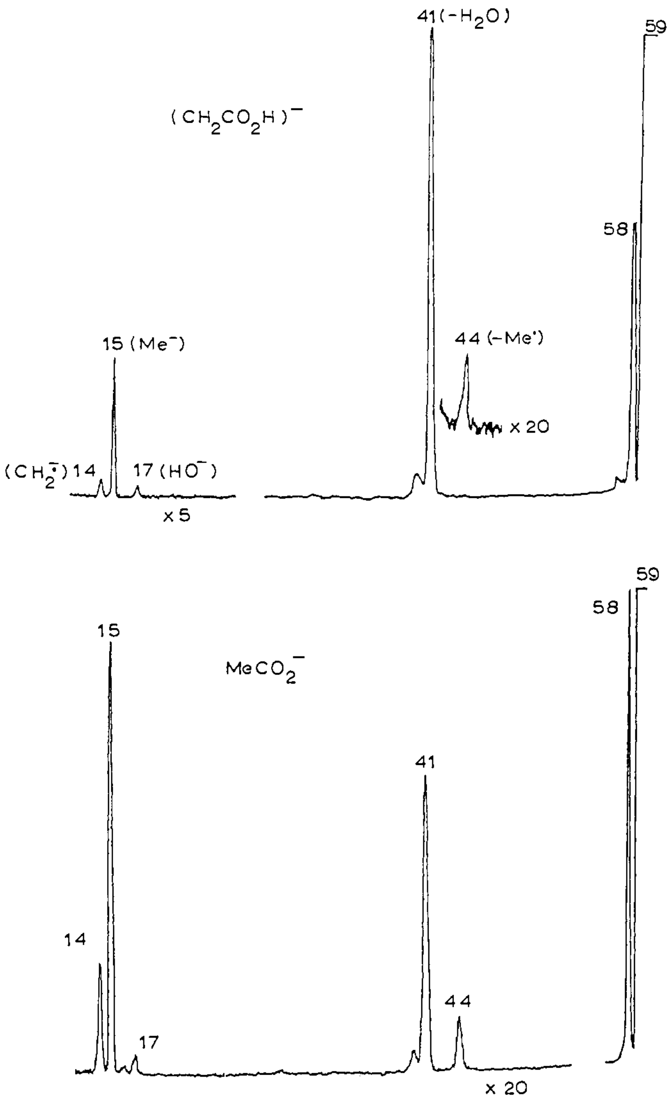


Figure 1. Collisional activation mass spectra of the acetic acid enolate anion and of the acetate anion.

question can be answered by a consideration of the collisional activation (CA) and charge reversal (CR)[13] mass spectra of I and II determined in a conventional mass spectrometer. Thus ions I and II were formed in the chemical ionization source of a ZAB 2HF mass spectrometer.[15,16] The CR spectra[17] are quite different, emphasizing the initial difference in structure of the two anions. For example, I shows major peaks corresponding to $CH_2^{\bullet +}$ and HCO_2^+, while II correspondingly yields CH_3^+ and $CO_2^{\bullet +}$. The CA mass spectra of the two anions are shown in Figure 1. The major fragmentation of I yields *m/z* 41 (eq 6), while II forms CH_3^- and eliminates $H^\bullet$ to yield $^\bullet CH_2CO_2^-$ (*m/z* 58). There is a minor formation of CH_3^- from "I", and this together with the formation of *m/z* 41 from "II"[18] indicates that the acetic acid enolate anion and the acetate anion are interconvertible under conditions of collisional activation.

$$\mathrm{I} \rightarrow [HO^-(CH_2CO)] \rightarrow HC{\equiv}CO^- + H_2O \qquad (6)$$

Acknowledgment. We gratefully acknowledge the support of this work by the National Science Foundation (Grant CHE-8503505 to C.H.D.) and the Australian Research Grants Scheme (to J.H.B.). R.A.J.O. thanks the University of Adelaide for a travel grant.

---

(14) We have calculated (6-311++G) that CH_3CO^- (DePuy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385) should convert by 1,2 H transfer to the acetaldehyde enolate ion over a barrier of 56 kcal mol^{-1} (Downard, K. M.; Sheldon, J. C.; Bowie, J. H. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *86*, 217). In practice this does not occur because of the availability of a more facile decomposition channel ($CH_3CO^- \rightarrow CH_3^- + CO$). Although we have not carried out the appropriate calculation, conversion of I → II should be a more likely process since the barrier for the 1,3 H^+ transfer should be lower than that for a 1,2 H transfer.

(15) V.G. Analytical Ltd., Wythenshawe, Manchester, M23 9LE, U.K., Model ZAB 2HF; helium collision gas, single collision conditions—for full experimental details of operation of the instrument, see: Stringer, M. B.; Bowie, J. H.; Holmes, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3888.

(16) Ions I and II were formed by the following reactions in the ZAB 2HF: $CH_3O^-(CH_3ONO) + (CH_3)_3SiCH_2CO_2H \rightarrow \mathrm{I} + (CH_3)_3SiOCH_3$ and $CH_3O^-(CH_3ONO) + (CH_3)_3SiOCOCH_3 \rightarrow \mathrm{II} + (CH_3)_3SiOCH_3$.

(17) CR (positive ion) mass spectra—*m/z* (abundance): I, 45 (65), 44 (18), 42 (100), 41 (22), 31 (23), 29 (49), 28 (21), 17 (5), 15 (4), 14 (26), 13 (6), 12 (4); II, 45 (27), 44 (100), 43 (36), 42 (46), 41 (18), 31 (4), 29 (28), 28 (30), 16 (1), 15 (31), 14 (18), 13 (3), 12 (1).

(18) The conversion of a carboxylate anion by 1,3 H^+ transfer to the enolate anion prior to fragmentation is a standard reaction of alkyl carboxylate anions, see: Stringer, M. B.; Bowie, J. H.; Eichinger, P. C. H.; Currie, G. J. *J. Chem. Soc., Perkin Trans. II* **1987**, 385.

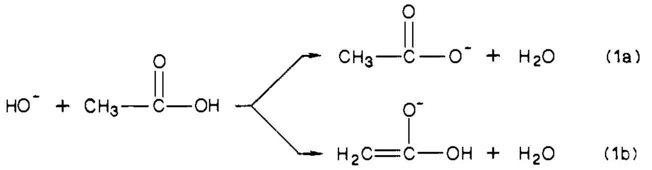
Gas-Phase Formation of the Enolate Monoanion of Acetic Acid by Proton Abstraction

Joseph J. Grabowski* and Xueheng Cheng

Department of Chemistry, Harvard University
12 Oxford Street, Cambridge, Massachusetts 02138

Received November 30, 1988

We wish to report that the hydroxide-induced deprotonation of acetic acid proceeds in the gas phase to give significant amounts of the carboxylate and enolate ions (eq 1).[1] The enolate anion of acetic acid is found to undergo no significant unimolecular isomerization, to display a chemical reactivity distinctive from that of the isomeric carboxylate, and to have a gas-phase basicity 20 kcal mol^{-1} greater than that of the isomeric acetate [ΔG°_{acid} $(CH_3COOH)^2$ = 341.5 ± 1.9 kcal mol^{-1}; ΔG°_{acid} (CH_3COOH) = 361.2 ± 3 kcal mol^{-1}].



$$HO^- + CH_3C(=O)OH \rightarrow CH_3C(=O)O^- + H_2O \qquad (1a)$$

$$HO^- + CH_3C(=O)OH \rightarrow H_2C{=}C(O^-)OH + H_2O \qquad (1b)$$

During our consideration of the detailed mechanism by which thermally equilibrated gas-phase anion-molecule reactions take place, the question was raised as to the selectivity exhibited in anion-induced proton-transfer reactions when the donor molecule contains protons of differing acidities. Lack of selectivity in proton transfers for positive ion systems has been exploited in determining differences in heats of formation of various reactive intermediates of organic chemistry.[3] However, kinetic versus thermodynamic control for proton-transfer reactions remains relatively unexplored in negative ion systems.[4] The test system we examine here is

---

(1) O'Hair, R. A. J.; Gronert, S.; DePuy, C. H.; Bowie, J. H. *J. Am. Chem. Soc.* **1989**, preceding paper in this issue.

(2) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement No. 1.

(3) (a) Ellenberger, M. R.; Eades, R. A.; Thomsen, M. W.; Farneth, W. E.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 7151-7154. (b) Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4845-4846. (c) Pau, C. F.; Hehre, W. J. *J. Phys. Chem.* **1982**, *86*, 321-322. (d) Pau, C. F.; Hehre, W. J. *J. Phys. Chem.* **1982**, *86*, 1252-1253. (e) Pau, C. F.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 16-18. (f) Shin, S. K.; Irikura, K. K.; Beauchamp, J. L.; Goddard, III, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 24-30. (The experimental results in ref f have recently been challenged: Grev, R. S.; Scuseria, G. E.; Scheiner, A. C.; Schaefer, H. F., III; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 7337-7339).

(4) (a) Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650-7653. (b) Ingemann, S.; Nibbering, N. M. M. *Can. J. Chem.* **1984**, *62*, 2273-2281. (c) Bartmess, J. E.; Kiplinger, J. P. *J. Org. Chem.* **1986**, *51*, 2173-2176. (d) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637-640.

0002-7863/89/1511-3106$01.50/0