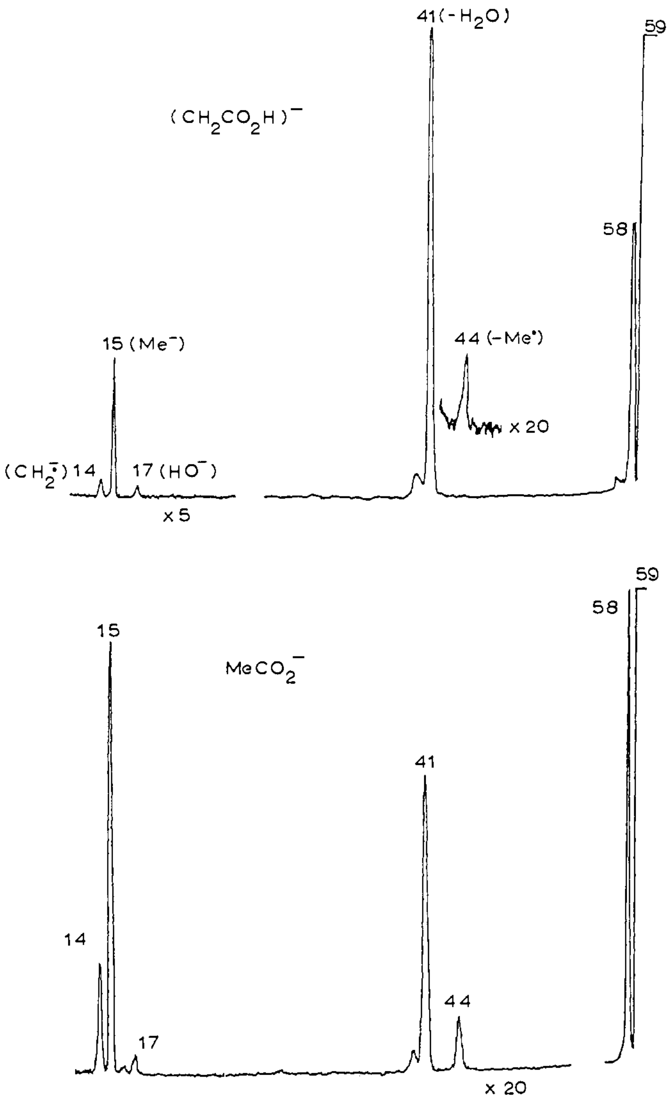

Figure 1. Collisional activation mass spectra of the acetic acid enolate anion and of the acetate anion.

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

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

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.

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[14] We have calculated (6-311++G) that CH$_3$CO$^-$ (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: $CH_3O^-(CH_3ONO) + (CH_3)_3SiCH_2CO_2H \rightarrow$ I + $(CH_3)_3SiOCH_3$ and $CH_3O^-(CH_3ONO) + (CH_3)_3SiOCOCH_3 \rightarrow$ 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

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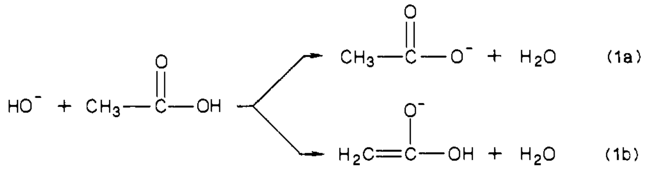
We wish to report that the hydroxide-induced deprotonation of acetic acid proceeds in the gas phase to give significant amounts of the carboxylate and enolate ions (eq 1).[1] The enolate anion



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 [$\Delta G^\circ_{\mathrm{acid}}$ (CH$_3$COOH)[2] = 341.5 ± 1.9 kcal mol^{-1}; $\Delta G^\circ_{\mathrm{acid}}$ (CH_3COOH) = 361.2 ± 3 kcal mol^{-1}].

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

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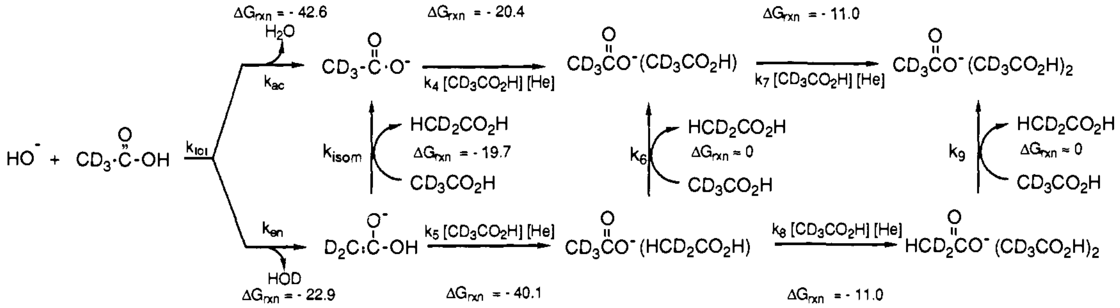
Scheme I[a]

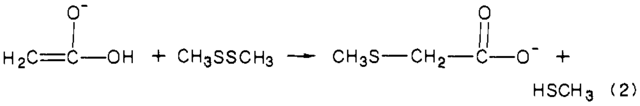


[a] Kinetic scheme that describes the reactions that occur when one allows HO^- to react with CD_3COOH in a flowing afterglow at 300 K and in a 0.30 Torr helium bath gas. The reaction exoergicities are in units of kcal mol^{-1} and are based upon acidities cited in the text and solvation energies obtained from ref 14.

hydroxide ion [$\Delta G°_{acid}$ (H_2O) = 384.1 ± 0.3 kcal mol^{-1}]^2 with acetic acid, in which both proton transfers are considerably exoergic, but wherein one proton resides on oxygen and the others on carbon.

In qualitative flowing afterglow experiments,[5] anhydrous HO^- is observed to form both $(M-H)^-$ and $(M-D)^-$ in good yield, from either CH_3COOD or CD_3COOH.[6] Also evident in the qualitative experiments is fast, acetic acid-catalyzed isomerization of the enolate ion to acetate ion as well as (presumably) termolecular formation of the acetate–acetic acid cluster ion.[7] Reactivity studies of the enolate anion of acetic acid were carried out under conditions in which both enolate and acetate ions were present. Authentic generation of the acetate ion (by dissociative electron attachment to acetic anhydride) and studies of its chemical reactivity, in combination with studies on the above mixture, allowed us to dissect the reactivity due to the enolate ion.

Thus, we find that the enolate anion reacts with dimethyl disulfide[8] as shown in eq 2, while the acetate anion, under identical



$$H_2C{=}C(O^-){-}OH + CH_3SSCH_3 \rightarrow CH_3S{-}CH_2{-}C({=}O){-}O^- + HSCH_3 \qquad (2)$$

conditions, yields only the cluster ion $CH_3CO_2^-(CH_3SSCH_3)$. Other chemical reagents that we have used to differentiate between the isomeric enolate and acetate ions include isoamyl nitrite[9] (the enolate anion gives $ONCH_2CO_2^-$ while acetate does not) and ethanol-O-D (the enolate anion forms $C_2DH_2O_2^-$ while acetate anion does not incorporate any deuterium). Bracketing studies indicate that the enolate anion will abstract a proton from aniline [$\Delta G°_{acid}(PhNH_2)$ = 359.0 ± 1.9 kcal mol^{-1}]^2 or any stronger acid (but not any weaker acid), while $(M-H)^-$ is observed from CH_3COOD with benzyl alkoxide ion [$\Delta G°_{acid}(PhCH_2OH)$ = 363.3 ± 1.9 kcal mol^{-1}]^2 and most stronger bases (but not for any weaker bases).

Complete kinetic studies are necessary to determine the yields of enolate and acetate ions from the proton abstraction by hydroxide from acetic acid because of rapid acid-catalyzed isomerization.[10] A further complication, but of little consequence in uniquely determining the initial product distribution, in the 0.30 Torr (helium) environment of the FA is acetic acid cluster ion formation. The results of our quantitative studies, analyzed according to the kinetic scheme of the type shown, are collected in Table I. We expect that the yield of $(M-D)^-$ for the CH_3COOD reactions reflects not only acetate ion but also a small amount of enolate ion formed from acetic acid that has suffered deuterium loss via H/D exchange on the walls of the apparatus.[11] The results for CD_3COOH are a more accurate representation of the abstraction process; for hydroxide 60% of the abstraction occurs from the carbon and 40% from the oxygen. Even fluoride [$\Delta G°_{acid}(HF)$ = 365.7 ± 0.5 kcal mol^{-1}]^2 gives appreciable amounts of the enolate anion (24%) upon interaction with acetic acid.

Table I. Quantitative Results for Enolate versus Acetate Formation in Proton Abstraction from Acetic Acid by Hydroxide and Fluoride Ions

$B^- + CL_3{-}C({=}O){-}OL'$	k_{en}/k_{ac}	n^a
$HO^- + CH_3{-}C({=}O){-}OD$	50:50	4
$HO^- + CD_3{-}C({=}O){-}OH$	60:40	2
$F^- + CH_3{-}C({=}O){-}OD$	18:82	2
$F^- + CD_3{-}C({=}O){-}OH$	24:76	2

[a] The number of independent experiments which were averaged to give the reported branching ratio.

While neither hydroxide nor fluoride show a statistical proton abstraction result, both demonstrate that competition among available exoergic proton-transfer channels is fierce (i.e., both observed!). A number of control experiments together with those experiments reported above allows us to discount unimolecular isomerization (300 K) and to eliminate acetic acid dimers as being active participants in the helium rich reaction environment. The absence of multiple H/D transfers within one ion–dipole collision complex is demonstrated by the lack of formation of m/z 61 ion (e.g., HCD_2COO^-) in the deuteron abstraction process between HO^- and CD_3COOD.[12] Other preliminary experiments indicate that a variety of carboxylic acids (propionic, isobutyric, and phenyl acetic acids) display the same lack of selectivity. With acetic acid, a large number of bases (amide, phenide, methoxide, ethoxide, benzyl alkoxide, in addition to hydroxide and fluoride) show both proton abstraction processes. The conjugate base of acetonitrile [$\Delta G°_{acid}(CH_3CN)$ = 365.2 ± 1.9 kcal mol^{-1}]^2 and propene [$\Delta G°_{acid}(CH_2{=}CH{-}CH_3)$ = 384.1 ± 1.9 kcal mol^{-1}]^2 are the only bases that we have examined which do not remove a carbon-bound proton from acetic acid, even though such reactions are exoergic. Further investigations into this and various other aspects of these competitive proton transfers are in progress in order to understand why CH and OH abstractions are competitive in spite of long-held beliefs which predict that OH (good hydrogen bonding site and an oxygen acid) should be much faster than CH.[13]

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(10) The lack of enolate ion formation noted in the reaction between HO^- and Et_2CHCO_2D may in fact be due to complete removal of the enolate, by acid-catalyzed isomerization, prior to probing the reaction mixture. Stringer, M. B.; Bowie, J. H.; Eichinger, P. C. H.; Currie, G. J. *J. Chem. Soc., Perkin Trans. II* **1987**, 385–390.

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Bis(ethylenedioxy)tetrathiafulvalene: The First Oxygen-Substituted Tetrathiafulvalene

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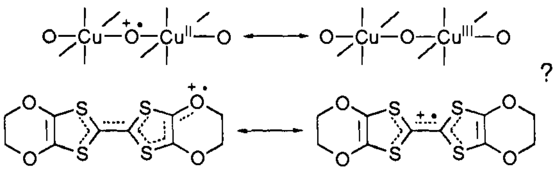
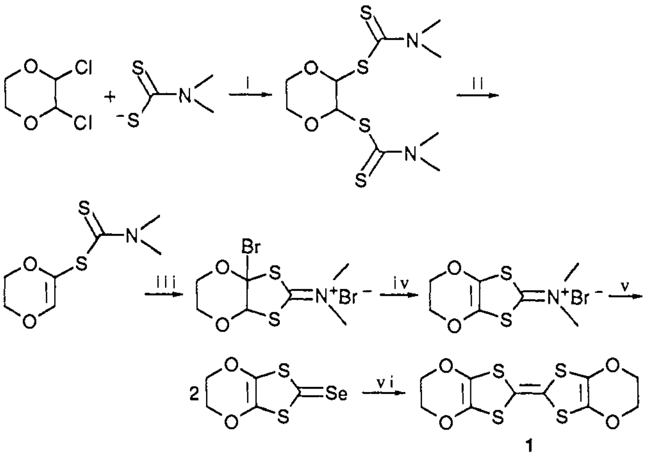
Since the discovery of the high conductivity of its chloride salt,[1] tetrathiafulvalene (TTF) and all its derivatives have become the most investigated donors for the generation of organic metals and superconductors. In the TTF family, the organic metallic state can be achieved with the unsubstituted and variously substituted sulfur, selenium, and tellurium heterocycles but the superconducting state can, so far, be achieved only with derivatives akin to tetramethyltetraselenafulvalene and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, a.k.a. "ET").[2] The highest recorded superconducting transition temperature for an organic superconductor is T_c = 11.2 K[3] for (BEDT-TTF-d_8)$_2$Cu(NCS)$_2$, previously reported by Saito's group[4] as T_c = 10.4 K for the protio sample. While these temperatures are considerably lower than those of the inorganic ceramic, copper oxide based, superconductors (125 K),[5] the rate at which the organic superconductor transition temperatures have been rising with time is still quite impressive [(TMTSF)$_2$PF$_6$, 0.9 K/25 kbar in 1980[6] (BEDT-TTF-d_8)$_2$Cu(SCN)$_2$, 11.2 K/1 bar in 1988[3,4]].

The eruption in solid state science publications caused by the discovery of the copper oxide superconductors[7] has inspired a number of theorists to suggest that the chemical species responsible for the mixed valence in these solids is not the copper couple (Cu^{II}/Cu^{III}) but essentially oxygen radical cations ("holes on oxygen").[8] Some have gone as far as suggesting that results of their calculations can be extrapolated to the design of organic polymeric superconductors.[8a] Inspired by these results, we have been thinking about the possibility of observing metallic and perhaps superconducting behavior with charge-transfer salts based on oxygen-containing donors. Indeed, if the organic superconductors were BCS superconductors,[2] the lighter the component atoms within a series of identical donors, the higher the T_c is expected to be (BCS isotope effect applied to organic superconductors). Also, assuming that the TTF core could be equated to copper, the following analogy may obtain:



However, TTF derivatives with *resonance* electron-donating substituents, such as sp^3-hybridized oxygen or nitrogen *directly* attached[9] to TTF do not exist; the same can be said for tetra-

Scheme I[a]



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[a] (i) CH$_3$CN/reflux, 48%; (ii) 110 °C/DMSO, 58%; (iii) Br$_2$/CH$_2$Cl$_2$, 0 °C, 84%; (iv) 110 °C/25 Torr, 92%; (v) H$_2$Se/MeOH, room temperature, 89%; (vi) (MeO)$_3$P/C$_6$H$_6$, reflux, 63%.

Table I[a]

compd	$^1E^{rev}_{1/2}$, mV	$^2E^{rev}_{1/2}$, mV	ΔE, mV	i^1_{pa}, μA	c, mM
TTF	367	748	381	50.1	1.58
BEDT-TTF	567	829	262	0.205[b]	0.03[b]
BEDO-TTF	435	699	264	18.4	0.53

[a] Conditions: acetonitrile/0.1 M TBAPF$_6$, T = 22 ± 1 °C, glassy carbon working electrode, scan rate 0.1 V/s, Ag/AgCl reference electrode. [b] Saturated solution, Pt electrode.

Table II. Interatomic Distances (Å)

bond	dist	bond	dist	bond	dist
S(1)-C(3)	1.754 (4)	S(3)-C(1)	1.758 (5)	O(3)-C(9)	1.444 (6)
S(1)-C(2)	1.757 (5)	C(1)-C(2)	1.357 (6)	C(3)-C(4)	1.336 (6)
S(2)-C(4)	1.752 (5)	C(7)-C(8)	1.329 (6)	C(3)-O(1)	1.365 (6)
S(2)-C(2)	1.771 (4)	C(7)-O(3)	1.366 (5)	O(2)-C(4)	1.368 (5)
S(4)-C(8)	1.759 (5)	O(4)-C(8)	1.372 (6)	O(2)-C(6)	1.441 (7)
S(4)-C(1)	1.761 (5)	O(4)-C(10)	1.448 (6)	O(1)-C(5)	1.452 (5)
S(3)-C(7)	1.752 (5)				

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