The Gas-phase Basicity and H/D Exchange Characteristics of the Parent Thiocarbonyl Enolate Anions

Lijian Zhang and Joseph J. Grabowski*

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, U.S.A.

The enethiolate anions corresponding to thioacetaldehye and thioacetone, synthesized *via* elimination reactions, undergo H/D exchange reactions, demonstrating the intermediacy of the thiocarbonyl tautomers, and proton transfer reactions, leading to $\Delta G^{\circ}_{\text{acid}}$ [$CH_3CH{=}S$] = 341 ± 3 kcal mol^{-1} and $\Delta G^{\circ}_{\text{acid}}$ [$(CH_3)_2C{=}S$] = 344 ± 3 kcal mol^{-1} (1 kcal = 4.184 kJ).

Thioformaldehyde, thioacetaldehyde, and thioacetone, the three prototypical thiocarbonyl compounds are extremely reactive, readily undergoing polymerization reactions under typical experimental conditions.[1] For example, thioacetone can be kept for a short time at temperatures below −50 °C, but at higher temperatures, it polymerizes quite rapidly.[2] Even in the vapour phase at ~30 mTorr of pressure, the lifetime of thioacetaldehye is of the order of 10 seconds while that of thioacetone is only several minutes.[3] Because of their rapid self-reaction and the difficulty in their generation, relatively little is known about the chemical reactivity of the prototypical thiocarbonyl compounds, as compared to their carbonyl counterparts, despite their obvious role in modelling biochemically important processes. Gas-phase ion-molecule techniques have proven to be invaluable for studying the energetics and dynamics of reactive species[4] but have not yet been applied to thiocarbonyl compounds or their anionic conjugate bases. Moran and Ellison have recently reported a study of the photoelectron spectrum of the molecular anion of thioformaldehyde, in which they found $EA(H_2C{=}S) = 0.465 \pm 0.023$ eV {44.9 ± 2.2 kJ mol^{-1}}[5] and we[6] are in the process of generating and examining other thiocarbonyl molecular anions. Here, we wish to report our findings concerning the generation, basicity, and H/D exchange reactions of the enolate anions of thioacetaldehyde and thioacetone.

All experiments reported herein were carried out under standard conditions in the flowing afterglow (*i.e.*, 300 K and 0.30 Torr of helium).[7] Ethyl vinyl sulphide was commercially available and was purified by distillation prior to use (observed b.p. = 90—92 °C). Ethyl isopropenyl sulphide was synthesized using a literature procedure[8] and was purified by distillation prior to use (observed b.p. = 113—115 °C; purity following distillation was found to be ⩾95% by GC and ^{1}H NMR spectral analysis). The ions F^- and MeO^- were prepared by direct electron ionization of NF_3 and MeOH respectively. Several of the exchange reagents used in this study [CF_3CH_2OD, $CF_3CF_2CH_2OD$, $(CH_3)_3CSD$, and $CH_3CH_2CH(CH_3)CH_2SD$] were prepared by mixing the corresponding protio compound with D_2O, separating the components and repeating the exchange several times. All other compounds or exchange reagents were commercially available and were used as received.

The enolate anions of thioacetaldehyde and thioacetone were generated in the flow tube by rapid, (presumably) *E*2 elimination reactions of F^- with the appropriate sulphide [equations (1) and (2) respectively].[9] For both reactions (1)

Table 1. Summary of bracketing (equation 5) and hydrogen/deuterium exchange (equation 6) experiments for thiocarbonyl enolate anions (R = H, Me).

$$H_2C{=}C(R){-}S^- + HA \rightarrow {?}\ A^- + C_2H_3RS \tag{5}$$

$$H_2C{=}C(R){-}S^- + DA \rightarrow {?}\ \text{H/D exchange} \tag{6}$$

HA[a]	ΔG°_{acid}[b]/ kcal mol^{-1}	ΔH°_{acid}[b]/ kcal mol^{-1}	Is proton transfer observed to. . .[c] R = H	R = Me
CF_3CH_2OH	354.2	361.8	—	No[d] (0)
CH_3SH	350.6	356.9	No	No
$(CH_3)_3CSH$	346.3	352.5	No (0)	No (≥3[e])
$CH_3CH_2CH(CH_3)CH_2SH$	~346[f]	~352[f]	No (≥1[e])	No (5)
H_2S	344.9	351.2	No	Trace
PhOH	342.3	349.2	No	Yes
CD_3CO_2H	—	—	Trace (2)	—
CH_3CO_2H	341.5	348.6	Indeterminate[g] (2)	Yes[d]
$CH_3CH_2CO_2H$	340.3	347.4	Yes (2)	Indeterminate[g]
HCO_2H	338.2	345.2	Yes	Yes
$CH_3COCH_2COCH_3$	336.5	343.7	Yes	—
$\therefore \Delta G^\circ_{acid}[CH_3C(R){=}S]$			341	344
$\{\therefore \Delta H^\circ_{acid}[CH_3C(R){=}S]\}$			(348)	(351)

[a] DA is the same acid as listed except for replacement of the most acidic proton by a deuterium. A dash in any column indicates that data is not available. [b] All acidities, unless noted, are from the standard compilation, ref. 11. [c] The number of H/D exchanges with DA, *via* equation 6, is shown in parentheses. [d] DA used instead of HA for proton transfer studies. [e] Exchange is extremely slow, such that kinetic limitations on observing all equivalent exchanges prevail. [f] Approximate acidity based on analogy to known compounds and some brief experimental work. [g] Because $CH_3CO_2^-$ and $H_2C{=}CHS^-$ [or $CH_3CH_2CO_2^-$ and $CH_2{=}C(CH_3)S^-$] have the same nominal *m/z*, proton transfer is indeterminable.

and (2), the yield of the enethiolate ion is better than 95%; small amounts of the HF*N* thioenolate cluster ion are also observed.[10] Methoxide anion was also used to generate the desired enethiolate ion of thioacetaldehyde in a process analogous to that depicted in equation (1); in this case, the enethiolate was formed in greater than 80% yield in this fast reaction. The results of our acid–base and exchange chemical studies of the enethiolate anions are summarized in Table 1.

$$\underset{m/z\ 19}{F^-} + H_2C{=}CH{-}S{-}CH_2CH_3 \rightarrow \underset{m/z\ 59}{H_2C{=}CH{-}S^-} + H_2C{=}CH_2 + HF \tag{1}$$

$$\underset{m/z\ 19}{F^-} + H_2C{=}C(CH_3){-}S{-}CH_2CH_3 \rightarrow \underset{m/z\ 73}{H_2C{=}C(CH_3){-}S^-} + H_2C{=}CH_2 + HF \tag{2}$$

Hydrogen/deuterium exchange has proven to be an extremely valuable tool for the analysis of gas-phase anion structures and reactivity.[12] In the present case, we find that CH_3CO_2D, CD_3CO_2D, and $CH_3CH_2CO_2D$ react with $H_2C{=}CH{-}S^-$ to give two exchanges (presumably forming $D_2C{=}CH{-}S^-$). In addition to the exchange which is moderately fast for acetic acid (we can readily make the D_2^- ion the most intense of the $L_2C{=}CL{-}S^-$ ions)† and somewhat slower for propionic acid, a trace of direct proton transfer is observed when acetic acid is used while direct proton transfer is the major process detected for propionic acid. 2-Methylpropane-2-[^{2}H]thiol was not observed to undergo any H/D exchange with $H_2C{=}CH{-}S^-$ while 2-methylbutane-1-[^{2}H]thiol underwent such extremely slow exchange that only a small amount of the D_1^- ion ($HDC{=}CH{-}S^-$) could be observed under the longest reaction times amenable to study. Both formic acid and acetyl acetone give rapid proton transfer products when allowed to react with $H_2C{=}CH{-}S^-$. Neither phenol, hydrogen sulphide, 2-methylbutane-1-thiol, 2-methylpropane-2-thiol, nor methanethiol give any proton transfer products with $H_2C{=}CH{-}S^-$. Taken in concert, these bracketing and exchange data which are summarized in Table 1 suggest that the absolute gas phase basicity (ΔG^0)‡ of $H_2C{=}CH{-}S^-$ is 341 ± 3 kcal mol^{-1} (1 kcal = 4.184 kJ).

While $(CH_3)_3SD$ reacts only by H/D exchange with the enethiolate anion of thioacetone, the process is so slow that we are able to observe only the first three exchanges. Under the most forcing of conditions, the observed pattern for the three exchanges in the $(CH_3)_3CSD$ system is exactly that expected for a five-exchange pattern in which the last two exchanges have disappeared into the noise of the mass spectrum. All five protons in $H_2C{=}C(CH_3)S^-$ are clearly observed to exchange with $CH_3CH_2CH(CH_3)CH_2SD$; under the longest reaction times tried, the observed distribution of the partially deuteriated enethiolate anions is approximately as follows:

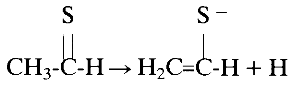
---

† Note that under such conditions, there is no indication of the third H/D exchange.

‡ Using the same data as reported in the text and making the additional assumption that entropy changes in these acid–base reactions are negligible allows one to assign the proton affinities (PA) as follows: PA[$H_2C{=}CH{-}S^-$] = 348 kcal mol^{-1} and PA[$H_2C{=}C(CH_3){-}S^-$] = 351 kcal mol^{-1} where PA[A^-] = ΔH^0_{acid} [AH]. Bartmess and co-workers[13] have previously estimated $\Delta H^\circ_{acid}(H_2C{=}CHSH)$ = 349 ± 8 kcal mol^{-1} based upon the known acidity of ethanethiol and half (an arbitrary guess) the known acidity difference between ethanol and vinyl alcohol.

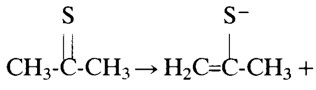
D_0^- (12%), D_1^- (28%), D_2^- (28%), D_3^- (18%), D_4^- (10%), and D_5^- (4%). With phenol, acetic or formic acids, facile, direct proton transfer reactions rapidly yield the conjugate base anions. Hydrogen sulphide is the weakest acid for which a trace of the direct proton transfer reaction is observed. No proton transfer could be deduced as having occurred between $H_2C{=}C(CH_3)S^-$ and 2-methylbutane-2-thiol, 2-methylpropane-2-thiol, methanethiol, or trifluoroethanol. The data for the enethiolate of acetone (see Table 1) clearly shows that it is a stronger base then the enethiolate of acetaldehyde: $H_2C{=}C(CH_3)S^-$ will abstract a proton slowly from hydrogen sulphide and rapidly from acetic acid; it will undergo exchange with 2-methylpropane-2-[^{2}H]thiol ($\geqslant$3 exchanges, slow) and 2-methylbutane-1-[^{2}H]thiol (5 exchanges, moderately slow)—all four processes are substantially different when $H_2C{=}CHS^-$ is the reactant ion.[13] We therefore conclude that the absolute gas phase basicity (ΔG^0)[14] of $H_2C{=}C(CH_3){-}S^-$ is 344 ± 3 kcal mol^{-1}.

The site of protonation of the enethiolate anions remains to be addressed. The observation of successful H/D exchange reactions indicates that protonation on carbon can and does occur. However, the difference in acidities of the two neutrals involved in the successful H/D exchange process here (only a few kcal mol^{-1}) is substantially smaller than that observed for the corresponding carbonyl compounds (*e.g.*, 22 kcal mol^{-1} for acetone enolate exchanging 5 protons with D_2O).[12a] These two observations can be reconciled by preferred kinetic protonation occurring on sulphur.[14] We note that the basicities found for the enethiolates, as compared to the corresponding thiols, are what one would expect for carbon protonation based on the known acidities[11] of the alcohols and carbonyl compounds: acetaldehyde enolate is 11.8 kcal mol^{-1} less basic than ethoxide (that is, $\delta\,\Delta G^0_{\mathrm{acid}} = 11.8$ kcal mol^{-1}) while $H_2C{=}CHS^-$ is 8 kcal mol^{-1} less basic than ethanethiolate and acetone enolate is 6.9 kcal mol^{-1} less basic than isopropoxide, while $H_2{=}C(CH_3)S^-$ is 3 kcal mol^{-1} less basic than propane-2-thiolate. Furthermore, acetone enolate is 2.9 kcal mol^{-1} more basic than acetaldehyde enolate and $H_2C{=}C(CH_3)S^-$ is 3 kcal mol^{-1} more basic than $H_2C{=}CHS^-$ while propane-2-thiolate is 1.9 kcal mol^{-1} less basic than ethanethiolate. These comparisons suggest that either the basicity data reported corresponds to carbon protonation or that enethiolates, which protonate on sulphur, show a different sensitivity to substituent effects than do the simple aliphatic thiols.[15] Therefore, we feel that the anionic basicities found here are indicative of the gas phase acidities of the thiocarbonyl compounds (equations 3 and 4).



$$\mathrm{CH_3{-}\overset{\overset{S}{\|}}{C}{-}H \rightarrow H_2C{=}\overset{\overset{S^-}{|}}{C}{-}H + H^+}$$

$$\Delta G^0_{\mathrm{reaction}} = \Delta G^{\circ}_{\mathrm{acid}}[\mathrm{CH_3CH{=}S}] = 341 \pm 3\ \mathrm{kcal\ mol^{-1}} \quad (3)$$



$$\mathrm{CH_3{-}\overset{\overset{S}{\|}}{C}{-}CH_3 \rightarrow H_2C{=}\overset{\overset{S^-}{|}}{C}{-}CH_3 + H^+}$$

$$\Delta G^0_{\mathrm{reaction}} = \Delta G^{\circ}_{\mathrm{acid}}[(\mathrm{CH_3})_2\mathrm{C{=}S}] = 344 \pm 3\ \mathrm{kcal\ mol^{-1}} \quad (4)$$

Several reactions were tried in an attempt to characterize the enethiolate reactivity beyond that of proton transfer reactions. However, no unambiguous reaction has been found yet that allows one to distinguish between carbon *vs.* sulphur reaction sites, though both dimethyltrisulphide and acetic anhydride are being pursued in this regard. For the most part, the reagent neutrals that are known to react distinctively with carbonyl enolate ions are unreactive or yield only the adduct ion when allowed to react with the enethiolates, as might be expected since the enethiolates are markedly less basic than the corresponding enolate ions.

In conclusion, we have determined the gas-phase basicity of the enethiolate anions corresponding to thioacetaldehyde and thioacetone, and further suggest that these values are very similar, if not identical, to the thiocarbonyl gas-phase acidities. The observation of H/D exchange for both enethiolates coupled with the current understanding of the gas-phase exchange mechanism clearly implies that the thiocarbonyls are readily formed during the exchange process and therefore must be similar in energy to the enethiols. We are continuing our investigations into this family of anions.

We gratefully acknowledge financial support of this work by a National Science Foundation Presidential Young Investigator Award (Grant CHE-8552742).

Received, 21st July 1989; Com. 9/03090E

References

1 R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 277; D. Paquer, *Int. J. Sulfur Chem., Part B*, 1972, **7**, 269.

2 R. D. Lipscomb and W. H. Sharkey, *J. Polym. Sci.*, 1970, **8**, 2187.

3 H. W. Kroto, B. M. Landsberg, R. J. Suffolic, and A. Vodden, *Chem. Phys. Lett.*, 1974, **29**, 265; H. W. Kroto and B. M. Landsberg, *J. Mol. Spectrosc.*, 1976, **62**, 346.

4 M. R. Ellenberger, R. A. Eades, M. W. Thomsen, W. E. Farneth, and D. A. Dixon, *J. Am. Chem. Soc.*, 1979, **101**, 7151; S. K. Pollack and W. J. Hehre, *ibid.*, 1977, **99**, 4845; C. F. Pau and W. J. Hehre, *J. Phys. Chem.*, 1982, **86**, 321; 1252; C. F. Pau, W. J. Pietro, and W. J. Hehre, *J. Am. Chem. Soc.*, 1983, **105**, 16; S. K. Shin, K. K. Irikura, J. L. Beauchamp, and W. A. Goddard, III, *ibid.*, 1988, **110**, 24; J. J. Grabowski and X. Cheng, *ibid.*, 1989, **111**, 3106.

5 S. Moran and G. B. Ellison, *Int. J. Mass Spectrom. Ion Processes*, 1987, **80**, 83.

6 J. J. Grabowski and X. Cheng, unpublished data.

7 J. J. Grabowski and S. J. Melly, *Int. J. Mass Spectrom. Ion Processes*, 1987, **81**, 147; J. J. Grabowski and L. Zhang, *J. Am. Chem. Soc.*, 1989, **111**, 1193.

8 D. Schuijl-Laros, *Recueil*, 1972, **91**, 785.

9 W. W. van Berkel, L. J. de Koning, and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1987, **109**, 7602.

10 D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1974, **96**, 3595; C. H. DePuy and V. M. Bierbaum, *ibid.*, 1981, **103**, 5034.

11 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, Supplement 1.

12 (a) J. H. Stewart, R. H. Shapiro, C. H. DePuy, and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1977, **99**, 7650; (b) C. H. DePuy, V. M. Bierbaum, G. K. King, and R. H. Shapiro, *ibid.*, 1978, **100**, 2921; (c) R. R. Squires, C. H. DePuy, and V. M. Bierbaum, *ibid.*, 1981, **103**, 4256; (d) J. J. Grabowski, C. H. DePuy, J. M. van Doren, and V. M. Bierbaum, *ibid.*, 1985, **107**, 7384.

13 J. E. Bartmesss, R. L. Hays, H. N. Khatri, R. N. Misra, and S. R. Wilson, *J. Am. Chem. Soc.*, 1981, **103**, 4746. In this manuscript, the authors interpret their observed product ions from the reaction of bases with 2,2-dimethyl-1,3-thioxolane as being consistent with thioacetone being less acidic than thioacetaldehyde.

14 However, slow exchange between EtSD and the conjugate base of 6,6-dimethylfulvene has also been noted and must be due to a different phenomenon: M. D. Brickhouse and R. R. Squires, *J. Am. Chem. Soc.*, 1988, **110**, 2706.

15 For simple aliphatic thioketone–enethiol tautomerism, it is believed that the tautomers are similar in energy; A. E. Bruno, R. P. Steer, and P. G. Mezey, *J. Comp. Chem.*, 1983, **4**, 104; R. Mayer, *Sulfur Org. Inorg. Chem.*, 1972, **3**, 325, and therefore, one can anticipate only small differences, if any, in basicities of the sulphur and carbon sites.