strength were set equal to one another. The combined data were then fitted by least-squares analysis to a quadratic expression in log (qK_a/p), and the lines indicated in the figures were obtained.

It is possible to relate the coefficients of such quadratic expressions to certain fundamental parameters by which proton transfer reactions may be characterized according to Marcus rate theory.[3] This treatment when applied to the data for the hydrolysis of ethyl isopropenyl ether gives an intrinsic barrier $\Delta G^{\ddagger}_0 = 4.0 \pm 1.2$ kcal/mol ($\Delta G^{\ddagger}_0$ is the free energy of activation for that member, in the present case hypothetical, of the series for whose reaction $\Delta G° = 0$; it is therefore the purely kinetic component of the reaction barrier[3,16]) and a work term $w^r = 9.1 \pm 1.7$ kcal/mol. (w^r is the energy required to bring the reactants together and to form them into a reaction complex.) For ethyl cyclopentenyl ether, the results are $\Delta G^{\ddagger}_0 = 2.1 \pm 0.3$ kcal/mol and $w^r = 13.5 \pm 0.4$ kcal/mol.

These values imply that relatively little of the considerable barrier which these moderately slow reactions experience comes from the actual proton transfer step itself; much of the energy required for reaction is expended in bringing the catalyst and substrate together, performing whatever desolvation is required, and then positioning the two reactants so that proton transfer may take place. Interesting as these results are, however, their significance can be questioned inasmuch as they are based upon a rather arbitrary combination of data for two different types of acid catalyst.

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Supplementary Material Available: Tables I and II of rates of hydrolysis (5 pages). Ordering information is available on any current masthead page.

References and Notes

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Ionization of Group 6 and 7 Protonic Acids in Dimethyl Sulfoxide

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Abstract: Enthalpies of deprotonation, ΔH_D, by K^+DMSYL^- in Me_2SO are reported for 21 alcohols, seven thiols, selenophenol, and the hydrogen halides. Evidence is presented supporting the notion that alkoxide ions interact strongly with counterions and with unionized alcohol. Thiols behave quite differently. By means of a previously reported correlation between ΔH_D and pK_a in Me_2SO, the pK_a's of all compounds discussed here are estimated and compared with scattered literature estimates of acidity. An excellent linear correlation of ΔH_D with Taft's σ^* values is found and shown to be dominated by solvation effects rather than structural effects on intrinsic acidity. The effect of variation of the central atom on the acidity of their hydrides is discussed for group 6 and 7 acids in the gas phase, Me_2SO, and H_2O. Finally, enthalpies of solvation for halide ions from the gas phase to Me_2SO are calculated and compared with published values for solvation in water.

Introduction

The hydrides of group 6 and of the halogens are of such fundamental importance to chemistry that they are considered in the most elementary textbooks. Their organic derivatives—the alcohols, mercaptans and alkyl halides—comprise a considerable fraction of the most useful reactants and intermediates for synthesis, industry, and living systems. Hydroxide, alkoxide, mercaptide, and halide ions are the prototype nucleophiles for mechanistic and synthetic chemistry. Therefore, it would be hard to exaggerate the significance of the Bronsted acid-base pairs of groups 6 or 7. It would be impossible to give a brief outline of their many crucial roles.

In sharp contrast to the importance of these acids and their anions is the dearth of information on their relative propensities to undergo the simplest (and perhaps only) reaction which they have in common—proton transfer.

The ionization of carboxylic acids and phenols to give resonance-stabilized anions has been a large and fertile area of solution thermodynamics for nearly a century[1-5] since their protolysis is readily studied in aqueous solution within the normal pH scale. However, most aliphatic alcohols are too weak and the hydrogen halides are too strong for convenient study under these conditions, and the few reliable studies of their acid strengths[6-9] have employed nonaqueous media or the use of halogenation to strengthen acidity. Although mercaptans have pK_a's within the pH range, they have received little attention until recently when several studies[10-17] have been reported.

Because of the wide range of acidities involved, and many other technical problems, no report that we know of has attempted a systematic comparison of alcohols, mercaptans, and hydrogen halides under a common set of conditions. Our approach to such a study, as presented in this paper, was made possible through development of a method[18] for measuring heats of deprotonation of acids of widely varied strength in dimethyl sulfoxide (Me_2SO). Elsewhere we have reported preliminary data on alcohol acidities[19] and on the solvation energies of alkoxy and other anions from the gas phase to Me_2SO.[19-22] We have also described[18,22] the remarkably good correlation between heats of deprotonation in Me_2SO (ΔH_D) and available pK_a values in this solvent which validate and extend the use of our measurements as a criteria of acidity.

The present article is intended as a full report of our techniques and results for the acids involved, most of which have not been previously published. We will also discuss them in the light of previous reports and current theories about such systems.

Experimental Section

Materials. Me_2SO was dried, purified, and converted to its alkali metal salt as described previously.[18] Water content was monitored by Karl Fischer (Photovolt Aquatest II), and the solvent was only used if it contained less than 100 ppm H_2O. Most of the proton donors were available from commercial suppliers (Fisher and Aldrich). Perfluoro-*tert*-butanol was obtained from PCR Inc. Professor K. B. Sharpless of M.I.T. generously provided selenophenol. Di-*tert*-butylcarbinol was prepared by reduction of di-*tert*-butyl ketone with $LiAlH_4$.

The authenticity of materials was checked by physical properties and NMR spectroscopy. They were purified until homogeneous to gas-liquid chromatography.

Calorimetry. The basic calorimeter system has been described previously,[18,23] and liquids and solids were introduced as before under protection of a blanket of argon. Gases were introduced using a system developed in this laboratory by Drs. F. M. Jones, III and James Wolf following a previous design reported by Stiles and Felsing.[24]

The calorimeter vessel shown in Figure 1 was a 250-ml silvered Dewar flask capped with a tight fitting Teflon head. This head contained the resistance heater coil, a thermistor, a stirrer shaft, a gas delivery bell, and a line for continuous argon purging. The Teflon head was bolted to the underside of a brass cap (½ in. thick) whose sides extended half-way down the outside walls of the Dewar. The Dewar was immersed in the bath to within 1 cm of its lip. This arrangement allowed the bath, Dewar, and Teflon head to reach thermal equilibrium and to minimize heat leaks. The bath in which the calorimeter was immersed was a Tamson regulated system, which maintained both temperatures constant to ±0.005 °C. Fluctuations in the temperature of the cooling water (circulated through a coil in the bath) had undesirable effects on the ability of the bath to hold a constant temperature. A second bath regulated to ±0.1 °C was used to cool and regulate the cooling water. The cooling water was maintained approximately 5 °C below the main bath setting.

The gas delivery bell was connected to a water-jacketed line, which was part of a small bore (~3-4 mm i.d.) vacuum line with a gas buret connected to a mercury bulb. The system was designed so that gas from a commercial cylinder could be distilled into the gas buret and then condensed in a storage flask with a liquid nitrogen cold trap. The condensed gas was redistilled from the storage flask when desired. Both the gas buret and the delivery line to the calorimeter were water jacketed. The gas was delivered from the buret to the calorimeter at a steady rate by means of a motor driven jack for elevating the mercury bulb. This allowed the gas to be introduced at the same rate it dissolved.[25] The system was calibrated by measuring the heat of solution of HCl in water (−17.90 ± 0.09 kcal/mol) with agreement to one-tenth of a percent with values determined by Gunn and Green[26] (−17.89 kcal/mol).

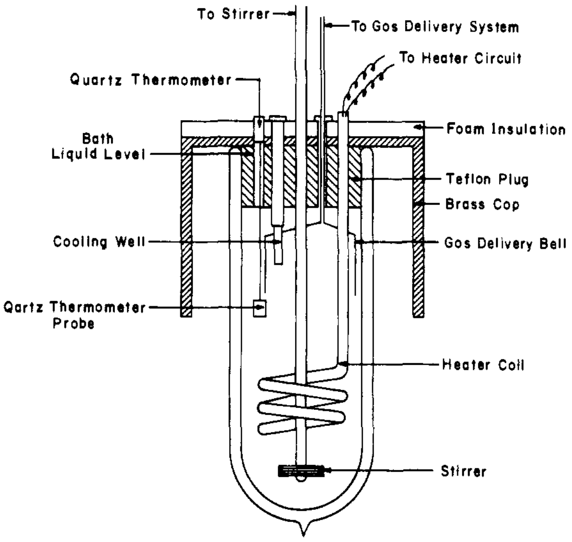


Figure 1. Cross section of gas calorimeter.

Heat of Solution of HF. Due to attack of hydrogen fluoride on glass, the small bore vacuum line could not be used to deliver the sample to the calorimeter. After several unsuccessful attempts with glass and plastic syringes (Becton-Dickenson), a Teflon syringe (Hamilton TF1010) was employed to collect 10 cm^3 samples of the gas. The sample was withdrawn directly from the lecture bottle septum (Hamilton No. 86600) fitted with Hamilton silicon rubber septa. Caution! Since hydrogen fluoride dissolves these septa in minutes, the septum had to be replaced after each sample collection. When 10 cm^3 of HF had been collected in the Teflon syringe, the sample was injected immediately into the calorimeter at a rate sufficient to allow the gas to react completely. Five to seven trials were averaged to give one heat of solution.

Results

We have defined the enthalpy of deprotonation, ΔH_D, of a weak acid in Me_2SO for process 1 as the heat of transfer from Me_2SO to a 0.1 M solution of K^+DMSYL^-

$$HA + DMSYL^- \rightarrow A^- + Me_2SO \qquad \Delta H_D \qquad (1)$$

in Me_2SO at 25 ± 1 °C:

$$\Delta H_D = \Delta \overline{H}_S{}^{DMSYL^-} - \Delta \overline{H}_S{}^{Me_2SO} \qquad (2)$$

The enthalpy of deprotonation can be converted to the enthalpy of ionization, ΔH_i, for the process

$$HA + Me_2SO \rightarrow A^- + Me_2SOH^+ \qquad \Delta H_i \qquad (3)$$

by measuring the heat of autoprotolysis (ΔH_{aut}) for the process

$$2Me_2SO \rightarrow Me_2SOH^+ + DMSYL^- \qquad \Delta H_{aut} \qquad (4)$$

The heat of autoprotolysis was determined through the heat of transfer from high dilution in Me_2SO for acids strong enough to be completely dissociated in Me_2SO to high dilution in a solution of K^+DMSYL^-. If we subtract eq 1 from eq 3, the result is eq 4. Results determined in this laboratory by Moriarity[18] for transfer of HSO_3F from Me_2SO to 0.1 M K^+DMSYL^- gave 48.0 ± 0.8 kcal/mol for the heat of autoprotolysis of Me_2SO. Obviously, the relative values $\delta \Delta H_i$ and $\delta \Delta H_D$ are identical.

Values reported for heats of solution in Table I are averages of six to eight measurements. Errors reported for ΔH_D and ΔH_i are the square roots of the combined variances of the $\Delta \overline{H}_S$ values used to calculate them. All ΔH_D values are in kcal/mol at 25 ± 1 °C.

Completeness of proton transfer is suggested, but not proved, by the reported pK_a's of alcohols (29) in this medium whose H_- is about 33. However, proof that only *clean* depro-

Table I. Thermodynamics of Solution and Deprotonation in Me_2SO with K^+DMSYL^- at 25 °C (all values in kcal/mol)

Compound	$\Delta\overline{H}_S^{Me_2SO\,a}$	$\Delta H_S^{DMSYL^-}$	ΔH_D	$\Delta H_i{}^a$	$\Delta G_i°$, kcal/mol[b]	$\Delta S_i°$, cal/mol-deg
		Alcohols				
Di-*tert*-butylcarbinol	+2.21 ± 0.0	−5.2 ± 0.2	−7.45 ± 0.3	40.6 ± 0.9		
tert-Butyl alcohol	+1.21	−8.0 ± 0.4	−9.2 ± 0.4	38.8 ± 0.9	39.8	−3.4
2-Propanol	+0.87	−8.6 ± 0.2	−9.5 ± 0.2	38.5 ± 0.8		
1-Adamantanol	+4.76 ± 0.30	−4.8 ± 0.2	−9.6 ± 0.4	38.4 ± 0.9		
Neopentyl alcohol	+2.05 ± 0.10	−8.6 ± 0.4	−10.6 ± 0.4	37.4 ± 0.9		
1-Butanol	+0.95 ± 0.03	−10.2 ± 0.1	−11.1 ± 0.1	36.9 ± 0.8		
Ethanol	+0.28	−10.9 ± 0.4	−11.1 ± 0.4	36.9 ± 0.9	37.4	−1.7
n-Amyl alcohol	+1.29	−10.1 ± 0.2	−11.4 ± 0.2	36.6 ± 0.8		
1-Propanol	+0.61	−11.0 ± 0.1	−11.6 ± 0.1	36.4 ± 0.8	38.2	−6.0
Water	−1.28	−13.5 ± 0.2	−12.2 ± 0.2	35.8 ± 0.8	>39.6	>−12.8
Benzyl alcohol	−0.67	−13.7 ± 0.8	−13.0 ± 0.8	35.1 ± 1.1		
Allyl alcohol	−0.37 ± 0.03	−13.4 ± 0.1	−13.1 ± 0.1	34.9 ± 0.8		
1-Heptanol	+1.95 ± 0.10	−11.3 (extrap)	−13.3 ± 0.1	34.8 ± 0.8		
2-Methoxyethanol	−0.56 ± 0.10	−14.3 ± 0.2	−13.8 ± 0.2	34.3 ± 0.8		
Triphenylcarbinol	+1.43 ± 0.10	−14.0 ± 0.5	−15.4 ± 0.5	32.6 ± 0.9		
Methanol	−0.34 ± 0.04	−16.3 ± 0.3	−16.0 ± 0.3[c]	32.1 ± 0.9	34	−7
2,2,2-Trifluoroethanol	−1.83 ± 0.10	−19.6 ± 0.6	−17.7 ± 0.6	30.3 ± 1.0		
Propargyl alcohol	−2.48 ± 0.05	−23.1 ± 0.6	−20.6 ± 0.6	27.4 ± 1.0		
Triphenylsilanol	+2.50 ± 0.11	−18.9 ± 0.4	−21.4 ± 0.4	26.6 ± 0.9		
Ethylene glycol	−0.91 ± 0.10	−22.8 ± 1.1	−21.8 ± 1.1[b]	26.2 ± 1.4		
Perfluoro-*tert*-butyl alcohol	−5.4 ± 0.10	−39.1 ± 0.5	−33.8 ± 0.5	14.2 ± 0.9		

Compound	$\Delta\overline{H}_S^{Me_2SO}$	$\Delta\overline{H}_S^{K^+DMSYL^-}$	ΔH_D	ΔH_i
		Thiols		
Methyl mercaptan	−5.31 ± 0.10	−33.6 ± 0.5	−28.3 ± 0.5	19.7 ± 0.9
tert-Butyl mercaptan	+0.96 ± 0.04	−27.4 ± 0.2	−28.4 ± 0.2	19.6 ± 0.8
n-Butyl mercaptan	+1.08 ± 0.06	−27.3 ± 0.6	−28.4 ± 0.6	19.6 ± 1.0
2-Propanethiol	+0.69 ± 0.02	−27.8 ± 0.3	−28.5 ± 0.3	19.5 ± 0.9
Ethyl mercaptan	+0.39 ± 0.02	−29.6 ± 0.4	−30.0 ± 0.4	18.0 ± 0.9
Hydrogen sulfide	−3.52 (extrap)	−35.9 ± 0.6	−32.4 ± 0.6	15.6 ± 1.0
Triphenylmethyl mercaptan	+4.24 ± 0.25	−28.5 ± 0.4	−32.8 ± 0.5	15.2 ± 0.9
1,2-Ethanedithiol	0.0	−57.8 ± 2.0	−57.8 ± 2.0	−9.8 ± 2.2
		Hydrogen Halides		
Hydrogen fluoride	−22.53 ± 0.3	−109.26 ± 6.0	−86.73 ± 6.0	38.8 ± 6.1
Hydrogen chloride	−17.37 ± 0.3	−52.37 ± 1.0	−35.00 ± 1.0	13.0 ± 1.3
Hydrogen bromide	−24.12 ± 0.4	−58.10 ± 1.0	−33.98 ± 1.1	14.0 ± 1.4
Hydrogen iodide	−25.25 ± 0.9	−66.27 ± 0.7	−41.02 ± 1.1	7.0 ± 1.4

[a] $\Delta H_i° = \Delta H_D + 48 \pm 0.8$ kcal/mol. [b] From data of Ritchie and Uschold (ref 37) corrected to Bordwell's pK_a scale (ref 45). [c] Tabulated in ref 9.

tonation reactions occur is forthcoming from a number of sources. (1) The heats of solution are usually evolved instantaneously or in seconds. (2) ^{1}H NMR studies on the alcohols in Me_2SO-d_6 and the alkoxides in K^+DMSYL^--d_5 gave spectra which were essentially identical, except that the hydroxyl proton was absent. ^{1}H NMR spectra of carbon acids in Li^+DMSYL^- in the first phase of this work were found to correspond exactly to published spectra for the carbanions when literature spectra were available.[12] (3) In two cases, di-*tert*-butylcarbinol and neopentyl alcohol, the K^+DMSYL^- solution was quenched with water, and only the starting alcohol was recovered as shown by gas chromatography and ^{1}H NMR.

Ion Pairing. The question of completeness of deprotonation referred to above is not dealt with satisfactorily merely by comparing the pK_a's of the alcohols and the much less acidic solvent, Me_2SO.

Steiner and Gilbert[27] discovered inconsistencies while titrating weak acids with K^+DMSYL^- in Me_2SO. Price and Whiting[28] had previously used Na^+DMSYL^- to titrate weak acids and had obtained stoichiometric end points. When the weak acids studied were alcohols or water, the end points occurred when only 0.33 to 0.54 molar equiv of acid were added. These inconsistencies were not peculiar to Me_2SO, being also observed in tetrahydrofuran (THF). The conclusion was that hydroxylic compounds drastically reduce the basicity of oxygen anions by hydrogen bonding and that metal cations do the same by ion pairing and aggregation. Other evidence for incomplete deprotonation of alcohols is provided by Ritchie[29] and Cram.[30]

We have attempted to reduce these effects by using low concentrations of alcohol and by employing cations which provide large metal alkoxide dissociation constants such as potassium or cesium since ion pairing of alkoxides is sensitive to cation variation.[28-30] Our ΔH_D's are measured at 10^{-2} to 10^{-3} M in alcohol. The concentration independence of ΔH_D for added alcohol suggests that we are measuring the same process over this range and that the presence of alcohol is unlikely. In order to provide further information on this subject, the enthalpy of deprotonation of 1-butanol was measured in the presence and absence of dibenzo-18-crown-6-ether. This macrocyclic ligand has been reported to complex potassium ion quantitatively and to effectively remove it from the acid-base equilibria.[18] When this experiment was performed with excess crown ether, the resulting $\Delta\overline{H}_S^{K^+DMSYL^-}$ was highly concentration dependent and constantly diminished with increasing alcohol concentration. If the data from this study shown in Figure 2 are extrapolated back to infinite dilution,

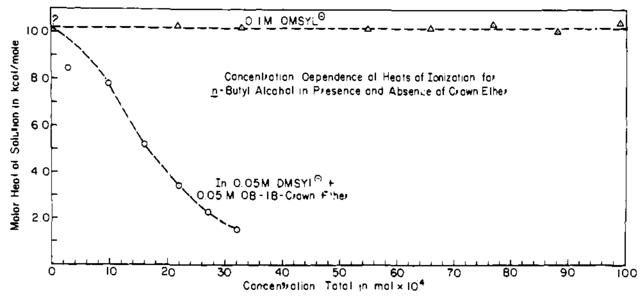


Figure 2. Plot of partial molar heats of solution in K^+DMSYL^- vs. total concentration of alcohol, with and without crown ether present.

Table II. Calculated Percent Dissociation of $K^{+-}O\text{-}Bu\text{-}t$[a]

$K^{+-}O\text{-}Bu\text{-}t \qquad K^+ + t\text{-}BuO^-$

Vol of alcohol injected, µl	Concn	% dissociation
50	0.0025	68
100	0.0055	55
200	0.0105	44
300	0.0160	38
350	0.0185	36

[a] From data in ref 31.

the resulting $\Delta H_S{}^{K^+DMSYL^-}$ with crown ether present is close to, if not identical with, that obtained without crown ether. This observation can be interpreted in terms of incomplete deprotonation in the presence of crown ether due to homoconjugate ion pairing to produce

$$RO^- \text{--} HOR$$

Me_2SO is a poor anion solvator. When the potassium counterion is effectively complexed, the alkoxide ion must resort to other means to obtain stabilization. The obvious possibility is through stabilization from homoconjugation with alcohol. This implies that alkoxide ions can compete effectively with the dimsylate ions for the proton. That alkoxide ions in Me_2SO are comparable in basicity with dimsylate ions and that proton abstraction from Me_2SO can be effected by alkoxides has been suggested by a number of studies.[29]

Our interpretation of the above results implies that in the absence of crown ether there must be significant stabilization of the alkoxide ions by ion pairing to K^+. Support for this conclusion is found in the conductance study of Exner and Steiner.[31] Data in Table II, calculated from their work, indicate that $K^{+-}O\text{-}Bu\text{-}t$ could be about 30–50 percent associated at our concentrations.

The effects of ion pairing and ion aggregation were examined further by changing the alkali metal counterion as shown in Table III. Varying the counterion from lithium to cesium for charge delocalized carbanions was shown previously to produce negligible effects on $\Delta \overline{H}_S{}^{M^+DMSYL^-}$ within experimental error.[32] However for alcohols, changing the counterion from lithium to potassium produced a 5–8 kcal/mol decrease (less exothermic) in $\Delta \overline{H}_S{}^{M^+DMSYL^-}$. The differences observed between potassium and cesium for these compounds was usually within the 1 kcal/mol of experimental error. The majority of work reported here is with K^+ as counterion.

The ion pairing constants reported by Exner and Steiner allow the degree of dissociation for the various metal salts to be calculated as shown in Tables II and IV. The counterion effect on increasing basicity is $Cs^+ > K^+ > Na^+ > Li^+$. The Tables explain at least in part the large differences observed between the lithium and potassium counterions.

Table III. Enthalpies of Reaction of Weak Acids with Different Alkali Metal Dimsylate Solutions at 25 °C[a]

	ΔH_D, kcal/mol		
	Li^+	K^+	Cs^+
1-Butanol	−18.2 ± 0.3	−10.2 ± 0.1	−9.4 ± 0.1
Ethanol	−18.7 ± 0.4	−10.9 ± 0.4	
Water	−21.2 ± 0.4	−13.5 ± 0.2	
Benzyl alcohol		−13.7 ± 0.8	−13.6 ± 0.2
Triphenylcarbinol	−20.7 ± 1.0	−14.0 ± 0.5	−15.8 ± 0.8
2,2,2-Trifluoroethanol	−24.9 ± 0.3	−20.1 ± 0.2	−19.7 ± 0.3
Phenol	−27.7 ± 0.8	−25.0 ± 0.4	−25.5 ± 0.4
tert-Butyl mercaptan	−25.3 ± 0.6	−27.4 ± 0.2	
n-Butyl mercaptan	−26.3 ± 0.2	−27.3 ± 0.6	−26.8 ± 0.8
Isopropyl mercaptan	−25.3 ± 0.7	−27.8 ± 0.3	
Thiophenol	−36.5 ± 0.3	−37.0 ± 0.6	

[a] In this table enthalpies of reaction = $\Delta \overline{H}_S{}^{M^+DMSYL^-}$ (kcal/mol).

Table IV. Calculated Percent Dissociation of Metal Dimyslate Salts[a]

$M^+DMSYL^- \qquad M^+ + DMSYL^-$

M^+	Ka	0.1 M, %	0.05 M, %
Li^+	370	15	21
Na^+	127	25	33
K^+	15	55	67
Cs^+	5	73	83

[a] From ref 31.

Crown Ether Effects on Alkali Mercaptides. The mercaptans, when subjected to the same crown ether experiments, did not display the behavior reported above for alcohols. For example, the $\Delta \overline{H}_S{}^{K^+DMSYL^-}$ for *n*-butyl mercaptan in the presence of dibenzo-18-crown-6-ether is the same within the experimental error as without crown ether. Since the ΔH_D values are not concentration dependent, two conclusions may be inferred: (1) mercaptide ions are not basic enough to partially deprotonate Me_2SO as alkoxide ions probably do; (2) under our calorimeter conditions, mercaptide ions are largely dissociated and undergo little if any homoconjugation.

Cation Effects. Ion pairing constants are not presently available for alkali mercaptides. However, Table III shows that cation variation from Li^+ to K^+ over the same range that produces a difference of 8 kcal/mol in $\Delta \overline{H}_S{}^{M^+DMSYL^-}$ for the alcohols shows no variation within experimental error for the mercaptans. The data with cesium as the counterion are sparse, but nonetheless show similarity to the data with K^+DMSYL^- both for alcohols and mercaptans. The apparent lack of a cation effect for the mercaptans can be attributed to the negligible importance of ion pairing for the mercaptide anion in Me_2SO.

Anomalous Reactions with Dimsylate Ion in DMSO. Not all of the compounds which we have studied gave heats of solution consistent with their acidities. Several β-chloroethanols listed in Table V underwent very exothermic reactions in K^+DMSYL^-. It is apparent that the heats of solution are almost directly proportional to the number of β-halogens. This fact suggests that dehalogenation is probably occurring along with proton transfer. These heats of solution are at least 50

Table V. Anomalous Enthalpies of Reaction in K^+DMSYL^- in kcal/mol

Compd	$\Delta\bar{H}_S{}^{Me_2SO}$	$\Delta\bar{H}_S{}^{K^+DMSYL^-}$
2-Chloroethanol		-77.5 ± 1.0
2,2-Dichloroethanol	-2.77 ± 0.08	-144.4 ± 1.1
2,2,2-Trichloroethanol	-2.79 ± 0.08	-243.0 (extrap)

kcal/mol more exothermic than would be expected if only deprotonation was occurring. Attempts to investigate these highly concentration dependent reactions under calorimeter conditions by NMR were unsuccessful.

Discussion

The results which we have presented are, to the best of our knowledge, the most extensive collection of data yet available for comparing Bronsted acidities of group 6 and 7 proton donors under a standard set of conditions. They are certainly not the only such study, and in this section we will explore their validity and significance by comparing them first with some other published investigations, then with each other (e.g., oxygen acids with sulfur acids) and finally with various theoretical expectations for the relative acidities of such systems.

In Table I we presented the three principal thermodynamic properties, $\Delta H_i°$, $\Delta G_i°$, and $\Delta S_i°$, for a number of the acids reported here. These $\Delta H_i°$ values were calculated from ΔH_D's and the autoprotolysis constant as described previously.[18] If our estimate of the latter value is not accurate it will simply change all $\Delta H_i°$, $\Delta S_i°$, and estimated (see below) $\Delta G_i°$ values by constant terms without affecting relative positions in any column. Unbracketed $\Delta G_i°$ values were measured by Bordwell[45] or Ritchie[46] and adjusted to Bordwell's scale in order to give the greatest possible consistency. Bracketed terms were estimated from ΔH_D using the formula

$$\Delta G_i° = 1.2\Delta H_D - (7.4 \pm 0.9)$$

based on the relationship between pK_a and ΔH_D[49] and the autoprotolysis enthalpy of Me_2SO. The values of $\Delta S_i°$ are obtained by the usual combination of $\Delta G_i°$, $\Delta H_i°$, and T. Since pK_a's were estimated by assuming $\Delta S_i° = 0$, these entropy terms are not listed. In Table VI the pK_a's estimated from our ΔH_D values are compared with a variety of other previously reported acidity data.

The ordinary aliphatic alcohols are well known to be weak acids in aqueous solution,[33,34] and only a few quantitative measures of their acid strengths have been reported. Hine and Hine[35] determined relative alcohol acidities in sodium isopropoxide/isopropyl alcohol by an indicator technique in 1952. Complications from differences in dielectric constant, ion pairing, and hydrogen bonding are apt to render comparison with the present results somewhat dubious.

The currently most reliable acidity measurements for alcohols in water were obtained from conductance studies by Ballinger and Long.[7] Dynamic ionization constants were determined for water and about 12 alcohols. The reported pK_a's gave an excellent ($r = 0.9909$) linear correlation with Taft's σ^* constants.

Probably the most reliable acidity measurements on alcohols in Me_2SO have been reported by Ritchie[9] using a modified glass electrode.[36,37] However, only four alcohols were included in his study.

All results so far show the same order of decreasing acidity regardless of the solvent: methyl > ethyl > isopropyl > *tert*-butyl and was previously ascribed to increasing electron release from the alkyl groups.

In dramatic contrast, relative gas phase acidities[38-40] lead to the acidity order: neopentyl > *tert*-butyl > isopropyl > ethyl > methyl and are attributed to ion-induced dipole interactions within the ion. The discrepancy between these series reveals the importance of solvation and/or ion pairing to acidity ordering in solution.

Quantitative study of the proton transfer reactions of aliphatic mercaptans have been largely overlooked by organic chemists. The data in the literature have primarily been reported by biochemists due to the importance of the sulfhydryl group in biochemical mechanisms.[10,17] Until 1946,[11] except for thiophenol and some of its derivatives, no pK_a's for mercaptans were available.

Most of the pK_a's reported in the literature[11-15] for mercaptans are of low precision. The reported error in some cases ranges from 10 to 32%. Obviously the need for further study is warranted.

The most reliable study of mercaptan acid strengths is probably that of Wadso,[16] who determined dissociation constants by UV spectrophotometry and heats of ionization by calorimetry. However, Wadso was primarily concerned with sulfur-containing amino acids, so only three aliphatic mercaptans were reported in the study.

Even the meager data available for the mercaptans show that they are much more acidic than analogous alcohols. Presently, there are no confirmed explanations for this although it is recognized that sulfur acids have bond dissociation energies for the S-H bond which are about 20 kcal/mol lower than for the O-H bond. Mercaptans are second period acids and have relatively low-lying 3d orbitals which may help to delocalize the charge on the mercaptide ion and contribute to ionization. Conversely, alkoxide ions are probably stabilized more strongly by ion pairing and/or hydrogen bonding in solution.

Hines' pK_e's are compared with our ΔH_D's in Table VI. Even though Hines' data are reported in a hydrogen bonding solvent of low dielectric constant, there is good qualitative agreement between the two acidity orders. However, a plot of the data yields only a poor linear correlation ($r = 0.909$). This is scarcely surprising since different counterions (Na^+ and K^+) were used in the two studies. Also, the dielectric constant of Me_2SO is almost three times that of isopropanol, and isopropanol can stabilize alkoxides by hydrogen bonding.

We were only able to compare $\Delta H_i°$ for seven alcohols with the pK_a's reported by Ballinger and Long[7] in aqueous solution, because of exothermic side reactions following the deprotonations of some of the halogenated alcohols. The lack of even qualitative agreement is quickly apparent, but not surprising, in view of the different standard states and methods involved. An important difference is that conductance studies measure the mobility of free ions, whereas our equilibrium heat measurements undoubtedly contain some contribution from ion pairing.

Obviously, since our $\Delta H_i°$ values correlate exactly with available pK_a's in Me_2SO, their failure to follow Hines' work[6] or Ballinger and Long's[7] implies considerable solvent effects on pK_a's on going from hydroxylic solvents to Me_2SO.

Barrow[41] studying the IR intensities of hydroxyl bands found that the order of the alcohols in terms of these intensities corresponded to the acidity order reported by Hine.[6] The correlation of OH stretching frequencies of alcohols in hydrogen bonding solvents was considered to represent the first stages of ionization. Similarly, Takahashi, Cohen, Miller, and Peake[42] found correlation between the carbonyl stretching frequencies of a series of esters of 3-phenyl propionate in CCl_4 and the acidities estimated from Ballinger and Long's study. Since our data do not correlate well with Hine's nor with Ballinger and Long's, it is not surprising that they also do not correlate well with the infrared studies.

Table VI. Estimated pK_a's of Group 6 and 7 Acids in Me_2SO at 25 °C Compared with Various Published Criteria of Acidity

	pK_a						
Compound	Estd	Lit	pK_e[a]	pK_{HA}[b]	pK_a[c]	pK_a[d]	$\Sigma\sigma^*$
Di-*tert*-butylcarbinol	30.5						−0.82
tert-Butyl alcohol	29.4	[29.2]	0.70		17.0		−0.79
2-Propanol	29.3		1.12		16.8	16.04	−0.68
1-Adamantanol	29.2						
Neopentyl alcohol	28.6				16.3		−0.66
1-Butanol	28.2		ca. 0.22		16.4	15.87	−0.62
Ethanol	28.2	[27.4]	0.02	15.90		15.83	−0.69
n-Amyl alcohol	28.0				16.3		
1-Propanol	27.9	[28.0]	ca. 0.30		16.4	15.92	−0.51
Water	27.5	[>29]	−0.08		15.2		0.0
Benzyl alcohol	27.0		−0.58		15.2	15.44	−0.27
Allyl alcohol	27.0		−0.43	15.50	15.6	15.48	
1-Heptanol	26.8						
2-Methoxyethanol	26.5		−0.90	14.80	15.9	14.87	0.03
Triphenylmethanol	25.5						0.11
Methanol	27.9	[27.0]	−0.60	15.50	16.2	15.07	−0.49
2,2,2-Trifluoroethanol	24.0			12.37	12.6	12.32	0.43
Propargyl alcohol	22.2			13.55	14.3	13.57	
Triphenylsilanol	21.7						
Ethylene glycol	28.4		−1.63	15.10	14.9	15.11	
Perfluoro-*tert*-butanol	13.8						2.27
Hexafluoro-2-propanol	18.2						1.35
Methyl mercaptan	17.3	10.32					
tert-Butyl mercaptan	17.2	11.05					
n-Butyl mercaptan	17.2	10.66					
2-Propanethiol	17.2	10.86					
Ethyl mercaptan	16.2	10.89,10.60					
Hydrogen sulfide	14.7	7.02					
Triphenylmethyl mercaptan	14.4						
1,2-Ethanedithiol	16.9						
Hydrogen fluoride	−19.3						
Hydrogen chloride	13.0						
Hydrogen bromide	13.6						
Hydrogen iodide	9.2						

[a] Reference 6. [b] Reference 7. [c] Estimated from infrared shifts in Ph.D. Thesis of T. Gorrie, Princeton University, 1972. [d] Estimated from data in ref 42.

In a previous communication[19] we combined gas phase acidities determined by McIver with ΔH_D values for some of the alcohols listed here to derive solvation enthalpies for the corresponding alkoxide ions and hydroxyl ion.

Our determination of alkoxide solvation enthalpies showed clearly that the relatively large substituent effects on ΔH_D in Me_2SO were produced by solvation energies in the order $MeO^- > EtO^- > i\text{-}PrO^- > t\text{-}BuO^-$ of such magnitude as to overwhelm gas phase stabilities of these ions in the opposite order. Furthermore, we showed a good correlation between the solvation enthalpy (representing external ion stabilization) and the gas phase deprotonation energy (representing the ability of the ion to stabilize itself internally). It is important to emphasize again that the solvation energies which we have derived for the alkoxide ions through formal application of the Born–Haber cycle probably do not refer to completely dissociated free RO^- ions in Me_2SO. Arguments presented in the Results section suggest that ion pairing to K^+ and homoconjugation by ROH may contribute strongly to the energies of these ions in this medium. Thus the nature of the solvated alkoxide ions may be quite different from that of other anions under the conditions of our study.

Further support for the validity of these data comes from Figure 3 where we have plotted solvation enthalpies of alkoxy ions in Me_2SO vs. corresponding values for primary ammonium ions in water.[43] The range of values for the latter values is about half that of the former as is consistent with the smaller reciprocal dielectric constant for water (0.0125) compared with Me_2SO (0.0286). It also may reflect the fact that the ammonium ions are completely dissociated in water whereas steric effects on ion pairing and solvation may be important for alkoxide ions in Me_2SO.

Taft σ^* Correlation. The close correspondence between ΔH_D's and pK_a's for acids in Me_2SO suggests the use of a linear energy plot. In Figure 4, ΔH_D for 15 alcohols are plotted against $\Sigma\sigma^*$ Taft's aliphatic substituent parameter.[44] The correlation coefficient is good (0.9867), and the slope (−8.00) shows a great sensitivity to what is normally regarded as the ability of the group to stabilize charge by the inductive effect. However, the foregoing analysis shows that the ΔH_D order for alcohols in Me_2SO is actually "anti-inductive" and is produced by ion solvation and ion pairing energies. We thus have for the first time, to our knowledge, a clear case where a good linear free-energy correlation for acid ionization leads to exactly the wrong conclusions about the distribution of charge within the ions produced. We doubt if this is a common occurrence, but it provides a warning against the uncritical use of substituent parameters.

Comparison of Aliphatic Alcohols and Mercaptans. Table VI allows a comparison of ΔH_D for aliphatic alcohols and mercaptans. At our calorimeter conditions the data for the mercaptans are independent of base concentration (0.05 to 0.1 M in M^+DMSYL^-) and independent of solute concentration.

The effect of replacing the hydroxyl group in R-OH with the sulfhydryl group results in a 16 to 20 kcal/mol exothermic

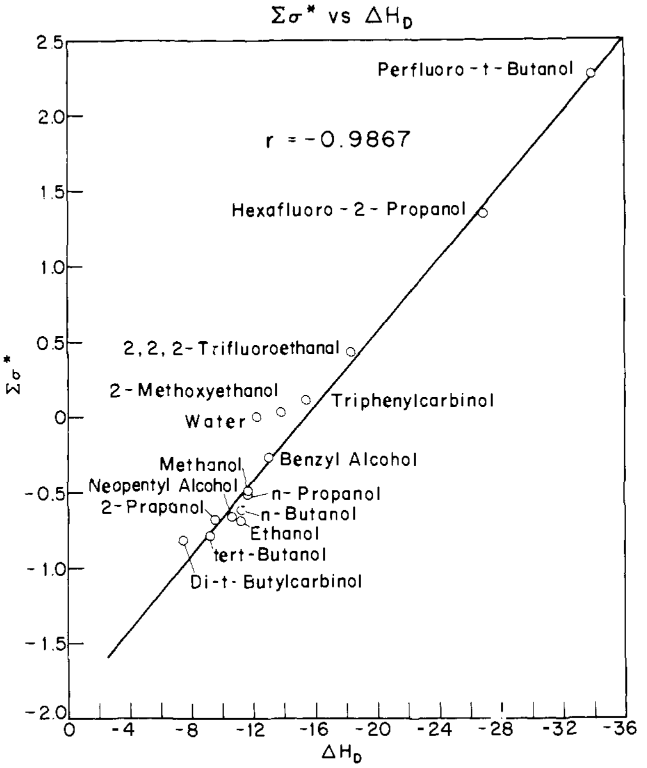


Figure 3. Plot of solvation energies of alkyl ammonium ions, $\delta\Delta_s^{g\text{-}H_2O}(BH^+)$ vs. solvation energies of alkoxide ions, $\delta\Delta_s^{g\text{-}DMSO}(RO^-)$.

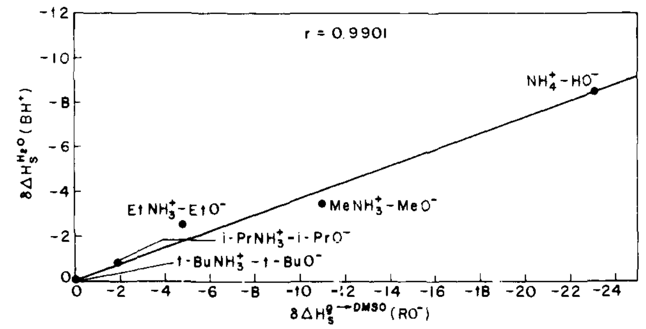


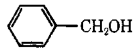
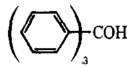
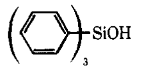
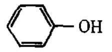
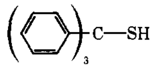
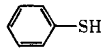
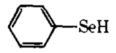
Figure 4. Plot of heats of deprotonation in K^+DMSYL^- vs. Taft's σ^* constants.

increase in ΔH_D. This is consistent with all previous reports that mercaptans are more acidic than alcohols. An interesting contrast has been noted by Zuika and Bankovskii,[47] whose extensive review documents the much weaker hydrogen-bonding ability of mercaptans compared with alcohols. Factors which could contribute to this enhanced acidity: the effects of a longer S-H bond distance, a lower dissociation energy, and a lower electronegativity.[17] Even more important may be the effect of vacant low-lying 3d orbitals, which may provide a greater degree of charge delocalization in the mercaptide anion, although a recent theoretical study[52] strongly discounts this interpretation.

The acidity order of the alcohols in Me_2SO largely followed the inductive order: methyl > ethyl > isopropyl > *tert*-butyl. The acidity order of the mercaptans shows no apparent trend. Kreevoy[13] reported a linear relationship ($r = 0.991$) for pK_a and Taft's σ^* constants. However, a direct comparison of Kreevoy's results to the present study is questionable in view of solvent (aqueous ethanol) and the different methods used to determine the dissociation constants.

Acidity, even in gas phase,[49,50] is a complex property. When it is compounded by solvation terms it is small wonder that acidities in solution have often led to erroneous interpretations at the molecular level. The surprising fact is that often, due to apparently fortuitous correlations, acidity orders in solution do at least reflect gas phase trends rather faithfully. The hydrogen halides in Table VII are a case in point (the alcohols discussed above are a counter example).

Table VII. Enthalpies of Deprotonation of Some Group 6 and 7 Acids

Compd	$\Delta H_D{}^{gas\,a}$	$\Delta H_D{}^{Me_2SO}$	pK_a (water)^a
HOH	390	$-12.2 \pm 0{:}2$	15.7
HSH	250	-32.4 ± 0.6	7.1
HF	370	$[-85.7 \pm 6.0]^b$	3
HCl	333	-35.0 ± 1.0	−7
HBr	324	-34.0 ± 1.0	−9
HI	314	-41.0 ± 1.1	−10
		-13.0 ± 0.8	
		-15.4 ± 0.5	
		-21.37 ± 0.4	
		-24.3 ± 0.4	10.00^c
		-32.8 ± 0.6	
		-36.2 ± 0.6	6.5^c
		-42.2 ± 0.4	

[a] Reference 49. [b] See text regarding correction of this value. [c] C. L. Liotta et al., *J. Am. Chem. Soc.*, 96, 7981 (1974).

A glaring anomaly in our data for the hydrogen halides is the enormous apparent heat of deprotonation of HF which we have placed in brackets in Table VII. Table I shows that the origin of this value is the tremendous exothermic heat of solution of HF in K^+DMSYL^- solution, since the heat of HF in Me_2SO is not out of line with the other hydrogen halides. Although we had considerable experimental difficulty in measuring our values for HF (see Experimental Section), we believe that the numbers presented here are correct within the experimental error shown. We tentatively attribute the large value for reaction with K^+DMSYL^- to formation of bifluoride ion in Me_2SO. The F^---HF hydrogen bond is the strongest presently known.[51]

We have already presented a heavily documented case for the incomplete dissociation of alcohols under these conditions. Since the F--HF bond is probably five times or more as strong as RO^---HOR bond, the argument holds a fortiori in the former case.

Returning to Table VII, it is apparent that for the hydrides of groups 6 and 7 the same orders of decreasing acidity are observed in the gas phase, in Me_2SO and in water: $H_2S > H_2O$ and HI > HBr > HCl > HF.

In both solvents the decrease in acidity on descending the periodic table are much smaller than in the gas phase. Furthermore, water has a much greater leveling effect than does Me_2SO, a result which can be attributed either to its hydrogen bonding ability or its greater dielectric constant. The ambiguity of this explanation could be resolved by an appropriate change of solvent.

Turning to the phenyl substituted cases it is clear that α-silicon strengthens oxy acids better than α-carbon, a result which conforms to previous reports.[53] Comparing triphenyl-

Table VIII. Relative Enthalpies of Ionization and Solvation of Hydrogen Halides and Their Anions in Me_2SO and Water at 25 °C (all values in kcal/mol)

	$\delta\Delta H_S{}^{g\text{-DMSO}}$ (HX) [H_2O]	$\delta\Delta H_D{}^{gas}$	$\delta\Delta H_D{}^{DMSO}$ [H_2O]	$\delta\Delta H_S{}^{g\text{-DMSO}}$ (A^-) [H_2O]	$\Delta H_{trans}{}^{Me_2SO\text{-}H_2O}$ Calcd	$\Delta H_{trans}{}^{Me_2SO\text{-}H_2O}$ Exptl[a]
HI	0 [0]	0	0 [0]	0 [0]	0	0
HBr	1.13 [1]	10	7.0 [−1]	−1.9 [−11]	−9	−4
HCl	7.88 [2]	19	6.0 [−1]	−6.10 [−19]	−13	−7.7
HF	2.77 [−6]	56	14 (corr) −45 (obsd) [11]	−42 (corr) −100.3 (obsd) [−52]	−10	

[a] Reference 56.

carbinol with triphenylmethyl mercaptan or phenol with thiophenol, we see again the same greatly enhanced acidity of sulfhydryl bonds vs. hydroxyl. This trend continues to the highly acidic selenophenol.

Large increases in acidity as the central atom increases in atomic number down a column in the periodic table is seen for all cases in Table VII. The principal factor producing the trend is decreasing bond strength which in turn may be related to the more diffuse bonding orbitals in the larger atoms. The trend is reflected strongly in the classification of these compounds by Hard Soft Acid Base[54] or by Drago's four parameter characterization.[55] We have already mentioned the introduction of $d\pi$-$p\pi$ bonding to explain enhanced acidities of hydrides of larger central atoms.

Solvation Enthalpies of Halide Ions. In other publications[19,21,22] we have discussed the calculation of enthalpies of solvation of anions by combining gas phase and solution acidities with thermodynamic properties of solution for neutral acids. The data presented in Table VIII present the results of such an analysis, using our data in Table I and gas phase data collected by Bell.[49] In each case the reported values are taken relative to HI since it is the strongest acid and is free of the complications described above for HF which might otherwise be the reference compound of choice. Where appropriate we have compared properties in Me_2SO with those in H_2O by showing the latter in brackets below the Me_2SO value. We use Bell's[49] values as a basis for calculating those in aqueous solution. The first column shows that both in Me_2SO and in water, HBr and HCl are somewhat less exothermically solvated from the gas phase than is HI whereas HF is considerably more exothermically solvated. We forbear from interpreting these numbers.

In the third column the relative enthalpies of deprotonation in Me_2SO and water are listed. For HF we list both the observed value, which is anomalously greater than would be expected both in magnitude and sign, and the corrected value which allows roughly for bifluoride formation (see above). The latter is quite consistent with the trends for the other halides in Me_2SO, water, and the gas phase which find HF to be the weakest acid of the series.

In column 4 are the results of combining data in the previous three columns to give relative solvation enthalpies of the halide ions from the gas phase into Me_2SO and water. Clearly, the solvation enthalpy is increasingly exothermic as the size of the ion decreases in conformity with simple electrostatics. However, the variation is somewhat irregular, probably reflecting the accumulation of experimental errors. In conformity with electrostatic theory, the largest variation in solvation enthalpies is found in going from the gas phase to water, the solvent of larger dielectric constant.

In column 5 the data in the previous column are combined to give an estimate of the single ion heats of transfer from Me_2SO to water. This allows a comparison with estimates of the same quantity in column 6 from Cox's recent review of the subject.[56] Although Cox's data are derived by entirely different routes (ours with much greater accumulated error), they are in rough agreement.

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Pyrolyses of Alkyl 2-Methyl- and 2,3-Dimethylcyclopropanecarboxylates and 2-Methylcyanocyclopropane. Effect of Substitution on Geometric and Structural Isomerization. Evidence for Cyclopropane Double Inversion via Reversible Formation of Enols Resulting from Homo-1,5-Hydrogen Shifts

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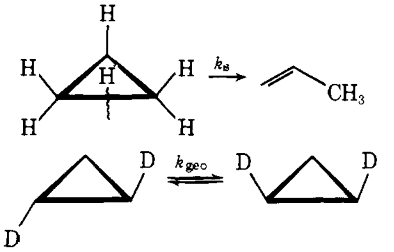
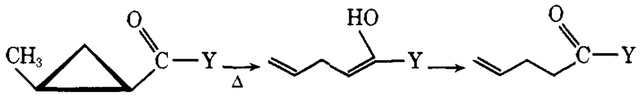
Abstract: Substitution of a carboalkoxy group on cyclopropane reduces the thermal geometric to structural isomerization rate ratio from 20–50 to 5–14, while cyano substitution gives a ratio of 33. Pyrolysis of methyl *cis*-2-methylcyclopropanecarboxylate did not lead to methyl 4-pentenoate, the product reported from homo-1,5-hydrogen shift and ester enol to ester tautomerization. Since ethyl *cis, syn*- and *trans*-2,3-dimethylcyclopropanecarboxylates interconverted at 230-275 °C with $\log k_f\ (s^{-1}) = 11.86 - (39\,900 \pm 700)/2.3\ RT$ and $\log k_b\ (s^{-1}) = 11.86 - (42\,800 \pm 700)/2.3\ RT$, while ethyl *cis,anti*-2,3-dimethylcyclopropanecarboxylate was stable at 275 °C, it is proposed that the cyclopropane double inversion occurs by reversible homo-1,5-hydrogen shift to a γ,δ-unsaturated ester enol which has at least a 45 kcal/mol barrier to undergo the 1,3-hydrogen shift to produce the γ,δ-unsaturated ester.

Structural and geometric isomerization of cyclopropane upon thermolysis is well known, with geometric isomerization being 10–20 times faster than structural rearrangement.[1] Recently, Berson showed that geometric isomerization occurred with stereospecific double inversion with unsubstituted and phenyl-substituted cyclopropanes.[2]



Alkyl,[3a,b] phenyl,[2b] or vinyl[3c] substitution on cyclopropane actually increases the k_{geo}/k_s ratio and, except for monophenyl substitution,[2b] retards double inversion to favor a randomized or "continuous" biradical intermediate.[3d-f] In addition, polar substituents enhance k_{geo} at the expense of k_s—witness Cram's work with geometric and optical isomerization of methyl 2-phenyl-1-cyanocyclopropane-1-carboxylate.[4] With simple carbonyl-substituted cyclopropanes no reactions have been reported save homo-1,5-hydrogen shift and subsequent tautomerization in *cis*-2-alkyl cases to γ,δ-unsaturated carbonyl derivatives.[5]



Y = alkyl or alkoxy

Our interest in alkyl cyclopropanecarboxylates stems from the observation that ethyl spiropentanecarboxylate undergoes structural rearrangement to ethyl methylenecyclobutanecarboxylate faster than geometric isomerization[6] despite the fact that unsubstituted and alkyl-substituted spiropentanes isom-