of the acetoacetyl derivatives, for a leaving group of pK_{LG} = 10, the oxy anion departs some 250-fold faster than the thiolate species; for pK_{LG} = 6.0, the advantage of oxygen over sulfur is some 1000-fold. Use has been made in the literature[7] of the *greater* leaving ability of RS^- than RO^- from sp^3 carbon, but we know of no case in which a direct comparison has been possible for a reaction of well-established mechanism.

As *S*-acetoacetyl coenzyme A was one of the thiol esters used to construct eq 2, its hydrolysis in aqueous solution must occur by the E1cB route and a ketene pathway. In E1cB-transfer reactions, the nucleophile attacks *after* the rate-determining step and exerts but little influence on the transition state.[5,6] We have found that the presence of up to 1.67×10^{-2} M aniline *decreases* rather than increases $k^{S}_{plateau}$ for *S*-acetoacetyl-*N*-acetylcysteamine, but at this alkalinity no acetoacetanilide is formed. Carbinolamine formation with the β-keto group may explain the inhibiting effect of aniline. For *S*-acetoacetyl-*N*-acetylcysteamine, $k^{S}_{plateau}$ is invariant down to about pH 9, where protonation of the conjugate base (ester, pK_a = 8.65 (spectrophotometric titration), 8.50 (kinetic pH profile)) begins to be detectable as a rate decrease.

In view of these observations, we are investigating a series of thiolacetates (including *S*-acetyl coenzyme A), to determine the participation, or otherwise, of a ketene route for their hydrolyses. Carbanions from thioacetates, if formed, would be expected to be very efficient in leaving group expulsion[11a] by analogy with a series of sulfonyl esters which exhibit E1cB hydrolysis (viz., $XSO_2OC_6H_4p\text{-}NO_2$; $k_{plateau}$ for X = $PhCH^- \gg MeN^- \gg O^-$, which is the order of ester pK_a values viz., ~21, 9, and 2, respectively).[11] In this light we might mention the elegant experiments performed to show that (*S*)-malate is formed by enzyme-catalyzed reaction of glyoxalate and *S*-acetyl coenzyme A, with inversion of configuration at the acetyl methyl group.[12] This has been held to implicate the planar (enzyme bound) enolate ion of *S*-acetyl coenzyme A, but is also consistent with collapse of this species to (enzyme bound) ketene, followed by reaction with glyoxalate in the active site. It is also appropriate to mention *S*-malonyl coenzyme A and other biological malonic thiol esters at this stage as malonyl thiol esters have been shown to form enolate ions in base.[4]

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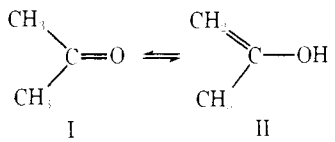
The Enol of Acetone

Sir:

In the condensed phase, acetone is known to exist almost entirely in its keto form (I).[1] The enol tautomer (II), although yet to be directly observed experimentally, has been estimated by bromine titration methods to lie at least 8.2 kcal/mol higher in free energy.[1a] Because prototopic tautomerism is, from all evidence, an extremely facile process, it has not been possible to prepare the enol forms of molecules such as acetone independently of their thermodynamically more stable keto tautomers. Therefore, all that is, in fact, known about the stabilities of such species derives from experiments on two-component equilibria in which the enol is by far the minor component.



I II

We describe in this communication a simple experiment which enables the determination of the thermodynamic stability of the enol form of acetone independent of that of its keto tautomer.[2] The predominant ion-molecule reactions which occur when a mixture of isopropylthiol, perdeuterioacetone, and a base, B, of known proton affinity are added to a pulsed ion cyclotron resonance (ICR) spectrometer[3] (in approximate proportions 100:10:1 and total pressure 3×10^{-6} Torr) are shown in Scheme I. Electron impact on *i*-PrSH leads to a buildup of the protonated compound by way of reaction of initially formed fragment ions with isopropylthiol itself. This in turn reacts exothermically with deuterated acetone to yield the oxygen-protonated compound and with B to produce BH^+. If B is a sufficiently strong base it will be able to abstract acetone's oxygen-bound proton, thus providing an additional source of BH^+. If stronger still, it will be capable of deuteron

Scheme I

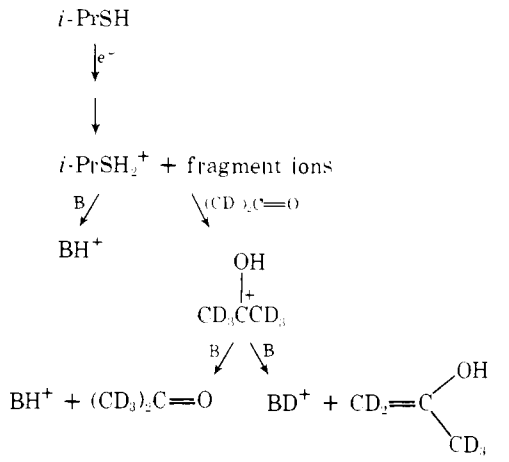


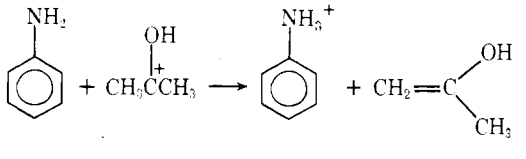
Table I. Observation by ICR Spectroscopy of Deuteron Abstraction from Carbon of Oxygen-Protonated Acetone

Abstracting base, B	Free energy of protonation of B relative to acetone,[a] kcal/mol	Is BD^+ observed?
$(CD_3)_2CO$	0.0[b,c]	No
THF[d]	2.5[b]	No
$(i\text{-}Pr)_2O$	9.1[e]	No
$(MeCO)_2CH_2$	10.7[f]	No
$(i\text{-}Pr)_2S$	13.0[f]	No
$C_6H_5NH_2$	13.9[e]	Yes
$HC{\equiv}CCH_2NH_2$	14.1[e]	Yes
$MeNH_2$	16.4[e]	Yes
$H_2C{=}CHCH_2NH_2$	18.8[e]	Yes
$EtNH_2$	19.1[e]	Yes

[a] Free energies for reactions, $BH^+ + (Me)_2CO \rightleftharpoons B + (Me)_2COH^+$. [b] Experimental data from J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, in press. [c] We have assumed a zero free energy for the reaction, $(CD_3)_2COH^+ + (CH_3)_2C{=}O \rightleftharpoons (CD_3)_2C{=}O + (CH_3)_2COH^+$. [d] Tetrahydrofuran. [e] Experimental data from R. W. Taft in "Proton Transfer Reactions," E. F. Caldin and V. Gold, Ed., Wiley-Halstead, New York, N.Y., 1975, p 31, with small corrections based on additional unpublished results. [f] Unpublished results of R. W. Taft.

abstraction from carbon, leading to formation of BD^+ and concurrently to acetone's enol tautomer. Therefore, by using a series of abstracting bases of known and increasing strength and by monitoring the onset of production of BD^+, it is possible to determine an approximate free energy of carbon deprotonation of acetone. Compared to the known free energy for oxygen deprotonation this yields a value for the heat of formation of the enol of acetone relative to that of its keto tautomer. Our data are displayed in Table I. Isopropyl sulfide (free energy of proton transfer, 13.0 kcal/mol greater than that of acetone) is the strongest base tested for which carbon dedeuteration is not observed. Aniline (free energy of proton transfer, 13.9 kcal/mol greater than that of acetone) does dedeuterate acetone from carbon as evidenced by the production of an ion of mass corresponding to molecular formula $C_6H_5NH_2D^+$. Deuterium incorporation due to reaction with fragment ions (i.e., those from isopropylthiol) is precluded by double-resonance experiments.[3] Specifically, the intensity of the resonance corresponding to an ion of mass BD^+ (for aniline and all stronger bases) was observed to decrease in response to ejection of protonated acetone from the system.

We conclude that proton transfer from protonated acetone to aniline is thermoneutral (i.e., that both the free energy and enthalpy for the process are 0 ± 2 kcal/mol).[4] It follows,



(1)

therefore, that the relative thermochemical stabilities of the keto and enol tautomers of acetone is approximately the same as the difference in free energies of protonation of aniline and acetone in the gas phase, or 13.9 ± 2 kcal/mol.[5] Such an estimate appears to be consistent with the lower limit of 8.2 kcal/mol established by Bell and Smith for the neat liquid.[1a] It seems to the present authors reasonable enough to suggest that specific hydrogen-bonding interactions between the enol of acetone and the solvent are of greater importance than those involving the keto tautomer. If for no other reason this is because a hydroxyl group can participate in three hydrogen bonds (acting once as a proton donor and twice in the capacity of an acceptor), whereas a carbonyl functionally can be involved in only two (in both, as a proton acceptor).[6]

Further experimental as well as theoretical studies are in progress. These are aimed both at elucidating the relative tautomer stabilities of other simple ketones and related systems, and at assessing the importance of solvation in dictating the direction of tautomeric equilibria.

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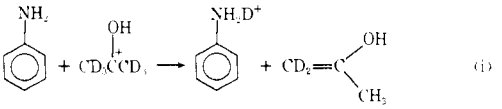

(i)

(5) Two sources of error beyond those already discussed may be identified: (a) the finite resolution of the proton affinity scale, and (b) the likelihood that slightly endothermic proton transfer reactions as well as thermoneutral and exothermic processes will occur. We suspect that the quoted 2 kcal/mol error limit is large enough to take account of these uncertainties.

(6) Note also, that recent experimental[7a] and theoretical[7b] investigations have shown that hydrogen bonds to OH groups which act simultaneously as acceptors and donors are stronger than those involving sites which can function in only one of these capacities.

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Transition Metal Complexes of Novel Ring-Bridged Bis(η^5-cyclopentadienyl) Ligands. Their Synthesis, Chemistry, and Structural Characterization

Sir:

The availability of ligands which constrain two metals to remain in proximity and also allow, but do not require, the formation of a metal–metal bond should lead to a greater understanding of the chemistry of bimetallic systems. For example, the reactivity of organic molecules with metal cluster systems is under intense investigation;[1] however, the reactivity of intact bimetallic metal–metal bonded systems has not been examined as extensively. The metal–metal bond is frequently the most reactive part of the molecule leading to cleavage of the system and the generation of two independent monometallic systems. We wish to report some studies concerning ligands that produce bimetallic systems in which the metals are constrained to remain in proximity. The ligands are of the type $(C_5H_5)_2Z$ and principally three ligands have been examined: α,α'-dicyclopentadienyl-*m*-xylene (**1**), $[m\text{-}C_6H_4(CH_2C_5H_5)_2]$; 2,4-bis[cyclopentadienyldimethylsilyl]-2,4-dicarbacloso-heptaborane (7) (**2**), $[2,4\text{-}B_5H_5C_2[Si(CH_3)_2C_5H_5]_2]$; and dicyclopentadienyldimethylsilane (**3**), $[(CH_3)_2Si(C_5H_5)_2]$. The bridging segments $m\text{-}C_6H_4(CH_2)_2$, $[2,4\text{-}B_5H_5C_2[Si(CH_3)_2]_2]$, and $(CH_3)_2Si$ were selected for these ligands because they were expected to favor complexation of