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DIRECT DETECTION OF THE ENOL OF ACETOPHENONE IN VAPOR PHASE DECARBOXYLATION OF A β-KETOACID

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The thermal decarboxylation of β-ketoacids in solution constitutes a method of ketone synthesis of wide application and interest.[1] These reactions are generally assumed to proceed via the enol (Scheme I) though evidence for this transient intermediate is indirect.[2] Deuterium isotope effects are consistent with unimolecular decomposition through a cyclic six-membered transition state.[3] The analogous reaction in the vapor phase has received little attention.

Additionally, enols such as **2**, which are thermodynamically unstable with respect to their keto tautomers[4] and are also chemically reactive[5] form an important class of organic compounds. These species are commonly cited as intermediates in a wide variety of organic chemical reactions through evidence for their existence in a given mechanistic pathway is generally indirect. Despite an early understanding of these compounds,[6] there exist few studies which provide even a marginal characterization of a member of this family.[7] McMillan, Calvert, and Pitts[8] have reported a partial gas phase infrared spectrum of enol-acetone (H-O stretch at 2.75µ, half-life 3.3 min. at 27°C and 750 torr total pressure). The persistence of this enol is not surprising since, in the absence of acid or base, tautomerization requires a unimolecular 1,3-suprafacial shift which is Woodward-Hoffmann "forbidden"[9] and may require in excess of 45 Kcal/mole activation energy in similar systems.[10] LCAO MO calculations predict an 85 Kcal/mole activation barrier for unimolecular tautomerization of acetaldehyde enol.[11] We now report the direct detection of the enol of acetophenone[12] in the vapor phase thermal decomposition of benzoylacetic acid **1a**,[13] supplying a partial characterization of this enol consisting principally of infrared spectral data at temperatures from ca. -196°C to 20°C.

When **1a** is decomposed by slow sublimation through a hot pyrex column[14] (100-350°C) at ca. 0.01 torr and the pyrolyzed material is collected at -196°C, one isolates only acetophenone (by NMR) after warming to room temperature.

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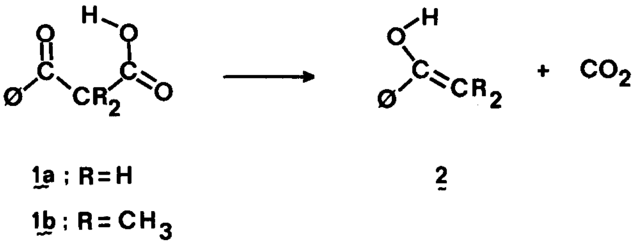

Scheme I

Introduction of excess bromine into the cooled receiver following the pyrolysis leads, upon warming to room temperature, to a mixture (by NMR integration) of acetophenone and ca. 15% α-bromoacetophenone suggesting that <u>at least part</u> of the gas phase decomposition of **1a** proceeds via the enol **2**. Indeed, when excess deuterium oxide is distilled into the cooled receiver following pyrolysis, a mixture (by NMR integration) of acetophenone and ca. 45% α-deuterioacetophenone is isolated. Both of these experiments are consistent with formation of enol **2** and persistence at -196°C for at least the five to ten minutes required for introduction of either bromine or deuterium oxide.[15]

More significantly, when the pyrolysis experiment was conducted with a precooled (ca. -196°C) infrared cell[16] in place of the receiver, the spectrum shown in Figure 1a was recorded. After warming the cell to room temperature, the spectrum in Figure 1b was recorded. <u>Spectra recorded twenty-four hours after warming to room temperature are weaker but qualitatively similar.</u>[17] The low temperature spectra consist principally of bands assignable to acetophenone but contain bands at 3580, 3330, 3215, 2955, 1710, 1610, 1310, 795, 710, and 655 cm^{-1} which are of other origin. Several of these bands are visible in Figure 1a and are marked with arrows. The strong, broad bands at 3330 and 3215 cm^{-1} disappear upon warming to room temperature and remain unassigned. The narrow band at 3580 cm^{-1} is particularly suggestive of a nonhydrogen-bonded enol[18] though *a priori* one might expect such a band from other hydroxylic species such as the β-ketoacid **1a**. This is a strong possibility since **1a** itself is capable of enolization and since the enolic tautomer may well survive pyrolysis, lacking a favorable transition state for loss of carbon dioxide. No such band, however, could be observed in spectra of **1a** under a wide variety of conditions.[19] This ambiguity is removed entirely by performing the analogous IR experiment on the corresponding α,α-dimethylbenzoyl acetic acid **1b**[20] which is not capable of enolization. Again, a persistent (even twenty-four hours after warming to room temperature) and narrow 3580 cm^{-1} band was observed along with bands at 1080, 698, and 600 cm^{-1} confirming the assignment for **2**.

A partial NMR spectrum of transient **2** has been recorded previously by taking advantage of the Chemically Induced Dynamic Nuclear Polarization phenomenon.[21] We are currently investigating the utility of NMR spectroscopy in our own studies.

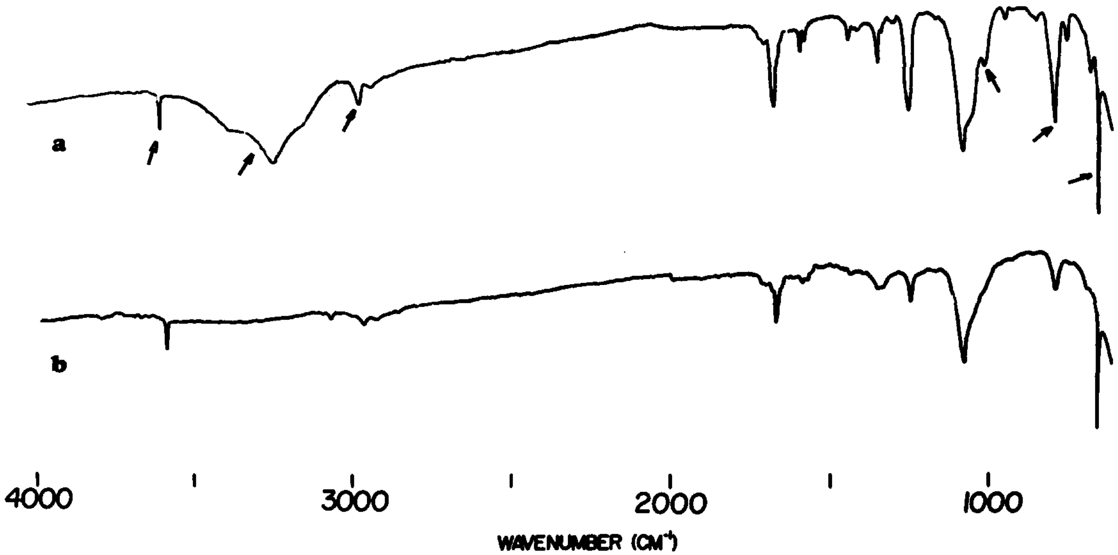

Figure 1. (a) Infrared spectrum of pyrolysate of **1a** collected at ca. -196°C. Arrows indicate bands not assignable to acetophenone or **1a**.
(b) Infrared spectrum of sample prepared as above and then warmed to room temperature.

Acknowledgements

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References and Notes

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2. K. J. Pedersen, *J. Phys. Chem.*, **38**, 559 (1932).
3. M. W. Logue, R. M. Pollack, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **97**, 6868 (1975).
4. S. K. Pollack and W. J. Hehre, ibid., **99**, 4845 (1977) and references therein.
5. One might argue that the term kinetically unstable is appropriate in this context. Since, however, the kinetic instability of these species is probably dependent upon the presence of strong acid or base we describe them as chemically reactive.
6. A description of enols and the phenomenon of tautomerization not unlike the current view can be found in numerous treatise on organic chemistry such as, "The Rise and Development of Organic Chemistry," 2nd Ed., C. Schorlemmer, MacMillan and Co., London, 1894.
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11. W. J. Bouma, D. Poppinger and L. Radom, ibid., 99, 6443 (1977).
12. The enol of acetophenone is both kinetically (in the presence of acid or base) and thermodynamically unstable with respect to acetophenone existing as $3.5 \times 10^{-4}\%$ of an equilibrium mixture with the parent ketone: A. Gero, *J. Org. Chem.*, 19, 1960 (1954).
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14. The glassware in this and subsequently described experiments was pretreated with 5% trimethylsilyl chloride in carbon tetrachloride for twenty-four hours.
15. A less likely explanation might be that the enol tautomer of 1a survives pyrolysis and is brominated or deuterated and then, before NMR analysis, decomposes to the brominated or deuterated acetophenone. In this connection, three deuteria per molecule are rapidly incorporated when a carbon tetrachloride solution of 1a is shaken with excess deuterium oxide. Incorporation of deuterium after formation of acetophenone is unlikely since no incorporation of deuterium is observed by NMR when solutions of acetophenone are shaken with excess deuterium oxide for periods up to one hour.
16. The infrared cell was loaned us by C. W. Brown (University of Rhode Island) and consists of a cesium iodide disk attached to a cold finger and encased in an evacuated chamber with sodium chloride end windows. The entire cell is separated from the vacuum line following the pyrolysis and placed in the sample beam of a Perkin-Elmer 521 Infrared Spectrometer.
17. The pyrolysis experiment yields similar results when the IR cell is cooled to several other temperatures between -196°C and 5°C.
18. This value compares favorably with the reported band at 3629 cm^{-1} for enol-acetone (reference 8) since a shift to higher frequencies is expected in the vapor phase. This peak appears not to be due to traces of water hydrogen-bonded to acetophenone since we were unable to detect such a band in spectra of acetophenone run under the conditions of the experiment.
19. Spectra of 1a were recorded in chloroform solution, as a thin film at -196°C, as a thin film at room temperature, as a potassium bromide pellet, and as a mull with acetophenone. Additionally, literature reports are in agreement with the lack of a 3580 cm^{-1} band in the spectra of 1a. See for example, M. Oki and M. Hirota, *Bull. Chem. Soc. Japan*, 33, 119 (1960).
20. M. W. Logue, *J. Org. Chem.*, 39, 3455 (1974).
21. S. M. Rosenfeld, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 95, 946 (1973).