

group of apparent $pK_a = 1.95$, close to the value expected for the carboxyl group.⁵

We believe that hydrolysis of the neutral species, in the lower pH-independent region, involves general acid catalysis by the carboxyl group; probably of the attack of a molecule of water on the carbonyl carbon atom of the ester, since this is most likely the slow step in the uncatalyzed hydrolysis of esters of this type² and since the attack of other nucleophiles is also catalyzed. Formate ion, for example, attacks the free acid 48 times faster than the anion.⁶ Mechanisms involving the salicylic-acetic anhydride can be ruled out with some confidence because solvolysis in 50% aqueous methanol produces a quantitative yield of 3,5-dinitrosalicylic acid.⁷

(5) This cannot be measured directly, because of rapid hydrolysis. The value obtained by subtracting $2\sigma_m$ from the pK of aspirin (3.36) is 1.94.

(6) A. R. Fersht and A. J. Kirby, unpublished results.

(7) Estimated spectrophotometrically.

A. R. Fersht, A. J. Kirby
University Chemical Laboratory
Cambridge, England
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Nuclear Magnetic Resonance Spectroscopy. Carbon-Carbon Coupling in Cyclopropane Derivatives¹

Sir:

The nature of the bonding in cyclopropane, the smallest and most highly strained carbocyclic ring system, has long been a lively and controversial topic. Walsh² has described the carbon-carbon bonding in cyclopropane as involving a three-center bond, while Coulson and Moffitt^{3a} and Trinajstić and Randić^{3b} have used quantum-mechanical treatments equivalent to bent bonds wherein the regions of highest electron density are not located along the C-C internuclear axes. Molecular orbital calculations of varying degrees of sophistication have been carried out.⁴ A recent summary of the description of bonding in cyclopropanes was given by Bennett.⁵

Nuclear magnetic resonance spectroscopy has been extensively used in the structural analysis of cyclopropane derivatives because the protons directly bonded to the ring give resonances at characteristically high fields.⁶ A comprehensive study of proton-proton coupling in substituted cyclopropanes has been carried out,⁷ and recently Watts and Goldstein⁸ have obtained accurate values of the one-bond carbon-proton coupling constant and the three proton-proton coupling constants in cyclopropane itself.

The carbon orbitals used to form the carbon-proton bonds in cyclopropane have been assigned 33% s character on the basis of the carbon-proton coupling

constant.⁹ Such correlations of carbon-proton coupling with the carbon orbital hybridizations seem valid in hydrocarbon systems. However, when electro-negative substituents are present, the parameter which most strongly influences the coupling constant appears to be the effective nuclear charge of the carbon 2s orbital.¹⁰ Frei and Bernstein¹¹ in their study of carbon-carbon couplings showed experimentally that such coupling constants are proportional to the product of the s characters of the two hybrid orbitals used in forming the bond. This approach was justified theoretically by the molecular orbital calculations of Pople and Santry.¹² Ethane, whose carbon-carbon bond is formed from two sp^3 orbitals (25% s character), has a carbon-carbon coupling constant of 34.6 Hz.¹³ The coupling constant for a carbon-carbon bond formed from an sp^3 - and an sp^2 -hybridized orbital, as in the methyl to ring bond in toluene, is 44.2 Hz.¹¹

Footo¹⁴ in a study of carbon-proton coupling in cycloalkanes has suggested that, because the carbon orbitals forming the carbon-proton bonds have more s character than a normal hydrocarbon, the carbon-carbon bonds must have more p character. If it is assumed that each carbon has a single 2s orbital which is used in forming its bonds¹⁵ and that the two orbitals used in forming the carbon-proton bonds have 33% s character each, this leaves 33% s character to be divided between the two orbitals forming the carbon-carbon bonds, or 17% s character in each hybrid orbital. This is roughly sp^5 hybridization.⁵

The predicted carbon-carbon coupling constant for a single bond between two 2s orbitals based on ethane as a model for an sp^3 - sp^3 bond is $34.6(4)^2 = 550$ Hz. The coupling constant predicted for a bond formed between two sp^5 hybrid orbitals is $550(1/6)^2 = 15$ Hz. The carbon-carbon coupling constants which have been observed for a series of cyclopropane derivatives are given in Table I and are in striking agreement with

Table I. ¹³C-¹³C Coupling Constants for Cyclopropane Derivatives

Compound	Bond	Coupling constant, Hz
Cyclopropyl bromide	1,2	13.3
Cyclopropyl iodide	1,2	12.9
1,1-Dichlorocyclopropane	1,2	15.5
Methylcyclopropane	$\alpha,1$	44.0

the concept of sp^5 hybridization of the orbitals used in forming the internal bonds and sp^2 hybridization for the external orbitals. Substituent effects and the approximations inherent in the simplified description of both the coupling constant and the bonding may account for the minor variations.

(1) Supported in part by the National Science Foundation and Public Health Service Research Grant 11070-04 from the Division of General Medical Sciences.

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The ^{13}C spectra were determined with complete proton decoupling on the Varian DFS-60 spectrometer.¹⁶ Several hundred scans were required to observe the ^{13}C satellites of the ^{13}C spectrum which arise from molecules whose natural abundance is only 0.02%.

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(17) National Science Foundation Predoctoral Fellow 1965-1967.

Frank J. Weigert,¹⁷ John D. Roberts

Contribution No. 3557

Gates and Crellin Laboratories of Chemistry

California Institute of Technology

Pasadena, California 91109

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Base-Catalyzed Hemithioacetal Decomposition at a Diffusion-Controlled Rate¹

Sir:

Measurements of the rate of hemithioacetal formation from acetaldehyde and thiols of differing acidity indicated that the rate of base-catalyzed hemithioacetal decomposition approaches the diffusion-controlled limit as the leaving thiol becomes more acidic.² The hydroxide ion catalyzed decomposition of the hemithioacetals formed by the condensation of acetaldehyde with benzenethiol, *p*-nitrobenzenethiol, and thioacetic acid has now been shown to proceed at a diffusion-controlled rate. In addition, the reaction is subject to general base catalysis with a Brønsted slope near 0.8.

The rate of hemithioacetal breakdown or formation was followed by ultraviolet spectroscopy with a stopped-flow mixing apparatus. Measurement of the equilibrium constants for thiol addition permitted calculation of both rate constants from rate measurements in either direction. The rate constants of the water and hydroxide ion catalyzed reactions were obtained over the range pH 0 to 6.5 from measurements in dilute hydrochloric acid or by extrapolation of rates obtained in buffer solutions to zero buffer concentration. Buffer catalysis was measured at two buffer ratios in most cases, and only the basic species was found to be catalytically active.

The rate constants for the hydroxide ion catalyzed breakdown of the three hemithioacetals are approximately $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, which is in the range expected for a diffusion-controlled reaction (Table I). The value of ΔH^\ddagger for this reaction, from measurements at 2, 25, 30, and 40°, is approximately 2 kcal/mole.

Table I. Decomposition of Hemithioacetals Formed from Acetaldehyde and RSH at 25° and Ionic Strength 1.0 M

RSH	pK_a	K_1^a M^{-1}	k_{H_2O} , sec^{-1}	$k_{OH^-} \times 10^{-10},^b$ $M^{-1} \text{ sec}^{-1}$	
				Obsd	Calcd
CH_3COSH	3.20	29	0.25	0.83 0.98°	0.83
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{SH}$	4.57	6.9	0.43	0.95	0.89
$\text{C}_6\text{H}_5\text{SH}$	6.33	29	0.010	0.68	0.69

^a $K = [\text{hemithioacetal}]/[\text{RSH}][\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}(\text{OH})_2]$.

^b Based on hydroxide ion activity. ^c Ionic strength 0.003-0.010.

(1) Publication No. 525. Supported by grants from the National Science Foundation and the National Institute of Child Health and Human Development of the Public Health Service (HD-01247).

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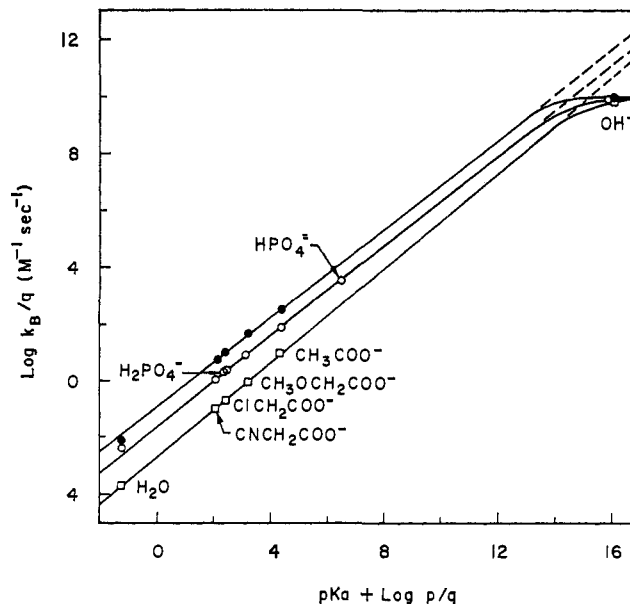
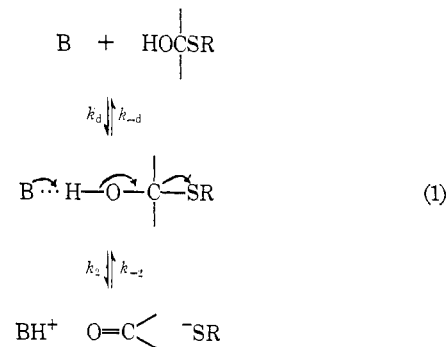


Figure 1. Brønsted plots for the decomposition of hemithioacetals formed from acetaldehyde and benzenethiol (\square), thioacetic acid (\circ), and *p*-nitrobenzenethiol (\bullet). Statistical corrections have been made according to R. P. Bell and P. G. Evans, *Proc. Roy. Soc. (London)*, **A291**, 297 (1966).

The rate constants, k_B , for catalysis by weaker bases follow Brønsted slopes of 0.80 ± 0.03 (Figure 1). These results suggest that the reaction proceeds according to the mechanism of eq 1 and that diffusion-



controlled encounter of the reactants is largely or entirely rate determining for the hydroxide ion reaction, whereas the k_2 step becomes rate determining for weaker bases or less acidic leaving groups. Calculations based on the steady-state rate equation for this mechanism (eq 2) using values of $k_d k_2 / k_{-d}$ from the Brønsted plots

$$k_B = \frac{k_d k_2}{k_{-d} + k_2} \quad (2)$$

and the assumption that $k_d = 0.9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ suggest that k_2 is partially rate limiting for the reaction of the benzenethiol compound with hydroxide ion (Table I).

An alternative mechanism in which a proton is removed in a fast step followed by general acid catalyzed expulsion of thiol is improbable for several reasons which include (1) a requirement for base catalysis of the removal of a proton from the free thiol in the reverse direction under experimental conditions in which the thiol is already 98% in the ionized form, and (2) the unlikelihood for this mechanism of similar values of