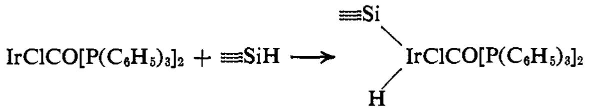
as well as subsequent exchange processes must occur with complete *retention* at the silicon center.



$$\mathrm{IrClCO[P(C_6H_5)_3]_2} + \equiv\mathrm{SiH} \longrightarrow \mathrm{(\equiv Si)(H)IrClCO[P(C_6H_5)_3]_2} \quad (6)$$

Research is continuing on the stereochemistry of reactions involving compounds containing silicon–transition metal bonds. A series of novel leaving groups including platinum as well as cobalt species are currently under investigation.

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Rate-Limiting Diffusion-Controlled Proton Transfer in an Acetyl Transfer Reaction[1]

Sir:

We wish to suggest that the rate-determining step of the intramolecular S to N acetyl transfer reaction of S-acetylmercaptoethylamine above pH 2.3 is a diffusion-controlled proton transfer and propose a mechanism for the reaction which appears to resolve the "thiazoline dilemma." [2] The evidence for this proposal is (a) a change in rate-determining step in this reaction at pH 2.3 can be accounted for by the proposed mechanism, but cannot be accounted for by steps which involve only bond formation or breaking with carbon, and (b) general acid catalysis of the reaction by carboxylic acids and phosphate occurs with an α value indistinguishable from zero, as expected for a diffusion-controlled reaction.

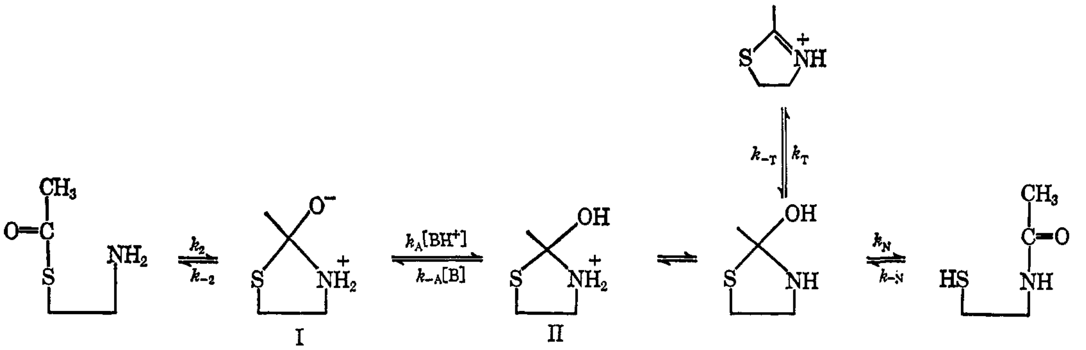
It is known that this intramolecular thiol ester aminolysis proceeds through a neutral transition state in acid solution and undergoes a change to a rate-determining step with a cationic transition state at pH 2–3; this step also proceeds through a neutral transition state above pH 4. Above pH 3 the reaction is subject to general acid catalysis. Martin and Hedrick first suggested that a slow proton-transfer step could account for these kinetic results and for the pH dependence of product yields from the hydrolysis of 2-methyl-Δ^2-thiazoline;[3] however, it was later pointed out that the proposed scheme does not account for all of the experimental data.[2]

Thiol ester disappearance or formation at 50° was followed spectrophotometrically at 230 mμ and thiazoline disappearance at 260 mμ. Above pH 2.3 the reaction of the cationic substrate is subject to general base catalysis with a Brønsted slope, β, of 0.97 for catalysis by carboxylate anions and phosphate dianion (Figure 1). This corresponds to a Brønsted slope, α, of 0.03 when the reaction is described by the kinetically equivalent k' for general acid catalysis of the reaction of the free amine (eq 1). This α value is equal, within experimental error, to the α value of zero expected for

$$v = k_B[SH^+][A^-] = k'[S][HA] \qquad (1)$$

a diffusion-controlled proton-transfer reaction,[4] and we suggest that the rate-determining step of the over-all reaction under conditions in which this catalysis is observed is, in fact, a diffusion-controlled proton transfer.

We have confirmed the earlier observation[5] that the ratio of thiol ester to amide product (1.0 at 50°) in thiazoline hydrolysis is independent of pH below pH 2 and have shown, by measuring initial rates of thiazoline disappearance and thiol ester formation, that the decrease in yield of thiol ester at higher pH values is not caused by secondary S to N acetyl transfer. The dependence on pH of the change in product ratio ("pK" = 2.37) corresponds to the change in rate-determining step in the intramolecular aminolysis reaction ("pK" = 2.30). The kinetic argument may be stated as follows. Below pH 2 the tetrahedral intermediate formed in thiazoline hydrolysis (eq 2) breaks down equally easily to thiol ester and to amide through transition states of zero charge. The decrease (a) in the rate of thiol ester aminolysis and (b) in the yield of thiol ester from thiazoline hydrolysis with increasing pH demands that *another step with a cationic transition state become rate determining* on the thiol ester limb of eq 2. This must be a simple proton-transfer step, and we suggest that it is step k_A of eq 2. The alternative assignment to k_3' of eq 3 would require a value of k_{-2}' of $\approx 10^{16}\,M^{-1}\,\mathrm{sec}^{-1}$ if the pK of the cationic intermediate is assumed to be 6.



(2)

Assuming that k_A for the solvated proton is $6.5 \times 10^{10}\,M^{-1}\,\mathrm{sec}^{-1}$ at 50°,[4,6] the values for most of the rate

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[2] R. B. Martin, R. I. Hedrick, and A. Parcell, *J. Org. Chem.*, **29**, 3197 (1964).

[3] R. B. Martin and R. I. Hedrick, *J. Am. Chem. Soc.*, **84**, 106 (1962).

[4] M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, 3, 1 (1964); M. Eigen, *Discussions Faraday Soc.*, 39, 7 (1965).

[5] R. B. Martin, S. Lowey, E. L. Elson, and J. T. Edsall, *J. Am. Chem. Soc.*, **81**, 5089 (1959); R. B. Martin and A. Parcell, *ibid.*, **83**, 4835 (1961).

[6] This assumes $E^{\ddagger} = 2$ kcal/mol and that ionic strength has little effect on diffusion coefficients.

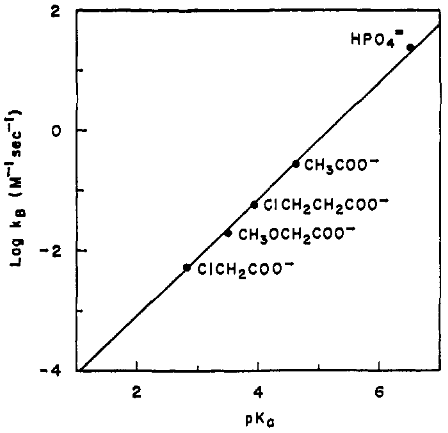
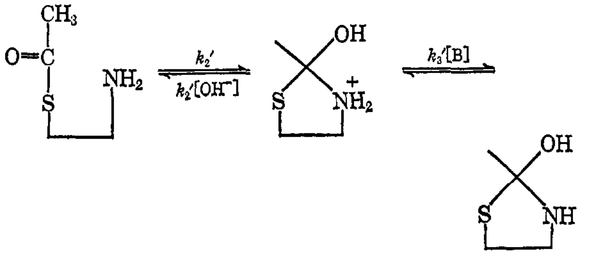


Figure 1. Brønsted plot for S to N transfer of S-acetylmercaptoethylamine.

constants of eq 2 can be estimated and are within reasonable limits. The values of k_A for four carboxylic acids and phosphate monoanion of 2.8 ± 0.4 × 10^9 M^{-1} sec^{-1} show the expected decrease relative to that for the solvated proton (Table I). Preliminary experiments indicate that acids with pK values greater than 7 show the decrease in rate constant expected for proton transfer to a base of pK about 7.5, in the thermodynamically unfavorable direction.[4] The water reaction shows a large positive deviation from the predicted value for such a weak acid, suggestive of a concerted intramolecular proton transfer from NH^+ to O^- through water. The previously reported[2] β value of 0.6 is based on points for H_2O, formate, phenolate, borate, and OH^- and is in agreement with the results reported here for catalysts of such widely varying acidity.



(3)

Table I. Catalysis of S to N Acetyl Transfer in S-Acetylmercaptoethylamine at 50° and Ionic Strength 1.0 M[a]

Acid	pK_a	k_B, M^{-1} sec^{-1}	k_A,[b] M^{-1} sec^{-1}
H_3O^+	−1.74	2.92 × 10^{-6}	6.50 × 10^{10}
$ClCH_2COOH$	2.83	5.20 × 10^{-3}	3.13 × 10^9
CH_3OCH_2COOH	3.50	2.01 × 10^{-2}	2.58 × 10^9
$ClCH_2CH_2COOH$	3.95	5.83 × 10^{-2}	2.64 × 10^9
CH_3COOH	4.64	2.62 × 10^{-1}	2.44 × 10^9
$H_2PO_4^-$	6.52	2.38 × 10	2.92 × 10^9
H_2O	15.00[c]	3.92 × 10^6	1.59 × 10^6

[a] Maintained with potassium chloride. [b] Calculated according to the mechanism of eq 2 (see text). [c] A. K. Covington, R. A. Robinson, and R. G. Bates, *J. Phys. Chem.*, **70**, 3820 (1966).

These results support the mechanism of eq 2, in which the initially formed dipolar addition intermediate I reverts to starting materials unless it is trapped by a diffusion-controlled encounter with an acid, to give II. The relatively slow over-all rate under conditions in which the k_A step is rate determining is caused by the unfavorable prior equilibria for the formation of free amine and I. This system (in reverse) is analogous to the diffusion-controlled proton removal by hydroxide ion from the (potential) carbonyl oxygen atom in the decomposition of hemithioacetals to aldehydes.[7]

(7) R. Barnett and W. P. Jencks, *J. Am. Chem. Soc.*, **89**, 5963 (1967).
(8) National Science Foundation Predoctoral Fellow, 1965–1968.

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Book Reviews

Electronic Absorption Spectra and Geometry of Organic Molecules. An Application of Molecular Orbital Theory. By Hiroshi Suzuki, Department of Chemistry, College of General Education, University of Tokyo, Tokyo, Japan. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xiii + 568 pp. 16 × 23.5 cm. $24.00.

In the author's words, "The main subject of this book is the relation between the electronic absorption of organic compounds and (the) geometry of molecules." The book fulfills this aim to a very great extent and in very beautiful fashion. As in many such books, the present one is divided informally into two parts: the theoretical part covering eleven chapters and almost exactly half its length, and the discussion of actual cases covering most of the rest of the book. Two brief chapters introducing new methodology are inserted fairly late in the text. The theoretical portions are well written and clear. Unfortunately, the emphasis is still largely on simple Hückel theory. Only Chapter 11 goes on to SCF methods (Pariser–Parr–Pople), and Chapters 19 and 20 deal with the composite molecule methods. Within this framework the book treats very nicely and adequately all the proper and important topics. In some places, particularly where the author has personal experience, it goes well beyond most previous treatments. Thus, it has an extensive section on molecules in the solid state. In the section discussing more specifically the relationship between spectra and geometry, the author has heavily leaned on his own work: "Chapters 12 to 15 are, to some extent, revised versions of papers I have published from 1959 to 1962." In this strong emphasis on the author's own work lies one of the major weaknesses of the book. Aside from this, the coverage of the literature seems to be rather out of date. A cursory examination shows very few references beyond 1962. Chapters 12 through 18 in 128 pages only contain two references to the literature past 1962. Thus, it is a tragic fact that Professor Suzuki's book, as it appears in this country, is about 5 years out of date.

The book is well printed and well bound. The figures are neat and legible and the whole presents a very pleasing appearance. In spite of its shortcomings, the book presents a significant contribution to the literature of organic electronic spectroscopy, largely because of its emphasis on the relation between geometry and spectra. It further represents a very nice summary and putting together in one place of Professor Suzuki's very extensive and important researches.

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