

single, sharp peak corresponding to P_4O_6 , with successive spectra becoming more and more complex (with as many as 20 first-order resonances showing up). Then, as the reaction proceeded further, the spectra become more and more simple, until only the single sharp resonance for the $P_4O_6[Ni(CO)_3]_4$ molecule remained.

When the reagents are combined in proportions corresponding to the Ni/P_4O_6 mole ratio being less than 4, bridging of P_4O_6 molecules by nickel atoms occurs and cross-linked polymers are obtained as glasses. Reaction also takes place when small amounts of nickel carbonyl are mixed with a large excess of P_4O_6 . In this case, the first pattern to appear in the P^{81} n.m.r. spectra is that of $P_4O_6[Ni(CO)_3]$, the same pattern which first shows up when the nickel carbonyl is present in large excess. However, succeeding reactions lead to replacement of up to three of the carbonyl groups on a given nickel by P_4O_6 molecules, with each carbonyl being replaced by a single P_4O_6 . We were unable to substitute four P_4O_6 groups on a given nickel atom, presumably because of steric hindrance. Successive replacement of carbonyl groups on a given nickel was found to require longer periods of time than the successive attachment of tricarbonylnickel groups to a given P_4O_6 molecule.

As expected, the family of compounds obtained by treating nickel carbonyl with the phosphorus trioxide bird-cage molecule shows two gel points, with infinite-network polymers appearing in the approximate composition region between Ni/P_4O_6 mole ratios of 0.25 and 4. Equilibrium is thought to be readily achieved in this system, except for the more highly cross-linked structures in which nearly every P_4O_6 molecule is bonded to four nickel atoms and nearly every nickel atom is bonded to three P_4O_6 molecules. For considerable cross linking, diffusion control would be expected to reduce greatly the rate of attainment of equilibrium.

(2) On leave from the University of Strasbourg, France, 1965.

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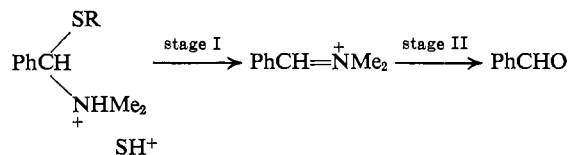
An Example of SN_1 Cleavage of a Sulfide¹

Sir:

It has been established that unimolecular carbon-sulfur heterolysis is the rate-controlling step in the conversion of alkyl α -dimethylaminobenzyl sulfides to N,N -dimethylbenzyliminium ion in aqueous acidic media (eq. 2). This appears to be the first authentic instance of an SN_1 cleavage of an alkyl-sulfur bond of a sulfide.

In pure water, the alkyl α -dimethylaminobenzyl sulfides are hydrolyzed to benzaldehyde practically instantly. In dilute aqueous acidic media, in which the substrate is present largely as the nitrogen conjugate acid, SH^+ , the reaction rate is slow enough to measure. The over-all reaction proceeds quantitatively in two states.

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-590-64.



This report concerns the kinetics of the first stage. First-order rate constants for stage I were obtained by an ultraviolet spectrophotometric method.²

For ethyl α -dimethylaminobenzyl sulfide in 0.08–1 M H_3O^+ , a plot of $\log k_{\text{obsd}}$ against $\log [H_3O^+]$ is linear with slope -1.0 (Figure 1). For t -butyl α -dimethylaminobenzyl sulfide at 0° k_{obsd} also is inversely proportional to $[H_3O^+]$, the rate law being $k_{\text{obsd}} = (2.00 \pm 0.9) \times 10^{-5}/[H_3O^+]$ over the range $[H_3O^+] = 2.82 \times 10^{-4}$ to 0.725 M . Since the ground state is SH^+ , the acidity dependence of k_{obsd} allows the conclusion that the transition state contains the elements of S (and possibly H_2O) but *no proton*.

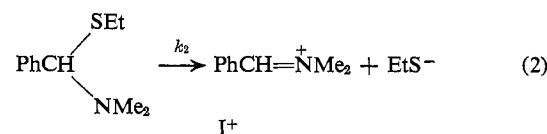
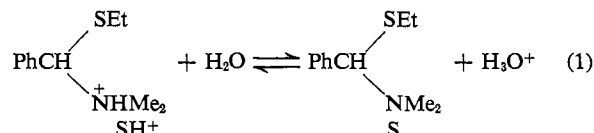
In formic acid buffers there is no detectable catalysis by molecular formic acid or by formate ion (Table I). This is consistent with the transition data containing *only* the elements of S.³

Table I. The Reaction $\text{PhCH}(\text{NMe}_2)\text{StBu} \rightarrow \text{PhCH}=\text{N}^+\text{Me}_2$ in Formic Acid Buffer at 0°

[HCO ₂ H], M	[HCO ₂ Na], M	[NaCl], M	10 ³ k_{obsd} , sec. ⁻¹ Method A ^a	Method B ^b
0.010	0.010	0.090		7.1
0.040	0.040	0.060	7.2, 7.2, 7.1	7.1
0.070	0.070	0.030		7.0
0.100	0.100	0.000	7.2, 7.1, 7.2	7.0

^a Slope of plot of $\ln(D_\infty - D)$ against time, where D is measured at 257 $m\mu$, the wave length at which the intermediate (I^+) and product (PhCHO) have the same molar absorptivity. ^b Average of several runs. Method of successive first-order reactions applied to optical density data at 250 $m\mu$.

At this point one can conclude that the most probable mechanism is that represented by eq. 1 and 2. The rate-controlling step is a solvolytic carbon-sulfur bond cleavage of the neutral thio ether.



$$k_{\text{obsd}} = k_2 K_I \frac{a_{\text{H}_2\text{O}}}{[\text{H}_3\text{O}^+]} \times \frac{f_{\text{SH}^+}}{f_{\text{H}_3\text{O}^+} + f_{\text{tr}_2}} \quad (3)$$

The rate expression for this mechanism is given

(2) In $>0.1 M$ H_3O^+ , stage II is much more rapid than stage I, and k_{obsd}^I was obtained from the change in optical density of the peak for benzaldehyde. In $<0.1 M$ H_3O^+ , the two stages have comparable rates, and values of k_{obsd}^I were obtained by applying equations for successive first-order reactions. These values were checked later by following the first-order change in optical density at the wave length at which the iminium ion and benzaldehyde have the same molar absorption (257 $m\mu$).

(3) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, Chapters IV and V.

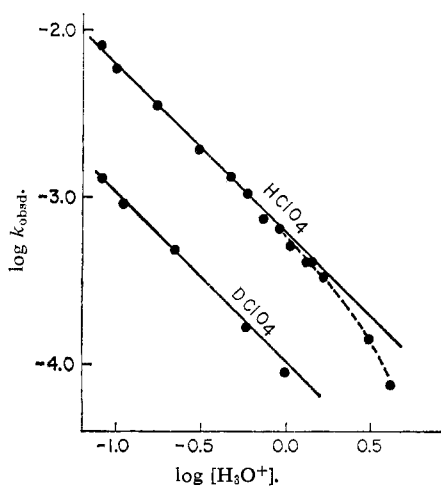
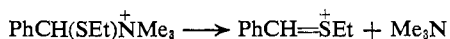


Figure 1. Plot of $\log k_{\text{obsd}}$ against $\log [\text{H}_3\text{O}^+]$ for the reaction
 $\text{PhCH}(\text{NHMe}_2)\text{SEt} \rightarrow \text{PhCH}=\text{NMe}_2 + \text{EtSH}$

by eq. 3, where $K_I = a_{\text{S}}a_{\text{H}_3\text{O}^+}/a_{\text{SH}}+a_{\text{H}_2\text{O}}$. The term $a_{\text{H}_2\text{O}}f_{\text{SH}}^+/f_{\text{H}_3\text{O}^+}f_{\text{EtS}^-}$ should change little in the predominantly aqueous solutions used, and hence k_{obsd} should be inversely proportional to $[\text{H}_3\text{O}^+]$, as observed. The assigned mechanism also accounts for the lack of catalysis by formate ion or molecular formic acid.

In complete agreement with the mechanism is the finding of a solvent isotope effect ($k_{\text{HClO}_4}/k_{\text{DClO}_4}$) of 5.9 ± 0.1 in several acidities for the ethyl sulfide (Figure 1). Since equilibrium 1 lies far to the left, the concentration of S should be significantly greater in protio than in deutero acid of the same molarity.⁴ It can reasonably be assumed that the solvent isotope effect on [S] is comparable to that on the acid dissociation constant of trimethylammonium ion. This is reported to be 4.0 but is more likely 5.0.⁵ The second step probably has a small positive isotope effect.^{7,10} The closest model is the reaction



for which $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ is 1.2.¹¹ Thus the estimated total solvent isotope effect agrees well with that observed.

The transition state of the rate-controlling step of the assigned mechanism has sulfide ion character. In agreement with this, the relative rates for various α -dimethylaminobenzyl thio ethers are: Ph (398), PhCH_2 (4.6), Et (1.0), *t*-Bu (0.8). A plot of $\log k$ vs. $\log K_{\text{RSH}}$, where K_{RSH} is the acidity constant of the thiol in water, is linear with slope -0.57 .

(4) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(5) In 1936, Schwarzenbach and Epprecht reported the following $K_{\text{HA}}/K_{\text{DA}}$ values: H_2O (5.4), NH_4^+ (3.1), $(\text{CH}_3)_3\text{NH}^+$ (4.0), $\text{CH}_3\text{CO}_2\text{H}$ (2.9), and H_2PO_4^- (2.9).⁵ No later values for $(\text{CH}_3)_3\text{NH}^+$ were found, but the generally accepted values for all the other acids are consistently larger than the earlier values, by a factor of 1.25 ± 0.05 : H_2O (6.5),^{7,8} NH_4^+ (4.06),⁹ $\text{CH}_3\text{CO}_2\text{H}$ (3.33),^{7,8} and H_2PO_4^- (3.62).⁸ Applying this factor to the early value for $(\text{CH}_3)_3\text{NH}^+$ gives $K_{\text{HA}}/K_{\text{DA}} = 5.0$.

(6) G. Schwarzenbach, A. Epprecht, and H. Erlenmeyer, *Helv. Chim. Acta*, **19**, 1292 (1936).

(7) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 42 (1961).

(8) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 188.

(9) F. A. Long, P. Salomaa, and L. L. Schlaeger, *J. Phys. Chem.*, **68**, 410 (1964).

(10) C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207, 3214 (1961).

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Mechanisms in which the transition state contains the hydroxide ion and the elements of SH^+ (such as in an $\text{S}_{\text{N}}2$ attack of OH^- on the sulfur-conjugate acid) are not ruled out by the acidity dependence of k_{obsd} . However, they are inconsistent with the other results obtained.

A literature search failed to reveal any unambiguous example of the $\text{S}_{\text{N}}1$ solvolysis of a neutral sulfide. Carbon-sulfur bond cleavage in general is much more difficult to achieve than carbon-oxygen bond cleavage.¹²⁻¹⁴ However, in this instance the "carbonium" ion formed, I^+ , has a relatively high stability. The iminium ion character of the transition state no doubt is of great assistance in promoting the $\text{S}_{\text{N}}1$ heterolysis of the carbon-sulfur bond.

(12) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951).

(13) N. Kharasch, Ed., "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., 1961.

(14) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

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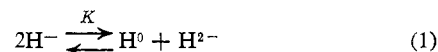
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Comments on the Proposed Dibenzocyclobutadiene Dianion

Sir:

We wish to report results of our spectroscopic measurements of equilibrium constants for disproportionation of anthracene (a^0) and biphenylene (b^0) radical anions in tetrahydrofuran (THF) solution (sodium gegenion)



Equilibrium data have been reported for disproportionation of the radical anions of stilbene,¹ tetraphenylethylene,² 1,2,3,4-tetraphenylbutadiene,³ and cyclooctatetraene,⁴ but no direct measurements of equilibrium constants for disproportionation of aromatic radical anions have been reported. Polarographic^{5,6} and potentiometric titrations^{7,8} indicate disproportionation of aromatic radical anions is small.

It was recently reported,⁹ based on visible spectral measurements, that in THF solutions biphenylene radical anion ($b^{\cdot-}$) (sodium gegenion) undergoes extensive disproportionation, but the equilibrium constant was not measured. The authors interpreted their observed disproportionation of $b^{\cdot-}$ as evidence that biphenylene dianion (b^{2-}) derives a special stability from being the closed shell $4n + 2$ π -electron molecule dibenzocyclobutadiene dianion.

(1) E. R. Zabolotny and J. F. Garst, *J. Am. Chem. Soc.*, **86**, 1645 (1964).

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(5) G. J. Hoijtink, J. van Schooten, E. deBoer, and W. Y. Aalbersberg, *Rec. Trav. Chim.*, **73**, 355 (1954).

(6) S. Wanzonek, E. W. Blaha, R. Berkey, and M. E. Runney, *J. Electrochem. Soc.*, **102**, 234 (1955).

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