fivefold lower concentrations of formate and formic acid were employed and 1 l. of water was used in the mixing chamber. It has proven essential to conduct a slow elution for optimal separation of products. Figure 1 shows the elution pattern. All efforts to date to separate the heptulose phosphates by other techniques have failed. Dephosphorylation with Polidase S[9] of portions of each fraction and subsequent paper chromatography with D-*allo*-heptulose and D-sedoheptulose[10] as standards established that fractions I and II, which were from overlapping peaks (Figure 1), both contained D-*allo*-heptulose 7-phosphate. The results also established that fraction III contained D-sedoheptulose 7-phosphate.

Fractions I, II, and III (Figure 1) were reduced to *ca.* 30% of the original volume and the barium salts were precipitated with cold alcohol and assayed enzymatically.[6] Table I shows the yield of each product and results of the assays, and compares results of elemental analyses (Galbraith Laboratories, Inc., Knoxville, Tenn.) with theory.

Table I. Analyses of Heptulose Phosphate Products

Fraction	Yield of monohydrate,[a] mg. (%)	S-7-P·H_2O by transaldolase assay, %	% C[b]	% H	% P
I	90 (3)	0	19.14	3.27	6.97
II	112 (4)	9	18.95	3.40	6.94
III	428 (16)	101	18.86	3.47	6.85

[a] Percentage yields assume that starting material was pure. [b] Theory for heptulose phosphate monohydrate for C, H, and P, respectively, is: 18.95, 3.41, 6.98.

In conclusion, the described condensation results in intermediate nitroalcohol salts which can be decomposed smoothly through the novel use of cold HBr. The principal product, D-sedoheptulose 7-phosphate, can be isolated in reasonable yield. We are currently investigating the scope of this reaction.

(9) I. Smith in "Chromatographic and Electrophoretic Techniques," Vol. I, I. Smith, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 527.

(10) We are indebted to Dr. N. K. Richtmeyer for samples of these sugars.

(11) Research Career Development Awardee (I-K3-AI-5268) of the National Institutes of Health.

Bruce A. McFadden,[11] Larry L. Barden
Norman W. Rokke, Marianne Uyeda, Theodore J. Siek
Department of Chemistry, Washington State University
Pullman, Washington

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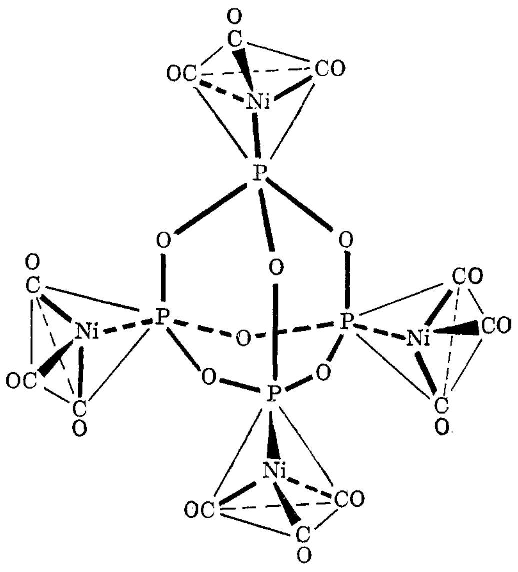
P,P′,P′′,P′′′-Tetrakistricarbonylnickel(tetraphosphorus hexaoxide)

Sir:

Phosphorus trioxide (P_4O_6) reacts with metal carbonyl complexes to give a new class of coordination compounds, including polymers, where P_4O_6 behaves as a polydentate ligand. When allowed to react with an excess of nickel carbonyl, the symmetric bird-cage structure of P_4O_6, which has four unshared pairs of electrons (one on each phosphorus), will coordinate with as many as four nickel tricarbonyl groups per P_4O_6 molecule to give the tetrahedrally symmetric P,P′,P′′,P′′′-tetrakistricarbonylnickel(tetraphosphorus hexaoxide) (I).



I

This is believed to be the first reported coordination complex built around a tetradentate phosphorus(III) molecule and is also the first complex having metal–phosphorus bonds where metal atoms are bridged by P–O–P linkages. Compound I is best obtained by treating 1 mole of P_4O_6 with 5 moles of $Ni(CO)_4$, mixed as neat liquids. Within about 10 min. at 24°, with evolution of 4 equiv. of carbon monoxide, I is formed as a white crystalline powder containing some unreacted $Ni(CO)_4$. It is essential to remove quickly this excess of $Ni(CO)_4$ in order to obtain a stable, storable product. The excess $Ni(CO)_4$ was removed by repeated crushing of the crystalline powder with Dry Ice cooled, dry pentane, followed by filtration. The pure compound shows unexpectedly good resistance to thermal decomposition and to reaction with moist air.

The structure of I is proven by the following: (a) a single sharp P^{31} n.m.r. peak at -32.9 p.p.m. for solutions (this is 10 p.p.m. downfield from P_4O_6 as expected[1] from the decrease of electron density on the phosphorus atoms in the complex); (b) the proper elemental analysis (Calcd.: P, 15.66; C, 18.22. Found: P, 15.47; C, 18.05); (c) a partial structure determination based on the X-ray powder diffraction pattern (1 mole per unit cell in the simple cubic system with a_0 = 8.81 Å.); and (d) the infrared stretching frequencies for the carbonyl which are close to those of the $Ni(CO)_4$ itself.

Additional structural evidence is obtained by following kinetically by P^{31} n.m.r. the formation of I. In this case, all of the intermediate species having from one to three tricarbonylnickel groups per P_4O_6 molecule are observed to form and maximize successively. These intermediate compounds exhibit the correct splitting patterns and reasonable n.m.r. chemical shifts and splitting constants for Ni–P bonding at the various $:P<$ sites of P_4O_6. Thus, the over-all P^{31} n.m.r. spectrum at the beginning of the reaction exhibits the

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(1) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, submitted for publication.

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^{31} 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.

Jean G. Riess,[2] John R. Van Wazer
Central Research Department, Monsanto Company
St. Louis, Missouri

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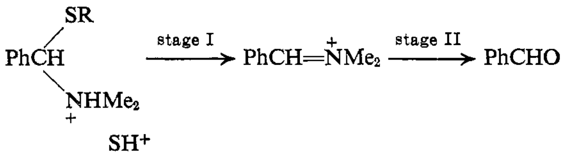
An Example of SN1 Cleavage of a Sulfide[1]

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-dimethylbenzaliminium ion in aqueous acidic media (eq. 2). This appears to be the first authentic instance of an SN1 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.



$$\underset{SH^+}{PhCH(SR)\overset{+}{N}HMe_2} \xrightarrow{\text{stage I}} PhCH{=}\overset{+}{N}Me_2 \xrightarrow{\text{stage II}} PhCHO$$

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_{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.*

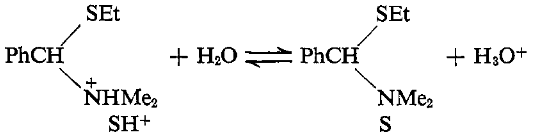
In formic acid buffers there is no detectable catalysis by molecular formic acid or by formate ion (Table I). This is consistent with the transition data containing *only* the elements of S.[3]

Table I. The Reaction $PhCH(NMe_2)StBu \rightarrow PhCH{=}\overset{+}{N}Me_2$ in Formic Acid Buffer at 0°

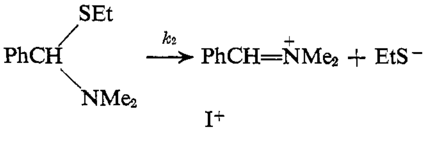
$[HCO_2H]$, *M*	$[HCO_2Na]$, *M*	$[NaCl]$, *M*	10^2k_{obsd}, sec.$^{-1}$ Method A[a]	Method B[b]
0.010	0.010	0.090		7.1
0.040	0.040	0.060	7.2, 7.2, 7.1	7.1
0.070	0.070	0.030		7.0
0.100	0.100	0.000	7.2, 7.1, 7.2	7.0

[a] Slope of plot of ln $(D_\infty - D)$ against time, where D is measured at 257 mμ, 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 mμ.

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.



$$\underset{SH^+}{PhCH(SEt)\overset{+}{N}HMe_2} + H_2O \rightleftharpoons \underset{S}{PhCH(SEt)NMe_2} + H_3O^+ \qquad (1)$$



$$PhCH(SEt)NMe_2 \xrightarrow{k_2} \underset{I^+}{PhCH{=}\overset{+}{N}Me_2} + EtS^- \qquad (2)$$

$$k_{\text{obsd}} = k_2K_{\text{I}}\,\frac{a_{H_2O}}{[H_3O^+]} \times \frac{f_{SH^+}}{f_{H_3O^+}f_{tr_2}} \qquad (3)$$

The rate expression for this mechanism is given

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

[2] In >0.1 *M* H_3O^+, stage II is much more rapid than stage I, and $k^{\text{I}}_{\text{obsd}}$ 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 $k^{\text{I}}_{\text{obsd}}$ 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 mμ).

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