EARLY EVENTS IN THE REACTION CHEMISTRY
OF PHOSPHORUS (P₄) AND SULFUR (S₈)

MARK E. JASON, TOAN NGO, and SHAHIDUR RAHMAN

Monsanto Company, Performance Materials
800 N. Lindbergh Blvd. T3W
St. Louis, MO 63167 USA

Abstract The oxidation of elemental phosphorus (P₄) by elemental sulfur (S₈) has been studied by a combination of ³¹P nmr and Raman spectroscopic techniques. At temperatures below the auto-ignition temperature, a molten mixture of the elements gives rise to a complex mixture of products which are dominated by phosphorus sulfides which have a high S/P₄ ratio. Both the rate at which the products are formed and their distribution support the formation of a reactive P₄S₈ intermediate which then cascades through a series of reactions, incorporating the sulfur atoms into the phosphorus cage. Two new phosphorus sulfides (of composition P₄S₆ and P₄S₈) have been identified in these product mixtures.

INTRODUCTION

The commercial production of P₄S₁₀ is performed by the high temperature (>300°C) reaction of P₄ with S₈, conditions which make difficult the study of the intermediate products and mechanisms involved in the transformation. However, a related study has shown that oxidation of phosphorus by sulfur takes place at a controlled and convenient rate at much lower temperatures (100-120°C). This observation provided the unique opportunity to follow the development of the product mixture during the course of the reaction, particularly the early portion (0-5% completion), in great detail. The initial survey of these reactions was performed with Raman spectroscopy from which qualitative rates and an understanding of the complexity of the product mixtures were obtained. ³¹P nmr spectroscopy, however, provided both the resolution and the sensitivity to characterize mixtures of twelve or more components at less than 1% total completion in molten reaction mixtures. From this effort has come a detailed picture of the products formed and a working hypothesis for the mechanism of their formation.
EXPERIMENTAL PROCEDURE

All reactions were performed either under vacuum or dry, oxygen free nitrogen using standard Schlenk techniques. The purity of the phosphorus (commercial vs. distilled) did not appear to affect the outcome of the chemistry.

The Raman spectroscopy experiments were performed by observing reaction mixtures through a quartz flat sealed to the bottom of a mechanically stirred quartz reaction vessel. The reaction zone was a cylinder 2 cm long and 1 cm in diameter, heated with nichrome wire wound around the cylinder. The spectra were recorded using a fiber optic probe placed in contact with the quartz flat. The reaction was profiled by recording spectra at regular intervals over the course of 8-24 hours, depending on the mixture and the reaction temperature.

$^{31}$P nmr spectroscopy was performed at 300 and 400 MHz (proton frequency) in standard 5 mm tubes. All reaction mixture nmr tubes were sealed under moderate vacuum (10-12 mmHg total pressure). Spectra were accumulated under semi-quantitative conditions because of long relaxation times for phosphorus in some of the sulfides. Integration of signals at low concentration provided relative product ratios with roughly 25% error limits, as judged by replicate measurements; at higher concentrations the integrals were obtained with approximately 5% error limits.

RESULTS AND DISCUSSION

The Raman spectra of a P$_4$/S$_8$ mixture at P$_4$S$_3$ stoichiometry at 80°C showed the loss of P$_4$ and S$_8$ and the growth of bands which can be attributed to P$_4$S$_3$, $\alpha$-P$_4$S$_5$, $\alpha$-P$_4$S$_7$, and $\alpha$-P$_4$S$_9$. Because the Raman spectra of all of the known phosphorus sulfides have not been published, these spectra could provide quantitative information only about the loss of the reactants.

The $^{31}$P nmr spectrum of a liquid mixture of P$_4$/S$_8$ at P$_4$S$_1$ stoichiometry showed a smooth appearance of 12 phosphorus sulfides: P$_4$S$_3$ (1), $\alpha$-P$_4$S$_5$ (2), $\alpha$-P$_4$S$_6$ (3), $\beta$-P$_4$S$_6$ (4), $\gamma$-P$_4$S$_6$ (5), $\alpha$-P$_4$S$_7$ (6), $\beta$-P$_4$S$_7$ (7), $\alpha$-P$_4$S$_8$ (8), $\beta$-P$_4$S$_8$ (9), $\gamma$-P$_4$S$_8$ (10), $\alpha$-P$_4$S$_9$ (11), and P$_4$S$_{10}$ (12). Two of these sulfides, 5 and 10, were observed for the first time in these reactions. The most rapidly formed products are 3, 6, and 11, in that order. Sulfides 1, 3, 4, 6, 7, and 11 appear to be primary products, where "primary" means only that the appearance profile has its steepest slope near $t=0$. Three of the other sulfides, 2, 8, and 9, are distinctly secondary; observable concentrations appear only after 2-4 hours of reaction, well after the major primary products have been established. The early portion of this profile is found in Figure 2. Using an initial
slope analysis of the 0-6 hour portion of this reaction profile, and assuming all of the products are derived from a common, initial reactive species, one can calculate an apparent first order rate constant at 80°C of $1.2 \times 10^{-6}$ s$^{-1}$ for the appearance of phosphorus sulfides in this molten mixture.

FIGURE 1. Structures of several of the phosphorus sulfides, and the proposed intermediates in the first three steps of the reaction of P$_4$ with S$_8$.

FIGURE 2. Reaction profile for P$_4 + \frac{1}{8}$S$_8$ at 80°C.
The stoichiometry of the major products indicates the mechanism involved in their build-up does not involve the formation of sulfides of low S/P₄ ratio followed by successive oxidation to the higher sulfides. This was confirmed by subjecting 1 to the conditions of a typical reaction. The rate of the reaction of P₄ with S₈ is similar though not identical to the rate of polymerization of sulfur, assuming the activation parameters derived from vulcanization studies. These two observations make possible the suggestion that the first steps in the reaction of phosphorus and sulfur is the ring opening of S₈ to give a diradical, 13, followed by addition to P₄ to give a new diradical, 14. Closure of 14 to give P₄S₈ isomer 15 is a logical consequence, and could explain the high S/P₄ ratios observed in the products. The transformations which link 15 to the major products 3, 6, and 11 should then preserve most of the sulfur atoms found in 15. These reactions should be faster than the initial formation of the S₈ diradical in order that they not be observed by nmr spectroscopy. However, a simple calculation places the maximum half-life of these unobserved intermediates at approximately 10 minutes. Similar structures are known to react rapidly enough to satisfy this requirement.

SUMMARY

The oxidation of phosphorus by sulfur displays a startling array of products when performed at low temperature. Two new phosphorus sulfides have been identified. The products and the kinetics of the reaction are adequately explained by the formation of the intermediate common to the polymerization of elemental sulfur, most likely the diradical.

REFERENCES