whereas in methanol[17] this electrolyte gives a large, positive B (0.67). Although there is evidence for hydrogen-bonded association of alcohols from a number of experimental approaches,[18-20] from the point of view of viscosity, methanol appears to be similar to the unstructured solvents, dimethylformamide and dimethyl sulfoxide, in which the alkali halide B coefficients are 0.6–0.7.

There have been several investigations of the viscosity of ethylene glycol and glycerol solutions of potassium iodide. Getman's data[21] are shown in Figure 1 but extrapolation leads to a negative value of A, in disagreement with Falkenhagen's expression.[10] Briscoe[22] measured the viscosity of glycerol solutions of potassium iodide at a number of temperatures but did not calculate B coefficients. Golik[23] reported that potassium iodide showed "negative viscosities" in ethylene glycol and glycerol, but the data at low concentration were too sparse and too scattered to permit calculation of B.

B coefficients of 0.0327 and -0.185 were obtained for potassium iodide in ethylene glycol and glycerol in the present study. In comparison to the methanol value ($B = 0.6747$), these results suggest considerable weakening of the hydrogen bonding in both solvents; in glycerol the effect is sufficiently pronounced to give a negative B.

It is interesting to note that the data in ethylene glycol are linear to about 0.9 M, far in excess of the limit of validity generally assumed for eq 1. The data in glycerol show two linear regions, one to about 0.3 M ($B = -0.185$) and then a second region beyond this concentration. Although more data are needed before an explanation of this phenomenon could be attempted, Fornwalt's data[17] for this salt in methanol exhibited the same behavior. Davis and Malpass[24] have suggested that ion pairing might explain the appearance of two linear regions. Cesium iodide (Figure 2) would be described as a "structure breaker" in both ethylene glycol ($B = -0.080$) and glycerol ($B = -0.408$). The latter value is more negative than any reported in water at any temperature. Although the data in ethylene glycol show some scatter, the data in the other solvent exhibit linearity to about 0.5 M, again in excess of the limit generally assumed for the Jones–Dole equation.

In water, the B coefficient of cesium iodide is more negative than that of potassium iodide. The same relationship holds for these two nonaqueous solvents. For both salts, the B coefficients become increasingly negative in going from ethylene glycol to water to glycerol. It is difficult to rationalize this trend in terms of one solvent parameter, i.e., viscosity, dipole moment, or compressibility. If the negative B coefficients are indicative of a weakening of the hydrogen bonding, the present data suggest that the extent of association should be least in ethylene glycol and most pronounced in glycerol.

The conductance data of Accascina and Petrucci[25] for potassium chloride in ethylene glycol and glycerol have been used to approximate the A coefficients for the systems studied, assuming that the limiting equivalent conductances of cation and anion were equal and independent of the alkali metal or halide. This gave calculated values of A of 0.0058 for ethylene glycol and 0.0034 for glycerol. The experimentally determined value for cesium iodide in the latter solvent was 0.0032, the agreement being somewhat fortuitous, as the values for the other systems were larger than the calculated values.

Further work is in progress to include other hydrogen-bonded solvents as well as an investigation of the temperature dependence of B in these solvents.

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The Reaction of Active Nitrogen with Phosphorus Vapor

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In the only study reported of the reaction of active nitrogen with phosphorus vapor, Strutt observed a "hang-fire" effect; i.e., the afterglow was extinguished part of the way down the reaction tube, after which there appeared a flame with a continuous spectrum.[1] When the vapor was introduced into the region of the flame, or further downstream, the dark zone disappeared, and the vapor burned at the jet. Red phosphorus was reported to be a product of the reaction (but this might have been mistaken for the nitride). No explanation was offered for the observed behavior.

For the present study, relatively simple modifica-

(1) R. J. Strutt, *Proc. Roy. Soc.* (London), **86**, 56 (1912).

Table I: Rate Constants for the Reaction of Phosphorus with Active Nitrogen

Temp, °C	Competitive reactant	Ratio of rates	Phosphorus rate, cm³/mol sec	Reaction system
100	C_2H_4	$k/k' \approx 25$	2.5×10^{11}	Poisoned, condensed discharge
200	C_2H_4	$k/k' = 15$	1.1×10^{11}	Unpoisoned, microwave discharge
300	C_2H_4	$k/k' = 14$	1.2×10^{11}	Unpoisoned, microwave discharge
200	cis-C_4H_8	$k/k'' = 2.8$	8.0×10^{10}	Unpoisoned, microwave discharge
300	cis-C_4H_8	$k/k'' = 2.3$	9.4×10^{10}	Unpoisoned, microwave discharge
400	$trans$-C_4H_8	$k/k''' = 6.3$	4.4×10^{11}	Unpoisoned, microwave discharge

$$k' = 1.6 \times 10^{10} \exp(-700/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}{}^{a}$$
$$k'' = 2.3 \times 10^{11} \exp(-1980/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}{}^{b}$$
$$k''' = 3.4 \times 10^{11} \exp(-2100/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}{}^{b}$$

[a] G. Paraskevopoulos and C. A. Winkler, *J. Phys. Chem.*, **71**, 947 (1967).   [b] J. T. Herron, *ibid.*, **72**, 2538 (1968).

tions were made to the apparatus and procedures described previously.[2] The nitrogen was activated by either a condensed or microwave discharge. Phosphorus vapor was carried into the reaction vessel by a stream of nitrogen, the flow rate of phosphorus being controlled by the temperature of the storage vessel. The reaction vessel was fitted with a movable jet for NO and with a tared glass sleeve on which the solid products from the reaction were collected and removed for analysis.

Excess phosphorus and products from other reactants, e.g., ethylene, butene, etc., were trapped in liquid nitrogen traps. Unreacted phosphorus was distilled into a tared flask and weighed. Solid products on the glass sleeve were analyzed for weight, nitrogen content (Kjeldahl method), and phosphorus content (digestion in concentrated H_2SO_4 and colorimetric estimation of the phosphorus[3]). The weight of unreacted phosphorus, together with the weight of phosphorus in the nitride, gave the total flow of phosphorus during the experiment, hence its flow rate.

When mixtures of phosphorus and hydrocarbon were allowed to react with active nitrogen, the trapped products were warmed and swept through consecutive bubblers containing sodium hydroxide and silver nitrate solutions to remove hydrogen cyanide and traces of phosphine, respectively. Excess phosphorus was distilled from the trap and weighed as before.

No "hang-fire" behavior, such as described by Strutt, was observed. The phosphorus vapor reacted with a pink flame immediately as it emerged into the yellow afterglow. The products of the reaction appeared to be mainly amorphous, probably polymeric phosphorus nitrides; red phosphorus was not formed in significant amounts.

With active nitrogen formed in either a condensed or microwave discharge, the rate of formation of the nitride, in a system "poisoned" with a trace of H_2O vapor, increased rapidly to a "plateau" value with increase of P_4 flow rate. At the "plateau" value, the amount of nitrogen bound as nitride corresponded to

the flow rate of atomic nitrogen estimated by the NO "titration," i.e., a ratio $[N]_{NO}/[N]_{PN} \approx 1$. With increase in the phosphorus flow rate, the atomic ratio $[N]/[P]$ in the nitride changed gradually from the value corresponding to an empirical formula P_3N_5 to a value approaching that for PN, and, for an "unpoisoned" system, it actually became equal to unity. The nitride changed correspondingly from colorless through yellow to brown and finally to dark brown.

It was not found possible to study the rate of the reaction by stopping it with a cobalt target after different reaction times,[2] owing to deposition of nitride on the target, which quickly rendered it ineffective for recombining nitrogen atoms. From this, it may be inferred that recombination of N atoms was not favored at walls coated with the nitride.

Attempts to stop the reaction after different reaction times, by "titrating" out the unreacted N atoms with NO, were limited to low flow rates of P_4 to reduce the rate of deposition of nitride and loss of visibility.

Complete consumption of N atoms occurred after quite short reaction times, even when the P_4 flow rate was one-tenth, or less, that of the N atoms. It is possible that recombination of N atoms occurred by a mechanism of the type

$$P_4 + N \longrightarrow [P_4N] \xrightarrow{[N]} P_4 + N_2 \qquad (1)$$
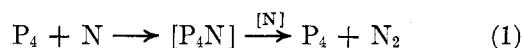
The initial rate of consumption of N atoms, calculated simply as $[N]_{reacted}/t$ for short reaction times, was found to be linear with the initial concentration of phosphorus. From the slope of the line and the initial N atom concentration, a second-order rate constant of about 5×10^{12} cm³ mol⁻¹ sec⁻¹ was obtained. This probably represents an *upper limit* to the rate constant for the initial rate of N atom attack on P_4, since it is estimated from data for the total consumption of N atoms by nitride formation and possibly also by reaction 1. It is possible, too, that P_4 may be regenerated
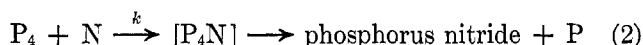
(2) E. M. Levy and C. A. Winkler, *Can. J. Chem.*, **40**, 686 (1962).
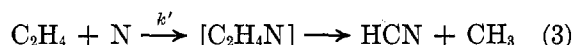(3) D. F. Boltz and M. G. Mellon, *Anal. Chem.*, **19**, 873 (1947).

during reaction 1 in some form that reacts with N more rapidly than does the tetrahedral molecule.

Rate constants for the N + P_4 reaction were also obtained from competitive reactions with C_2H_4 and C_4H_8. The relative extents of the two reactions were estimated from the relative amounts of nitrogen contained in the phosphorus nitride and in the HCN produced from the olefin.

In one set of experiments, with active nitrogen from a condensed discharge, in a "poisoned" system, the composition of the P_4 + C_2H_4 mixture was varied from 0 to 100 mol % P. As the mole per cent of P was increased, consumption of active nitrogen to form the nitride increased rapidly and eventually became equal to the NO "titration" flow rate of N atoms (8 μmol sec^{-1}). At the same time, the yield of HCN decreased rapidly, in a manner to suggest that the reaction with P_4 was considerably faster than that with C_2H_4. A rough estimate of the relation between the two rates was made, on the assumptions that cross-induced reactions were not significant and that the rate-controlling steps of the two reactions are, respectively

$$P_4 + N \xrightarrow{k} [P_4N] \longrightarrow \text{phosphorus nitride} + P \quad (2)$$

and

$$C_2H_4 + N \xrightarrow{k'} [C_2H_4N] \longrightarrow HCN + CH_3 \quad (3)$$

On this basis

$$\frac{d[PN]/dt}{d[HCN]/dt} = \frac{k}{k'} \frac{a[P_4]}{b[C_2H_4]}$$

where

$$a = \frac{[N]_{PN}}{[P_4]_{reacted}}, \qquad b = \frac{[HCN]_{produced}}{[C_2H_4]_{reacted}}$$

From the data for flow rates of P_4 and C_2H_4 sufficient to react completely with the active nitrogen present ("plateau" values), a ratio of $k/k' \approx 25$ was obtained.

Similar studies were made with active nitrogen from a microwave discharge, in an "unpoisoned" system, using C_2H_4, cis-C_4H_8, or trans-C_4H_8 as the olefin in competition with P_4. The results are shown in Table I, where k' refers to C_2H_4, k'' to cis-C_4H_8, and k''' to trans-C_4H_8, as the competitive reactant. (The reasonably good agreement between the values inferred from the C_2H_4 and C_4H_8 systems, in spite of the tenfold difference in rate with which these hydrocarbons themselves react with active nitrogen, suggests that cross-induced reactions were not significant.) The rate constant thus obtained for the P_4–active nitrogen reaction was of the order 10^{11} cm^3 mol^{-1} sec^{-1}.

During the competitive reactions of C_2H_4 and P_4 with active nitrogen, some PH_3 was formed ($\sim$0.004 μmol/sec). This is in accord with the formation of hydrogen

atoms in the ethylene reaction with active nitrogen.[4,5–10] The formation of PH_3 also suggests that, in these competitive reactions, hydrogen atoms react faster with phosphorus or phosphorus fragments than with ethylene.

The mechanism of the active nitrogen reaction with P_4 is probably quite complex after the initial rupture of the P_4 tetrahedron. Phosphorus species ranging from P to P_4 may exist in the system, together with a range of phosphorus nitride species. Such species might interact in a variety of ways to yield the solid products of variable composition observed with different relative flow rates of the reactants. Only an exhaustive study of the intermediates present would permit details of the mechanism to be elucidated.

(4) See footnote a of Table I.

(5) J. H. Greenblatt and C. A. Winkler, Can. J. Res., 327, 721 (1949).

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The Reaction of Colloidal Sulfur with Sulfite[1]

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In an idealized experiment designed to study reaction kinetics in a colloidal system in which particles are growing or being consumed, it would be possible to observe a typical particle and to follow its change in size as a function of composition of the medium and particle concentration. This situation is, to a limited extent, realized in the system in which colloidal sulfur having a narrow particle size distribution reacts with sulfite ions to form thiosulfate

$$S(\text{colloid}) + SO_3^{2-} \longrightarrow S_2O_3^{2-} \quad (A)$$
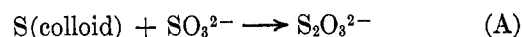
It is the purpose of this report to describe studies of this reaction in which the change in average particle size in a suspension of colloidal sulfur is measured by light-scattering techniques as a function of pH, total sulfite concentration, and particle number.

The preparation and properties of colloidal sulfur suspensions having a narrow range of particle sizes have been thoroughly described by the late Professor La Mer