

were incurred in measuring broad weak signals and in those cases where collapsed lines were superimposed on uncollapsed spectra.

In all cases we have assigned the faster rate to the free ions on the basis of the following evidence. (1) The larger rate constants have essentially the same value and, furthermore, these reactions all have low activation energies (≈ 5 kcal/mole). This is not consistent with the formation of different ion pairs. (2) The smaller rate constants all agree with Weissman's data. Conductance studies of aromatic anion radicals show that except in Na-DME all of the combinations of cation and solvents favor the formation of ion pairs at room temperature.⁹ Thus in the slow exchange limit the measured rates must apply to reaction 2. The free ions show up so prominently in the collapsed spectra because of their narrow lines. This does not exhaust our arguments but should suffice.

The major discrepancy in Table I arises with the dissociated ion in the Na-THF system. We are not sure of the reason for this difference, but would like to point out that unwanted line width contributions are much more likely to introduce errors when one is working at the slow exchange limit. Our estimates of the rate constants for the ion pairs are in agreement with previous work but are not as accurate since the spectra could not be collapsed with reasonable naphthalene concentrations. Unfortunately, esr measurements give only a limited amount of information about the total system. We plan to supplement this work by means of a pulsed nmr study of ²³Na relaxation and, in particular, to determine the rate of dissociation of the ion pair.

In addition to providing access to previously concealed rate processes the technique described here shows considerable promise for complex systems since the esr spectra do not have to be either well resolved or analyzed. Our experiments on stilbene and other systems show that experimental second moments can easily be obtained which fall within 10% of those calculated from stick spectra. Solubility may present a problem, but if necessary it can be partially circumvented by deuterating the radicals to decrease the exchange rate required to collapse their spectra. We plan to make a more detailed report of our work at a later time.

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Reactions of Phosphorus Trioxide with Some Compounds of the Group III Elements

Sir:

Phosphorus trioxide (P_4O_6) is expected¹ to donate lone-pair electrons to Lewis acids to give addition complexes without disruption of the P_4O_6 birdcage structure. On the other hand, exchange of parts between P_4O_6 and, for example, tricoordinated boron compounds might also be possible. Both situations have actually been observed.

When diborane is slowly bubbled through a solution of P_4O_6 in dry chloroform at 25°, a reaction takes place

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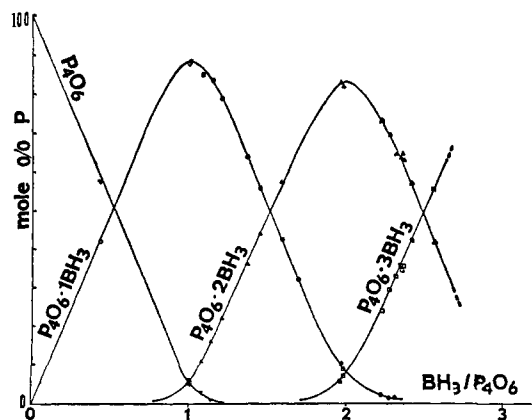


Figure 1. Distribution of species at equilibrium in the system P_4O_6 vs. B_2H_6 in chloroform solution at 25°. The open symbols refer to samples prepared by bubbling B_2H_6 through a chloroform solution of P_4O_6 and the half-shaded symbols to samples obtained by addition of P_4O_6 to a previously equilibrated sample or by admixing two such samples. The full-shaded symbols refer to samples obtained from $P_4O_6 \cdot 3BH_3$ crystals.

which has been followed quantitatively by P^{31} nmr. Successive nmr spectra show a sequential reaction similar to that already observed between P_4O_6 with $Ni(CO)_4$.¹ The observed coupling constant and chemical shifts correspond to successive coordination of one, two, and three BH_3 groups around the P_4O_6 . The P^{31} and H^1 nmr data for the individual species are presented in Table I.

Table I. Nmr Data for Phosphorus Trioxide-Borane Complexes^a

	From P^{31} spectra		From H^1 spectra		
	$\delta_{\text{coord P}}$	$\delta_{\text{uncoord P}}$	J_{P-O-P}	δ_H	J_{B-H} J_{P-B-H}
$P_4O_6 \cdot BH_3$	-90.4	-118.2	27.5	-0.7	102 18
$P_4O_6 \cdot 2BH_3$	-98.7	-119.2	24.7	-0.65	~100
$P_4O_6 \cdot 3BH_3$	-103.6	-114.6	21		

^a P^{31} spectra in *n*-hexane and H^1 spectra in $CHCl_3$. P^{31} chemical shifts, δ in ppm, are referenced to 85% H_3PO_4 but were measured with respect to P_4O_6 at -113 ppm. Proton chemical shifts, δ in ppm, are referenced to tetramethylsilane. Coupling constants J , are in cps. ^b J_{P-O-P} represents the coupling constants between coordinated and uncoordinated phosphorus atoms.

The rate of incorporation of diborane at 1 atm pressure in the P_4O_6 solution is approximately constant until it stops at a ratio of total uncoordinated P to total P of ca. 1:3. The product then consists of an equilibrium mixture of ca. 64% $P_4O_6 \cdot 2BH_3$ and 36% $P_4O_6 \cdot 3BH_3$.

Well-formed crystals of the $P_4O_6 \cdot 3BH_3$ complex are observed to form when concentrated chloroform solutions corresponding to the maximum possible incorporation of diborane under 1 atm are cooled by Dry Ice. The crystals of $P_4O_6 \cdot 3BH_3$ are so unstable that we have been unable to dry them. When redissolved in chloroform, they decompose in a few minutes with evolution of B_2H_6 to give the above equilibrium mixture.

The reaction is seen to follow the same path when diborane is allowed to react with P_4O_6 in the absence of a solvent, but the $P_4O_6 \cdot 2BH_3$ complex then precipitates and the coordination of further BH_3 groups is thus prevented. This compound has been recrystallized as

needles from *n*-hexane and an X-ray study is underway. The nmr spectrum of its chloroform solution is identical with that observed for the directly prepared mixture exhibiting the same over-all composition.

Structural proofs in addition to the nmr were obtained by treating mixtures of various over-all compositions, as well as the isolated $P_4O_6 \cdot 2BH_3$ species, with an excess of nickel tetracarbonyl. First the uncoordinated phosphorus atoms were seen to react with the $Ni(CO)_4$. Then the BH_3 groups are stripped off and replaced by $Ni(CO)_3$ groups. Finally, the well-characterized $P_4O_6[Ni(CO)_3]_4$ complex¹ is obtained, proving that the basic birdcage structure of the P_4O_6 persisted throughout the reactions with diborane.

Equilibria are reached rapidly between the various $P_4O_6 \cdot xBH_3$ complexes in solution, and the distribution of species at equilibrium (see Figure 1) depends only on the over-all BH_3/P_4O_6 mole ratio in solution and has been achieved by using various combinations of starting materials to give the BH_3/P_4O_6 ratio.

When P_4O_6 dissolved in 4 moles or more of $BF_3 \cdot O(C_2H_5)_2$ (less than 4 moles gives two phases) is allowed to stand at room temperature, a slow reaction is observed which is accompanied by the evolution of gaseous products including PF_3 , $(C_2H_5)_2O$, and PF_2OPF_2 . New peaks also appear in both the P^{31} and F^{19} nmr spectra and have been shown tentatively to include the end and middle groups of the $BF_3-B_2O_3$ scrambling system. Finally, gels and glasses are obtained for a large range of composition. These data mean that, under these conditions, exchange of bridging oxygens with fluorine atoms takes place between P_4O_6 and BF_3 , but an equilibrium is not reached since the PF_3 and PF_2OPF_2 are allowed to escape. Similarly, decomposition of the $P_4O_6 \cdot xBH_3$ complexes is observed at elevated temperatures or long standing.

PF_2OPF_2 is the first recorded member of the μ -oxo-perfluoropolyphosphorus family of compounds. It has been isolated and exhibits a molecular weight of 154 (mass spectrometry); calculated 154. In the P^{31} nmr spectra, it was found that $\delta_P = -114.6$ ppm, $J_{P-F} = 1380$ cps.

Highly reactive, amorphous, insoluble compounds were immediately precipitated by mixing phosphorus trioxide with BCl_3 , BBr_3 , BI_3 , $AlCl_3$, $AlBr_3$, $GaCl_3$, and $InCl_3$ in various unreactive solvents.

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Weak Bases in Strong Acids. I. On the Hydration of Anilinium Ions in Aqueous Sulfuric Acid¹

Sir:

The relative base strengths of various classes of amines in dilute aqueous solution were explained a number of years ago in terms of different degrees of specific hydration of the corresponding ammonium ions²⁻⁴ through hydrogen bonds from the acidic am-

monium hydrogens to water as an acceptor. An important argument in support of this idea was the regular difference of about 5 cal/mole deg between the entropies of ionization for the methyl representatives of each class of ion: ammonium, primary, secondary, and tertiary. This observed entropy effect was taken as plausible evidence for the ion hydration concept because any ordering of the hydration water molecules should be reflected in the entropy term and the free energy variation through the series from ammonia to trimethylamine is largely entropy controlled.

This interpretation has since gained considerable acceptance⁵ and has led to some elaborate equations relating free energy terms such as pK_a 's and activity coefficients to hydration numbers.⁶ The hydration concept was soon extended, through the leadership of Bell,⁷ Wyatt,⁸ and Taft,⁹ to explain the differing response of weakly basic amines to increasingly strong aqueous acid in which water for hydration of the ammonium ions becomes decreasingly available.¹⁰ However, no data on variation of entropy or heat capacity of the relevant ions have been available for the strong acid-weak base systems to support or refute these extensions from the strong base-weak acid reference point. It is the chief purpose of the present communication to show that the entropy criterion for hydration cannot be used for the aqueous sulfuric acid system over the 10-70% range.

In Tables I and II are presented the thermodynamic data for transfer of anilinium and dimethylanilinium ions from dilute aqueous sulfuric acid to a series of more concentrated acids up to 70%. In each case, the comparison is made relative to the tetraethylammonium ion as an unhydrated standard. The free energy data are calculated from the elegant solubility study of Boyd,¹³ and the heats of transfer were measured in a calorimeter described by us recently.¹⁴ Our enthalpy measurements were usually done at amine salt concentrations near 10^{-3} M, but $\Delta\bar{H}_s$ was independent of concentration up to 1.5×10^{-2} M, showing that solute-solute interactions are negligible at these levels.¹⁵ The partial molar heats of solution of anilinium bisulfate and N,N-dimethylanilinium bisulfate were calculated from the heats obtained by direct injection of the amine from its pure liquid state (l) into the series of sulfuric acid solutions. The reaction in

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(15) The thermodynamic properties described here are not to be confused with those derived in this laboratory through extrapolation for a series of ionic equilibria involving weak bases in dilute aqueous solution.¹⁰

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