range in polar media *via* singlet excited states.[14] Comparison of 2,4-heptadienone with conjugated dienes, the only highly flexible compounds whose excited states are characterized in comparable detail, reveals that lack of intersystem crossing and efficient internal conversion from S_1 to S_0 are common features. Possibly the wealth of vibrational modes in S_1 allows internal conversion and isomerization to compete effectively with intersystem crossing. A striking difference between dienes and dienones is the low efficiency of triplet isomerization for dienones.

Acknowledgment. We wish to thank Professor Steven Hixson for stimulating discussion and the National Science Foundation for a grant.

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Magnesium Ion Catalysis of the Hydrolysis of Phenyl Phosphosulfate in Acetonitrile–Water Mixed Solvent

Sir:

Magnesium ion is an essential cofactor in enzymatic reactions of 3′-phosphoadenosine 5′-phosphosulfate which acts as a sulfate group donor to numerous phenols, steroids, and carbohydrates, etc.[1] However, in nonenzymatic hydrolysis of phenyl phosphosulfate (PPS) in water, essentially no magnesium ion catalysis was detected.[2] The effects of metal ion on nonenzymatic polyphosphate hydrolysis have also been extensively studied but the catalysis observed is not large.[3] Rate acceleration has been observed only in the hydrolysis of esters which have a neighboring functional group for chelation with metal ions.[4]

For an efficient catalysis to occur, a metal ion and phosphate (or sulfate) must form a complex. This would be, however, an unfavorable process in water because of favored hydration of the metal ion and ester, whereas, in an enzymatic reaction, the medium at the active site is not necessarily water but rather would be hydrophobic in favor of metal ion–substrate binding. We now report that the magnesium ion catalyzed hydrolysis of PPS is highly sensitive to the water content of an acetonitrile–water mixed solvent.[5]

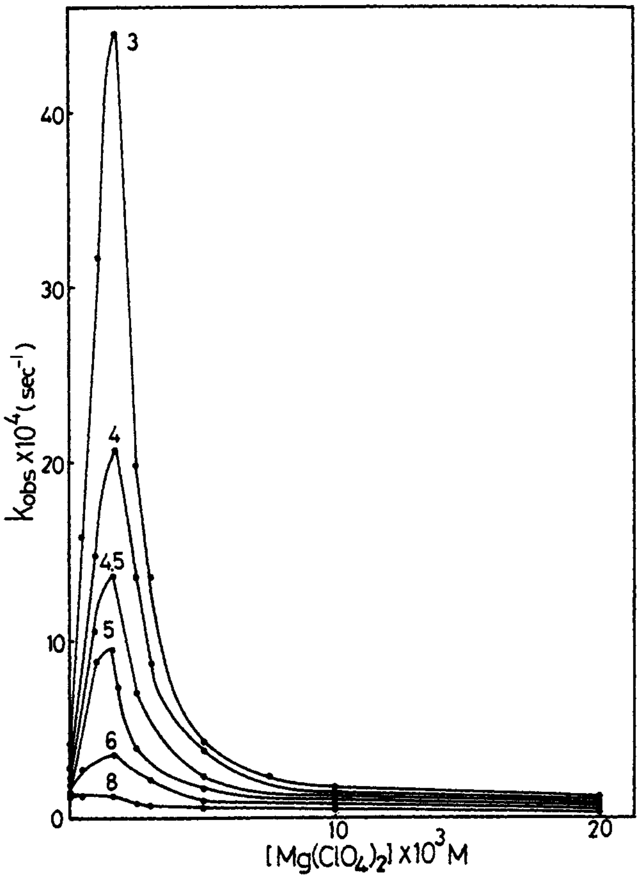

Figure 1. Effect of magnesium ion on the hydrolysis of phenyl phosphosulfate (PPS): $[PPS] = 1.8 \times 10^{-3}$ *M*; $[HClO_4] = 1.0 \times 10^{-3}$ *M*; $[n\text{-}Bu_4N^+ClO_4^-] = 0.02$ *M*; 25°. The numbers in the plots are the molar concentrations of water in acetonitrile–water mixed solvent.

The hydrolysis of the diammonium salt of PPS has been carried out in acetonitrile–water containing tetra-*n*-butylammonium perchlorate as the buffer reagent, and magnesium perchlorate and perchloric acid as the catalysts. Most reaction mixtures were homogeneous during the reaction, although, in the solvents of low water content (less than 3 *M*), ammonium sulfate occasionally precipitated out at the end of the reaction. The rate of reaction was followed spectrophotometrically by quenching the reaction mixture with aqueous sodium hydroxide according to the previous method[2] except for centrifugation of the quenched solutions to remove magnesium hydroxide.[6] The results are shown in Figure 1. (1) The rate acceleration by magnesium ion is not observable when the water content of the medium exceeds 8 *M*; rather, the addition of magnesium ion tends to inhibit the acid catalysis (shown by intercepts). (2) A large rate acceleration takes place in a medium of low water content showing a maximum in each plot of k_{obsd} *vs.* $[Mg(ClO_4)_2]$ where the concentration of magnesium ion is very close to the initial concentration of the substrate ($[PPS] = 1.8 \times 10^{-3}$ *M*).[7] For example, in the solvent of $[H_2O] = 3$ *M*, the k_{obsd} at the maximum ($k_{max} = 4.45 \times 10^{-3}$ sec^{-1}) is ten times larger than the k_{obsd} in the absence of

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(1) F. Lipmann, *Science*, **130**, 1319 (1959); A. B. Roy, *Advan. Enzymol.*, **22**, 204 (1960).

(2) (a) S. J. Benkovic and R. C. Hevey, *J. Amer. Chem. Soc.*, **92**, 4971 (1970); (b) W. Tagaki, T. Eiki, and I. Tanaka, *Bull. Chem. Soc. Jap.*, **44**, 1139 (1971).

(3) B. S. Cooperman, *Biochemistry*, **8**, 5005 (1969), and references therein.

(4) (a) Phosphate hydrolysis: R. Hofstetter, Y. Murakami, G. Mont, and A. E. Martell, *J. Amer. Chem. Soc.*, **84**, 3041 (1962); Y. Murakami, J. Sunamoto, and H. Sadamori, *Chem. Commun.*, 983 (1969); S. J. Benkovic and L. K. Dunikoski, Jr., *J. Amer. Chem. Soc.*, **93**, 1526 (1971). (b) Sulfate hydrolysis: R. W. Hay and J. A. G. Edmonds, *Chem. Commun.*, 969 (1967).

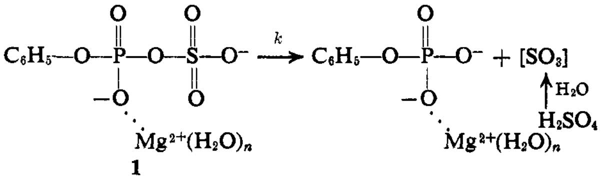
(5) A model reaction of hydrolytic enzymes has also been examined in acetonitrile of low water content: G. Wallerberg, J. Boger, and P. Haake, *J. Amer. Chem. Soc.*, **93**, 4938 (1971).

(6) Good pseudo-first-order rate constants were obtained up to 90% completion of the reaction, in the range of $[HClO_4] = 0.3\text{–}3.0 \times 10^{-3}$ *M*, both in the presence and absence of $Mg(ClO_4)_2$, although significant deviation from the first-order kinetics due to autocatalytic rate acceleration was observed below $[HClO_4] = 0.3 \times 10^{-3}$ *M*. The rates were invariant to the change of salt ($n\text{-}Bu_4{}^+NClO_4{}^-$) concentration from 0.02 to 0.2 *M* for all the mixed solvents as well as pure water (see also p 4973 in ref 2a). Hydrolysis of neither the product (phosphate) nor solvent (acetonitrile) was detected.

(7) Similar curves were also observed when $[HClO_4] = 0.5 \times 10^{-3}$ *M*.

Mg^{2+} ion ($k_0 = 4.44 \times 10^{-4}$ sec^{-1}). These k_{max} and k_0 are dependent on both water and acid concentration, and the ratio (k_{max}/k_0) appears to increase linearly with decreasing water concentration, and exponentially with decreasing acid concentration,[8] at least in the range of [H_2O] = 3–8 *M* and [$HClO_4$] = 0.3–3 × 10^{-3} *M*.

The above observations suggest that the 1:1 complex of the ester and magnesium ion **1** is catalytically active, while the higher order complexes are stable and inert to hydrolysis. The absence of the salt effect[6] may eliminate the possibility that the inhibition at higher Mg^{2+} concentration is due to such an effect. Presumably, **1** decomposes unimolecularly to form a phosphate–magnesium ion complex and sulfur trioxide.[9]



Much remains to be clarified in order to know the detailed mechanism of this magnesium ion catalysis, in particular to derive a reasonable rate law. Nevertheless, it may be of considerable importance to note that a change of medium alone causes a profound influence on the effectiveness of metal ion catalysis, even in the absence of a suitably located functional group for coordination with metal ion.

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[8] Preliminary experiments showed that the plots of log k_{obsd} *vs.* log [$HClO_4$] are linear with slopes of 1.6 (when [PPS] = [$Mg(ClO_4)_2$] = 1.8 × 10^{-3} *M*) and 3.2 in the absence of $Mg(ClO_4)_2$, respectively, in a range of [$HClO_4$] = 0.3–3.0 × 10^{-3} *M*. The slope appears to be invariant to the change of water concentration from 4 to 6 *M*.

[9] Similar unimolecular fission of the S–O bond has been suggested in the acid-catalyzed hydrolysis of PPS.[2]

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Synthesis of Unsymmetrical Secondary and Tertiary Amines from Amines by Palladium Catalyst

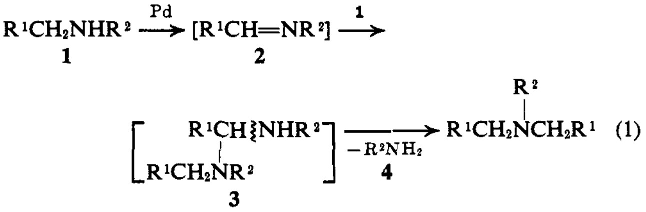
Sir:

Unsymmetrical amines are synthesized by Hofmann alkylation[1] or reductive alkylation[2] of either ammonia or amines and by modifications of these reactions.[3]

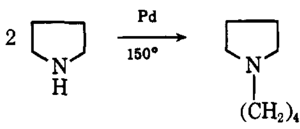
We wish to report a new process for the synthesis of unsymmetrical secondary and tertiary amines by dehydrogenation of primary or secondary amines by palladium black. The method is operationally simple, highly selective, and efficient, hence offers advantages over previous methods.

In a general procedure, a suspension of palladium black (5 wt%) in amines (5–10 g) was heated at 25–200° with stirring for 3–20 hr. After filtration of palladium the products were distilled. The distillate was analyzed by vpc, and the structure of the products was assigned by comparison of their spectral data with those of authentic samples.

Treatment of primary amines having activated α hydrogens with Pd at 25° afforded secondary amines and/or imines as shown in Table I. Thus, allylamine was converted to *N*-propylideneallylamine (95%), while benzylamine led to *N*-benzylidenebenzylamine (45%) and *N*,*N*-dibenzylamine (45%). These reactions can be illustrated by addition of the amine **1** to the intermediate imine **2** derived from dehydrogenation[4] of **1** followed by elimination of ammonia[5] (**4**, R^2 = H) as shown in eq 1.



Analogous reactions were generally performed on secondary amines giving tertiary amines with two identical substituents. Reaction of *N*-methylbenzylamine with Pd afforded *N*-methyldibenzylamine in 85% yield in addition to methylamine. *N*-Methylaniline was also converted to *N*,*N*-dimethylaniline along with aniline. Liberation of amines such as methylamine and aniline in these reactions would be rationalized by cleavage[6] of the C–N bond of the intermediate **3**. This is clearly demonstrated by formation of 1-pyrrolidinebutylamine (**5**, 98%) on treatment of pyrrolidine with Pd at 150° for 5 hr.



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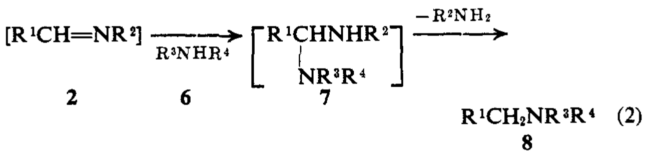
In analogy with formation of tertiary amines in eq 1, amine exchange reactions might be expected by introducing a primary amine (**6**, R^4 = H) or a secondary amine (**6**) at the stage of addition of the amine to the intermediate imine **2** followed by extruding R^2NH_2 (eq 2). Indeed, as shown in Table II, reaction of *N*-methylbenzylamine with aniline afforded *N*-phenylbenzylamine (48%) and *N*-benzylideneaniline (52%) by exchanging the methyl group for the phenyl group. Further, addition of a secondary amine to **2** to give **7** followed by extruding R^2NH_2 can also be achieved selectively. Thus, reaction of *N*-methylbenzylamine with *N*-methylbutylamine gave *N*-butyl-*N*-methyl-



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[2] W. S. Emerson, *Org. React.*, **4**, 174 (1948).

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[5] K. W. Rosenmund and G. Jordan, *Chem. Ber.*, **58B**, 51 (1925).

[6] Palladium must play an important role in the cleavage of the intermediate **3**, since thermal reaction of *N*-benzylidenemethylamine with *N*-methylbenzylamine without Pd led to *N*-benzylidenebenzylamine, but not to *N*-methyldibenzylamine, the ordinary product of the reaction of *N*-methylbenzylamine with Pd.