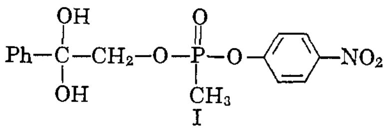
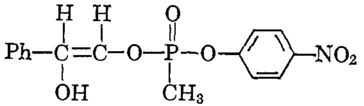
serve as models of the reactions which occur at the active sites of enzymes. We report the marked enhancement of the solvolytic displacement of *p*-nitrophenol from a phosphonate ester by a neighboring ketonic carbonyl group. *p*-Nitrophenyl phenacyl methylphosphonate[3] is hydrolyzed with $k_{OH^-} = 5.106 \times 10^3\ M^{-1}\ sec^{-1}$ in 5% aqueous dioxane, 25°, over the pH range 7.2–8.0 in the presence of 0.1 *M* tris(hydroxymethyl)aminomethane (TRIS), and at pH 7.22 at constant ionic strength in TRIS buffer over the concentration range 0.1 to 0.04 *M*.[4] The reaction is first order in phosphonate, hydroxide ion, and in TRIS·base. The results are consistent with the rate expression $k_{obsd} = k_1[OH^-] + k_2[TRIS \cdot base] + k_3$, where $k_2 = 0.412\ M^{-1}\ sec^{-1}$ and $k_3 = 1.4 \times 10^{-4}\ sec^{-1}$. At pH 7.81, $t_{1/2} = 41.0$ sec for the hydrolysis of *p*-nitrophenyl phenacyl methylphosphonate. Under these conditions ethyl *p*-nitrophenyl methylphosphonate hydrolyzes with $t_{1/2} = 3.63 \times 10^5$ sec. The carbonyl group thus increases the hydrolysis rate by a factor of *ca.* 9000 times.

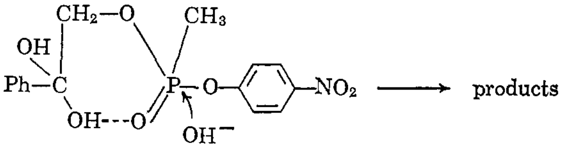
Enhancement in reaction rate can be explained in several ways. Hydration of the carbonyl group to give I, in which the rate enhancement would be due either to hydrogen-bonding assistance (eq 1) or to attack by the corresponding anion (eq 2). Alternatively, the active species could be the enol II, which could also participate *via* reactions of either type 1 or 2. Further considerations are activation of the phosphonyl group by an inductive effect or through orbital overlap with the carbonyl π-bonding electrons.



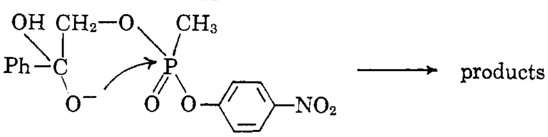
I



II



(1)



(2)

In the analogous hydrolysis of dimethylphosphoacetoin, in which, however, acetoin is the product of hydrolysis, Ramirez[5] indicated a preference for reaction path 2, *via* the enol corresponding to II, based upon his observation that certain cyclic saturated oxyphosphoranes hydrolyze in ether or benzene to yield cyclic phosphotriester. On the other hand, Cox and Farmer[6] argue in favor of path 1 as being consistent with their finding of the incorporation of one oxygen atom derived from solvent into the displaced dimethyl phosphate ion. In several cases where enolization cannot occur, rate enhancement of carboxylate ester hydrolysis by aldehydic carbonyl has been ascribed to the hydrated carbonyl group *via* route 2.[1d,7] In our study, compelling evidence against the enolization mechanisms is our observation that the hydrolysis of 1-anthraquinonyl *p*-nitrophenyl methylphosphonate in 25% *p*-dioxane–75% TRIS buffer of pH 8.00 was only 60 times slower than *p*-nitrophenyl phenacyl methylphosphonate under the same conditions. Furthermore, hydrolysis *via* the enol mechanisms is considered most unlikely since one should then expect to observe, to at least some extent, hydrolysis *via* the competitive pathway to give *p*-nitrophenyl methylphosphonate.[8] None was observed.[4] To be compatible with our results, reaction *via* intermediate I requires a very rapid preequilibrium step, since no deviations in reaction kinetics were observed, the first point being taken at 25 sec.[9] Based upon ultraviolet absorption in dioxane and dioxane–H_2O (50:50) the extent of hydration or hydroxyamination by 0.1 *M* TRIS (measured at pH 6.88) is at most minor.[10] Unlike the observation of Shalitin and Bernhard,[1d] addition of KCN had only a very small effect upon rate (20% enhancement at pH 7.9). On the other hand, in the presence of 0.02 *N* hydroxylamine hydrochloride at pH 3.5, a 10-fold increase in the rate of displacement of *p*-nitrophenol was observed.

It is noteworthy that with *ketonic group* participation in carboxylic ester hydrolysis, Newman and Hishida[7b] found an acceleration factor of *ca.* 10×, and Shalitin and Bernhard[1d] one of 40×, whereas in this study we have observed in phosphonate ester hydrolysis a rate enhancement several magnitudes larger. A detailed study of the reaction mechanism is in progress.

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[3] Satisfactory elemental analyses were obtained on all compounds.

[4] Excellent first-order plots were obtained to >4 half-times. The production of *p*-nitrophenol, determined as the anion at 402 mμ, is stoichiometric; phenacyl methylphosphonic acid has been isolated in 80% yield.

[5] F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962).

[6] J. R. Cox, Jr., and J. J. Farmer, unpublished results, cited in ref 2.

[7] (a) M. L. Bender and M. S. Silver, *J. Am. Chem. Soc.*, **84**, 4589 (1962); (b) M. S. Newman and S. Hishida, *ibid.*, **84**, 3582 (1962).

[8] *p*-Nitrophenyl methylphosphonate anion is quite stable under these conditions, 0.25% hydrolysis in 27 hr at pH 7.9.

[9] Slow equilibrium with solvent was eliminated as a possibility since storage of the phosphonate ester in dioxane-water (25:1) for 4 days resulted in no change in hydrolysis rate.

[10] Maximum at 273 mμ unchanged in wavelength; reduced 3.7% in absorbance. Maximum at 243 mμ shifted to 248 mμ; no change in absorbance.

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Synthesis of the Tetranitratoborate Anion

Sir:

The simple nitrate of boron has never been isolated despite efforts by several investigators.[1-3] The products of the reactions are invariably B_2O_3 or possibly $BONO_3$. We wish to report the synthesis of tetramethylammonium tetranitratoborate, $[Me_4N][B(NO_3)_4]$, from the action of liquid dinitrogen tetroxide on the corresponding tetrachloride. The complex has proven

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[1] M. Schmeisser, *Angew. Chem.*, **67**, 483 (1955).

[2] M. Schmeisser and K. Brandle, *ibid.*, 73, 388 (1961).

[3] D. Lutzow, Dissertation, Munich, 1955.

to be remarkably stable and possesses rather unexpected properties.

The synthesis was accomplished by adding dinitrogen tetroxide to solid $[Me_4N][BCl_4]$ at −78° (mole ratio $N_2O_4/BCl_4^- > 8:1$); the system was then allowed to warm to 0° over a period of approximately 2 hr. The removal of the excess dinitrogen tetroxide, along with the nitrosyl chloride produced in the reaction, was effected at room temperature, leaving a white, crystalline solid with the approximate composition for the desired product. Prolonged contact with dinitrogen tetroxide, or carrying out the reaction at room temperature, increased the oxynitrate or boric oxide content. Extraction with ammonia removed the complex nitrate, leaving the oxide behind. The solid recovered from the filtrate was analyzed. *Anal.* Calcd for $[Me_4N][B(NO_3)_4]$: C, 14.41; H, 3.69; B, 3.30; Me_4N^+, 22.22; N (Devarda), 16.81. Found: C, 14.6; H, 4.8; B, 3.32; Me_4N^+, 22.42; N (Devarda), 16.94.[4]

The X-ray powder pattern of the solid was obtained by using Cu Kα radiation and is shown in Table I. The pattern shows no reflections for tetramethylammonium nitrate, a likely impurity.

Table I

d, A	RI[a]	*d*, A	RI	*d*, A	RI
7.25	s	3.39	s	2.35	w
5.70	m	3.29	w	2.32	w
5.15	s	3.19	w	2.20	vw
4.90	vw	3.15	w	2.15	vw
4.70	vw	3.05	m	2.02	w
4.40	m	2.82	w	1.98	w
3.90	vw	2.64	w	1.94	w
3.80	vs	2.60	w	1.91	w
3.60	w	2.49	w	1.88	w
3.45	w	2.45	w		

[a] Relative intensity.

The infrared spectrum in Nujol and KBr shows lines at 669, 743, 755, 767, 887, 950, 1007, 1297, 1311, 1356, 1385, 1416, 1489, 1582, 1612, and 1626 cm.$^{-1}$ The absorptions for ν_4 at 1582 to 1626 cm^{-1} and for ν_1 at 1297 and 1311 cm^{-1} are the two prominent bands. The 1582- and 1626-cm^{-1} lines appear as shoulders on the 1612-cm^{-1} lines. This splitting of the ν_4 and ν_1 absorptions together with the (ν_4–ν_1) separation of 271 to 339 cm^{-1} are expected for unidentate nitrato bonding.[5,6] Ionic nitrate vibrations at ~1330 cm^{-1} for tetramethylammonium nitrate were absent from the spectrum.

Table II

Concn[a]	Λ[b]	Concn	Λ
0.123	135	0.012	157
0.06	132	0.006	170
0.024	157	0.0024	184

[a] Molal. [b] In ohm^{-1} cm^{-2}.

Molecular weight determinations in acetonitrile in a concentration range of 0.045 to 0.288 *m* gave a value of 185 ± 15. The theory for $[Me_4N][B(NO_3)_4]$, assuming complete dissociation into two ions, is 166.5. Conductance measurements support dissociation. Equivalent conductance values obtained in acetonitrile at 18° are listed in Table II. A plot of Λ against the square root of the concentration is linear and extrapolates to an equivalent conductance of 210 ohm^{-1} cm^{-2} at infinite dilution. Berns and Fuoss[7] report an equivalent conductance for $[Me_4N]NO_3$ in acetonitrile at 25° of 200.5 ohm^{-1} cm^{-2} at infinite dilution. Thus dissociation into two ions is clearly indicated. If the conductivity data are used to calculate the measured molecular weight in the concentration range indicated, a value of about 205 is obtained which checks well with the measured value of 185 ± 15. A preliminary ^{11}B nmr spectrum shows the single expected peak with a chemical shift value of 44.0 ppm relative to $NaBH_4$ in acetonitrile. If the δ value for $NaBH_4$ in acetonitrile is comparable to its value in H_2O, $[Me_4N][B(NO_3)_4]$ has a chemical shift value comparable to $NaB(C_6H_5)_4$ and $NaB(OMe)_4$.

The complex is not noticeably soluble in, nor hydrolyzed by cold water. Some solubility is indicated in hot water. It is readily soluble in methanol, acetonitrile, ammonia, and dimethylformamide from which it can be recovered unchanged. Reaction occurs with sulfur dioxide to give products as yet unknown. As mentioned previously, a slow reaction occurs in dinitrogen tetroxide producing the boron oxide linkage.

$[Me_4N][B(NO_3)_4]$ is stable at room temperature; samples have been stored for periods of more than 2 months without noticeable decomposition. The compound is insensitive to shock when struck sharply with a hammer.

Acknowledgments. This work was sponsored by the Office of Naval Research under Contract ONR Nonr 3943(00). We also wish to thank J. S. Bellissimo for laboratory assistance and Professor R. W. Parry for consultation and the nmr analysis.

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(4) The total nitrogen by the Dumas method was 19.6% *vs.* the theoretical value of 21.02%. It has been our experience, however, with tetramethylammonium compounds and complex nitrates in general, that values slightly lower than theoretical are to be expected. The nitrogen balance obtained by adding Devarda (NO_3^-) and tetramethylammonium analyses was 21.18%, or nearly theoretical (21.02%).

(5) K. W. Bagnell, D. Brown, and J. G. H. duPreez, *J. Chem. Soc.*, 5523 (1964).

(6) B. O. Field and C. J. Hardy, *Quart. Rev.* (London), **18**, 385 (1964).

(7) D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **83**, 1321 (1961).

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Spin–Spin Coupling in Primary Alcohols

Sir:

We have measured the spin–spin coupling constant, J_{HCOH}, for a wide variety of primary alcohols in CCl_4 solution[1] and have found that J_{HCOH} for 0.22 *M* solutions (see Table I) increases as the electronegativity of the hydroxyl carbon is increased.[2] This conclusion

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(1) Measurements were made at 23° on a Varian HR-100 nmr spectrometer, using calibration by the usual audio side-band technique and CCl_4 dried over Linde Type 13-X molecular sieve. When the hydroxyl proton failed to show sharp splitting initially, the alcohol was purified by distillation, or by drying over molecular sieve, or by passing through a column of alumina or silica gel–molecular sieve; for troublesome cases a small amount of activated alumina was added to the nmr sample tube.

(2) A positive sign for J_{HCOH} has been established for 2-methyl-2-