isotopic $N_2$ molecules and in this case produce 9.86% $N^{15}N^{15}$.

## Experimental

**Potassium Nitrite-$N^{15}$.**[6]—10.0 ml. of 1.67 *N* nitric acid containing 31.4 atom per cent. excess $N^{15}$ was titrated to *p*H 7 with 2 *N* potassium hydroxide using a glass electrode. Evaporation of the solution on the steam-bath gave a quantitative yield of potassium nitrate-$N^{15}$. Of this, 0.950 g. was finely powdered and intimately mixed with 1.950 g. of pure powdered lead in the bottom of an eight-inch Pyrex test-tube. The temperature of the lower end of the tube was slowly raised to 350° in a small wire-wound furnace. The tube was cooled and the contents were rinsed into a centrifuge tube with two 5-ml. portions of distilled water. The lead oxide was centrifuged down and the clear supernatant liquid transferred to an evaporating dish. Evaporation gave a 0.682-g. residue, which contained 94% potassium nitrite as determined on a small sample by addition of standard acid permanganate and back-titration.[7] The yield was therefore 80.2%.

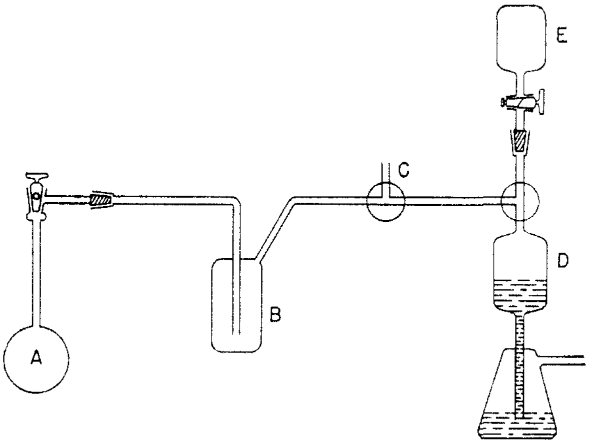

Fig. 1.

**3,5-Dinitrobenzazide.**—The procedure used was that of Sah and Ma.[8] By the use of 0.171 g. of the potassium nitrite-$N^{15}$, 0.412 g. or 89.7% yield of the dinitrobenzazide was obtained.

**Thermal Decomposition of 3,5-Dinitrobenzazide.**—A suspension of 0.150 g. of 3,5-dinitrobenzazide-$N^{15}$ in 10 ml. of water was placed in bulb A of the apparatus (Fig. 1). The suspension was frozen by cooling the bulb with a Dry Ice–acetone-bath, and the entire system was then evacuated by pumping at C. The stopcock on vessel A was closed, and the contents of A were gradually warmed to 100° by an external water-bath. Heating was continued for half an hour, and the contents were then allowed to cool. A liquid nitrogen-bath was placed around trap B, and A was connected by means of the various stopcocks to the reservoir of the Toepler pump D. The gaseous products were slowly toeplerred into a gas storage bulb E, avoiding sudden rushes through the trap B. Mass spectrometric analysis of the gas showed it to be nitrogen of 99.5$^+$% purity, and to contain 31.1 atom per cent. $N^{14}N^{15}$ and 0.1% $N^{15}N^{15}$.

**Deamination of 3,5-Dinitroaniline.**—The aqueous suspension from the decomposition reaction was extracted with two 10-ml. portions of ethyl acetate. The ethyl acetate was removed in a current of air, and the residue refluxed with 3 ml. of concentrated hydrochloric acid for three hours, during which time the solution was gradually concentrated to approximately 1 ml. The whole was taken up in 10 ml. of 50% sulfuric acid and transferred back to reaction vessel A. The solution was chilled to −10°, and 1 ml. of 5 *M* sodium nitrite solution added. The liquid in the bulb was frozen and pumped out as before, then the stopcock was closed and the contents gradually warmed to 100°, at which temperature it was held for 15 minutes. The liquid was then refrozen, and the gaseous products toeplerred through a liquid nitrogen-cooled trap into a storage bulb, as before. Mass spectrometric analysis showed no difference in isotopic composition from tank nitrogen.

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[6] A new method for the preparation of sodium nitrite-$N^{15}$, giving better yields has been described by K. Clusius and M. Hoch, *Helv. Chim. Acta*, **33**, 2122 (1950).

[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis." The Macmillan Co., New York, N. Y., 1945.

[8] Sah and Ma, *J. Chinese Chem. Soc.*, **2**, 159 (1934).

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RECEIVED MAY 21, 1951

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[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

# Comparison of Hydrogen Bonding Abilities of Some Organic Compounds of Phosphorus

BY GENNADY M. KOSOLAPOFF AND JOHN F. MCCULLOUGH

The maximum heats of mixing of chloroform with fifteen organophosphorus compounds were determined. Representative members of the families of types: $R_2P(O)OR$, $RP(O)(OR)_2$, $(RO)_3PO$, $(RO)_2P(O)Cl$, $ROP(O)Cl_2$, $(RO)_3P$ and $(RO)_2POH$ display differences in their hydrogen bonding ability, as reflected by the heat of mixing. These differences are qualitatively predictable from the structures of the compounds, showing enhanced activity with increased electron density at the central group.

Some time ago the heat of mixing of chloroform with phosphorus oxychloride[1] and with triethyl phosphate[1,2] was used as a method for estimation of the ability of the latter substances to form hydrogen bonds. It was of interest to extend such a study to the several rather readily available families of organophosphorus compounds in order to secure direct comparison of the hydrogen bonding tendencies in substances with various structures.

Accordingly, representative specimens of dialkyl phosphites, trialkyl phosphates, dialkyl chlorophosphates, alkyl dichlorophosphates, dialkyl alkanephosphonates and alkyl dialkylphosphinates were examined using the technique of the previous investigators.[1,2]

The results, which are summarized in Table I, readily show that the changes of structure bring about variations of the hydrogen bonding ability that can be qualitatively expected from considerations of the structural theory. Replacement of alkoxy groups (OR) by radicals (R) that are directly bonded to the central atom raises the hydrogen bonding ability. Replacement of chlorine atoms by alkoxy radicals causes a similar shift. The series: phosphorus oxychloride, alkyl dichlorophosphate, dialkyl chlorophosphate, trialkyl phosphate, shows the progressive manifestation of this effect very well. The relatively small change which takes place upon substitution of the first alkoxy group is rather unexpected, but the results are qualitatively in line with the grossly observable chemical behavior of the alkyl dichlorophosphates.

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[1] Audrieth and Steinman, THIS JOURNAL, **63**, 2115 (1941).

[2] Marvel, Copley and Ginsberg, *ibid.*, **62**, 3109 (1940).

TABLE I

| Compound | B.p., °C. | Mm. | $n_D$ | Max. molar heat of mixing with $CHCl_3$ | Mole fraction of $CHCl_3$ |
|---|---|---|---|---|---|
| $Bu_2P(O)OBu$ | 125–126 | 1 | $1.4445^{24}$ | 1430 | 0.540 |
| $BuP(O)(OBu)_2$ | 171 | 26 | $1.4321^{17}$ | 1380 | .542 |
| $PrP(O)(OEt)_2$ | 102 | 17 | $1.4156^{25}$ | 1233 | .573 |
| $EtP(O)(OEt)_2$ | 85–87 | 16 | $1.4094^{30}$ | 1155 | .570 |
| $(iso\text{-}PrO)_3PO$ | 99 | 11 | $1.4059^{20}$ | 1150 | .585 |
| $(PrO)_3PO$ | 84–86 | 1 | $1.4160^{17}$ | 1125 | .566 |
| $(BuO)_3PO$ | 140 | 2 | $1.4233^{17}$ | 1122 | .615 |
| $(EtO)_3PO$ | 112 | 22 | $1.4060^{17}$ | 1065 | .575 |
| $(BuO)_2POH$ | 131 | 18 | $1.4052^{23}$ | 980 | .628 |
| $(EtO)_2POH$ | 82 | 19 | $1.4051^{25}$ | 838 | .566 |
| $(BuO)_2P(O)Cl$ | 109 | 4 | $1.4302^{23}$ | 709 | .605 |
| $(BuO)_3P$ | 130 | 17 | $1.4302^{24}$ | 680 | .560 |
| $(EtO)_2P(O)Cl$ | 54 | 1 | $1.4156^{24}$ | 653 | .599 |
| $BuOP(O)Cl_2$ | 92–93 | 16 | ..... | 440 | .534 |
| $EtOP(O)Cl_2$ | 66–67 | 15 | ..... | 373 | .525 |
| $POCl_3$ | 105 | 740 | ..... | 368 | .574 |

It was impossible, unfortunately, to complete the entire series of possible structural variations by inclusion of trialkylphosphine oxides and trialkylphosphines in our study. The former substances are solids, while the latter have such obnoxious physical characteristics that close work with them in the currently used apparatus was effectively precluded. Therefore, it was impossible to establish conclusively whether or not the site of the hydrogen bond formation is a singular atom. The possibility of some bonding at the ester oxygen atoms, at the halogen atoms, and at the phosphorus atom (in the phosphites) still exists. Such multiple sites for hydrogen bonding would tend to cause a shift of the relative concentration of the components toward the chloroform side at the point of maximum heat evolution.[1] Conceivably, however, possible is a factor which may have a simultaneous but opposite effect on the location of the maximum. All systems studied here have rather low degree of stability; they are readily separated into components by simple distillation. As such they may be expected to obey the law of mass action, with substances having the greater heat of mixing with chloroform requiring a lesser preponderance of the latter in the mixture to display the heat maximum. Since all substances studied here have several potential bonding sites, the magnitude of this effect cannot be estimated, with the first effect apparently taking the predominant role.

Among the practical significant points resulting from this study the apparently superior characteristics of the esters of phosphinic and phosphonic acids may be pointed out. While many other factors are involved in the action of plasticizers, the hydrogen bonding effect is one of the more important ones and in this respect compounds of types $RP(O)(OR)_2$ and $R_2P(O)OR$ stand somewhat above trialkyl phosphates.

## Experimental Part

The apparatus used was constructed along the lines that were used previously.[1,2] The mixing chamber and the associated equipment were mounted as a unit on the cover of the calorimeter in order to facilitate the removal of this portion of the apparatus for recharging between runs. A glass stirrer was used within the mixing chamber instead of the silver wire,[1] in order to reduce heat exchange with the surroundings.

The substances used in the study were prepared by conventional methods and their constants are given in Table I. One new compound, butyl dibutylphosphinate, was prepared as follows.

A solution of 5.65 g. of sodium in 100 ml. of *n*-butanol was treated with 48.3 g. of dibutylphosphinyl chloride (prepared according to Kosolapoff and Watson[3]), with stirring and ice-cooling. The mixture was diluted with 200 ml. of dry benzene and was allowed to stand overnight. After filtration, there was obtained 35.8 g. (62.4%) of butyl dibutylphosphinate, a colorless liquid, b.p. 125–126° at 1 mm., $n^{24}\mathrm{D}$ 1.4445, $d^{24}_4$ 0.9271. Found: *MR*, 67.20; P, 13.32. Calcd. for $Bu_2P(O)OBu$: *MR*, 67.33; P, 13.22.

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[3] Kosolapoff and Watson, THIS JOURNAL, **73**, 4101 (1951).

AUBURN, ALABAMA

RECEIVED MAY 28, 1951

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

# Effect of Structure on Reactivity.[1] IV. Aminolysis of Esters with Secondary Amines

BY EDWARD McC. ARNETT,[2] JOHN G. MILLER AND ALLAN R. DAY

In the aminolysis of esters, secondary amines have been found to be very unreactive relative to primary amines. A number of secondary amines have been studied in the aminolysis of methyl lactate and phenyl acetate both in the presence and absence of ethylene glycol. The relative reactivities are: dimethylamine > piperidine > morpholine > diethanolamine > diethylamine > di-*n*-butylamine > di-*n*-propylamine.

Previous papers[3] in this series have dealt with the ammonolysis and aminolysis, using primary amines, of esters. The present paper reports the use of secondary amines for the aminolysis of esters.

The results show clearly that secondary amines are much less reactive than most primary amines. It was also noted that ethylene glycol which acts as a catalyst for the ammonolysis and primary aminolysis of esters actually hinders the reaction, in certain cases, when secondary amines are used.

## Experimental

The experimental method was modified slightly from that of the preceding papers in the series. To increase the accuracy with which the reaction systems were prepared, the ester was delivered to the reaction system by means of a buret before final dilution was made. The densities of the esters and the catalysts were determined immediately before

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(1) From a thesis submitted in April, 1949, by Edward McC. Arnett to the University of Pennsylvania.

(2) du Pont Fellow 1948–1949. Present address: Max Levy and Company, Wayne Avenue and Berkeley Street, Philadelphia, Pa.

(3) (a) M. Gordon, J. G. Miller and A. R. Day, THIS JOURNAL, **70**, 1946 (1948); (b) M. Gordon, J. G. Miller and A. R. Day, *ibid.*, **71**, 1245 (1949); (c) E. McC. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950).