opened at D; the bulb was quickly introduced into the dry-box where a sample of its contents was removed for analysis.

From 0.0531 g. of the solid, hydrolysis generated 126 cc. (5.63 mmoles) of hydrogen; the lithium content proved to be 0.0382 g. (5.50 mmoles). The ratio (1/1.02) of hydrogen generated to the lithium content is thus in excellent agreement with the equation

$$LiH + H_2O \longrightarrow LiOH + H_2$$

The total quantities of hydrogen and of lithium were, however, only about 88% of those expected of 0.0531 g. of lithium hydride. The nature of the impurity was not ascertained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Addition of Boron Trifluoride, Sulfur Trioxide and Sulfur Dioxide to Trimethylphosphine Oxide

BY ANTON B. BURG AND WILLIAM E. MCKEE[1]

Trimethylphosphine oxide reacts with boron trifluoride to form the vacuum-stable new compound $(CH_3)_3POBF_3$ (m.p. 149°, water-soluble, with reversible removal of BF_3 by the water). With sulfur trioxide, the less stable $(CH_3)_3POSO_3$ is formed; unlike $(C_2H_5)_3NOSO_3$ this is readily alcoholized, to form $(CH_3)_3POHOSO_3C_2H_5$ (m.p. 87°). Pressure–composition isotherms indicate a weak interaction between $(CH_3)_3PO$ and SO_2, whereas $(CH_3)_3NOSO_2$ is very firmly bonded. It appears that the oxygen atom in $(CH_3)_3PO$ is somewhat weaker as an electron donor than the oxygen atom in a trialkylamine oxide—a comparison bearing upon the question of the P–O bond order in $(CH_3)_3PO$.

Introduction

Trimethylphosphine oxide, $(CH_3)_3PO$, is formally similar to trimethylamine oxide, $(CH_3)_3NO$, which has been shown to form very stable compounds by addition to electron-acceptor substances.[2-5] Hence it is of interest to try the preparation of similar addition compounds of $(CH_3)_3PO$, in order to make a general comparison of the electron-donor powers of oxygen in these oxides. As a step toward this comparison, we have studied the behavior of BF_3, SO_3 and SO_2 with $(CH_3)_3PO$.

One might expect $(CH_3)_3PO$ to be a far weaker electron-donor than $(CH_3)_3NO$, since the latter has a strictly single-bonded oxygen atom, with a considerable negative formal charge, whereas the PO bond could have chiefly double-bond character through the use of hybridized 3d orbitals on the phosphorus atom. However, the well-known base-strengthening effect of the methyl group would tend to induce electron density toward oxygen, increasing the donor powers. A fuller discussion of oxygen in such situations appears elsewhere.[6] The present results indicate that $(CH_3)_3PO$ is a fairly strong electron donor, but evidently weaker than $(CH_3)_3NO$.

Experimental Part

Preparation of $(CH_3)_3PO$.—The method of Pickard and Kenyon[7] was modified for convenience: a solution of 0.167 mole of $POCl_3$ in 200 ml. of ether was added slowly to 0.50 mole of CH_3MgCl in one liter of ether, well stirred and cooled by ice–salt. The ether was evaporated off and the powdery residue was treated first with water and then with 500 ml. of a hot solution of Na_2CO_3 (slightly over 1 molar), to precipitate magnesium. After filtration, the solution was evaporated to a thick sirup, with occasional removal of solid NaCl. Finally the $(CH_3)_3PO$ was extracted by hot chloroform and purified by vacuum sublimation; yield 52%, based on CH_3MgCl; m.p. 137.5–138.5°.

The Compound $(CH_3)_3POBF_3$.—The addition of BF_3 to $(CH_3)_3PO$ was done first by leading a stream of BF_3 into a solution of 272 mg. of $(CH_3)_3PO$ in 5 ml. of $CHCl_3$. Most of the precipitate was collected on a sintered glass filter-stick and weighed as 295 mg. (68% recovery). After purification by sublimation in high vacuum, it melted in the range 148–150° (reproducible after heating at 215°). Titration of boric acid, after hydrolysis in boiling water and removal of fluoride as CaF_2,[3] gave 4.87% B (calcd. 4.77). Micro-combustion[8] gave 22.60% C (calcd. 22.53) and H as 5.67% (calcd. 5.67), confirming the formula $(CH_3)_3POBF_3$.

The compound $(CH_3)_3POBF_3$ was established also by synthesis without a solvent. Two glass U-tubes were sealed together in series and a 1:4 mixture of BF_3 and N_2 was passed over a weighed sample of $(CH_3)_3PO$, contained in the U-tube nearest to the gas inlet. After 45 minutes (room temperature) the gain in the weight of the system indicated completion of the addition reaction, but for certainty the gas stream was continued at 110°, with the second U-tube serving to catch any sublimate. The weight-gain was 216.5 mg. per 292.7 mg. of $(CH_3)_3PO$, or 1.003 BF_3 per $(CH_3)_3PO$. The entire product sublimed cleanly *in vacuo* and melted at 148–150°, demonstrating a quantitative synthesis.

Behavior of $(CH_3)_3POBF_3$ toward Water.—Although weight-stable in the open air, $(CH_3)_3POBF_3$ dissolves in water (very slowly unless pulverized), and lowers the freezing point nearly three times as far as expected from the formula weight. Thus 94.9 mg. of this complex, in 10.5 ml. of water, lowered the f.p. by 0.31°, or 2.9 times the expected 0.106°; also, 238.2 mg. in 10.2 ml. gave a lowering of 0.66°, or 2.44 times the expected 0.271°. Such results could be understood in terms of the equation $(CH_3)_3POBF_3 + 2H_2O \rightleftarrows (CH_3)_3PO + H_3O^+ + HOBF_3^-$, the reversibility of which would explain the higher average molecular weight in the more concentrated solution. This reversibility was further indicated by an 80% recovery of $(CH_3)_3POBF_3$ (m.p. 149–150°), obtained by evaporating the solution *in vacuo* and subliming the residue *in vacuo*.

This reversal of the hydrolytic decomposition was fully confirmed by the preparation of $(CH_3)_3POBF_3$ from an aqueous solution of $(CH_3)_3PO$. A 660-mg. sample of this oxide was dissolved in 5 ml. of water and treated with 1.5 ml. of $(C_2H_5)_2OBF_3$, diluted by 3 ml. of ether. After shaking to extract the BF_3 from the ether, the volatile solvents were evaporated off *in vacuo* and the residue was sublimed at pressures below 0.1 mm. (bath temperature 140°); yield

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(1) Most of the details of this work are to be found in the M.S. thesis of William Edgar McKee, University of Southern California Libraries, 1950 (available on microfilm).

(2) A. B. Burg, THIS JOURNAL, **65**, 1692 (1943).

(3) A. B. Burg and J. H. Bickerton, *ibid.*, **67**, 2261 (1945).

(4) W. K. Godfrey, M.S. Thesis, University of Southern California Libraries, 1948.

(5) H. Z. Lecher and W. B. Hardy, THIS JOURNAL, **70**, 3789 (1948).

(6) C. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

(7) R. H. Pickard and J. Kenyon, *ibid.*, **89**, 262 (1906).

(8) This analysis was done by Dr. A. Elek, of Elek Microchemical Laboratories, Los Angeles, Calif.

542 mg. (47%); m.p. 150°. An analysis by long digestion with $CaCl_2$ at 70° (equation: $3Ca^{++} + 2H_2OBF_3 + 2H_2O \rightarrow 3CaF_2 + 6H^+ + 2HBO_2$) gave 2.93 m.e. of H^+ and 1.06 m.e. of HBO_2 per m.e. of $(CH_3)_3POBF_3$.

These results suggest that $(CH_3)_3POBF_3$ is slightly more stable than H_2OBF_3, although the latter preponderates, in ionized form, when there is a great excess of water.

The Compound $(CH_3)_3POSO_3$.—The preparation of $(CH_3)_3POSO_3$ was done first by the use of the double U-tube system: SO_3 was evaporated from the first U-tube and carried by a stream of nitrogen over $(CH_3)_3PO$ in the second. The sample was kept at room temperature or lower, since a working temperature of 70° led to charring. After considerable absorption had occurred, liquid SO_3 was three times condensed upon and evaporated from the solid; finally the excess SO_3 was carried off by the nitrogen stream, while the product was gradually heated to 140°. The gain in weight then corresponded to 1.05 SO_3 per $(CH_3)_3PO$. The white solid product, very reactive toward water, melted with irreversible decomposition, in the range 180–200°. Vacuum sublimation proved impossible.

In an attempt to purify this product, a sample was dissolved in anhydrous ethanol, and ether was added to precipitate a solid which melted at 87–88°. Analyses gave 27.15% C, 6.46% H, and 20.18% ethoxy-groups,[9] corresponding to another new compound, $(CH_3)_3POH^+OSO_3C_2H_5^-$ (calcd. C, 27.51; H, 6.94, and C_2H_5O, 20.20). This alcoholysis indicates a weaker bonding of $(CH_3)_3PO$ to SO_3 than that in $(C_2H_5)_3NOSO_3$, which could be washed with cold ethanol without reaction.[5]

A better sample of $(CH_3)_3POSO_3$ was prepared by leading sulfur trioxide over a solution of 300 mg. of $(CH_3)_3PO$ in 2 ml. of 1,2-dichloroethane, again in the double U-tube system, with care to avoid an excess of SO_3. The precipitate was washed with fresh solvent and dried in high-vacuum at 35°. Again the melting involved decomposition (165–200°). *Anal.*[9] C,20.32; H, 5.40 (calcd. 20.93 and 5.27; deviations attributable to 3% absorption of moisture). The rapid destruction of this substance by water was shown by the drop in *p*H from 6.9 to 2.1 within 5 seconds after formation of a 0.1% solution. The $BaCl_2$ test for sulfate also was immediate, and an electrometric titration showed the expected quantity of acid.

The Behavior of $(CH_3)_3PO$ toward SO_2.—In sharp contrast to the vigorous process of formation and strong bonding of $(CH_3)_3NOSO_2$,[2] trimethylphosphine oxide smoothly absorbs SO_2 to form a liquid with a saturation limit of about 50 mole per cent. $(CH_3)_3PO$. The saturation pressure of SO_2 over this liquid is scarcely one-tenth that expected in terms of Raoult's law; hence some kind of weak combination is indicated. A series of pressure–composition isotherms at −23, 0, 8 and 18°, for the system $(CH_3)_3PO$–SO_2, showed a virtually constant pressure at each temperature until all of the solid had dissolved; then the pressure rose very sharply and almost linearly with increasing SO_2 content. These results are summarized in Table I, in which P_s refers to the pressure of SO_2 in equilibrium with the saturated liquid and x_s is the molar ratio of SO_2 to $(CH_3)_3PO$ at the saturation point. S, the slope of the pressure–composition graph beyond the level region, is expressed as mm. change of pressure per unit change of the ratio of SO_2 to $(CH_3)_3PO$.

The values of p_s at the four temperatures determine the equation $\log_{10} p = 6.592 - 1325/T$, from which the check values were computed. Such linearity would be expected if the saturated liquid were assumed to represent a single compound such as $(CH_3)_3POSO_2$, but the evidence is not sufficient for this specific interpretation.

TABLE I

PRESSURE–COMPOSITION ISOTHERMS FOR $(CH_3)_3PO$–SO_2

t, °C.	p_s (mm.) (obsd.)	p_s (mm.) (calcd.)	x_s	S
−23	19.2	19.4	1.10	61
0	54.5	54.1	1.05	216
8	76.6	74.5	0.98	244
18	106.5	108	0.92	278

LOS ANGELES 7, CALIFORNIA RECEIVED MAY 14, 1951

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[9] Analyses by Joseph Pirie, of this Department.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KANSAS]

Further Observations on Reissert Compounds

BY WILLIAM E. MCEWEN, J. VERNON KINDALL, ROBERT N. HAZLETT AND ROBERT H. GLAZIER

The yellow compound obtained in the reaction of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with hydrochloric acid has been investigated. On the basis of a molecular weight determination, the ultraviolet and visible spectra, the hydrolysis products, the oxidation products, and by analogy with other known substances, the compound is assigned the structure VII, 2-(1′-isoquinolyl)-4,5-diphenyloxazole. Evidence is offered regarding the mechanism by which it is formed. A rearrangement affording 2-quinolylphenylmethylcarbinol (XI) from a reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (VIII) with methylmagnesium bromide is also discussed.

Some time ago a mechanism was proposed for the acid-catalyzed formation of aldehydes from Reissert compounds, and evidence in support of that mechanism was presented.[1] Mention was also made of the isolation of a yellow compound of unknown structure, together with benzaldehyde, isoquinaldic acid, benzoin and benzoin isoquinaldate (V), on reaction of 2-benzoyl-1,2-dihydroisoquinaldonitrile (I) with concentrated hydrochloric acid. The yellow compound had previously been reported by Reissert, who assigned the molecular formula $C_{34}H_{23}N_3O$, on the basis of the analysis for its elements.[2]

We have now determined that the yellow compound is 2-(1′-isoquinolyl)-4,5-diphenyloxazole (VII) on the basis of the following facts: (1) It is not possible to distinguish between the molecular formulas $C_{34}H_{23}N_3O$ and $C_{24}H_{16}N_2O$ by combustion analyses.[3] (2) A molecular weight determination by the Rast method gave a value of 353, as compared to a theoretical value of 348 for a compound of the molecular formula $C_{24}H_{16}N_2O$. (3) The conventional tests of qualitative organic analysis indicate the absence of carbonyl-containing cyano, hydroxyl or primary or secondary amino groups. (4) The ultraviolet and visible absorption spectrum (Fig. 1) shows a maximum at 410 mμ, which is reasonable for a compound having several aromatic rings in conjugation with one another. (5) The compound is very resistant to hydrolysis under both acid and alkaline conditions, but a 6% yield of benzoin and a 5% yield of isoquinaldic acid, together with an 85% recovery of starting

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[1] W. E. McEwen and R. N. Hazlett, THIS JOURNAL, **71**, 1949 (1949).

[2] A. Reissert, *Ber.*, **38**, 3415 (1905).

[3] *Anal.* Calcd. for $C_{34}H_{23}N_3O$: C, 83.39; H, 4.73; N, 8.61. *Anal.* Calcd. for $C_{24}H_{16}N_2O$: C, 82.73; H, 4.63; N, 8.04.