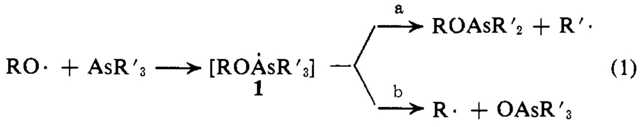
An Electron Spin Resonance Study of the Reaction of *tert*-Butoxy Radicals with Triphenylarsine[1]

Sir:

It has been proposed[2] that the reaction of trivalent arsenic compounds (AsR'_3) with oxy radicals ($RO\cdot$) involves as an intermediate the four-coordinate arsenic radical, **1**.



$$RO\cdot + AsR'_3 \longrightarrow \underset{\mathbf{1}}{[RO\dot{A}sR'_3]} \begin{cases} \xrightarrow{a} ROAsR'_2 + R'\cdot \\ \xrightarrow{b} R\cdot + OAsR'_3 \end{cases} \qquad (1)$$

The reaction of triethylarsine with *tert*-butoxy radicals has been studied by esr spectroscopy,[3] and although the spectrum from the ethyl radical (*via* reaction 1a) could be detected, there was no evidence for the intermediate arsenic radical.[4]

In this communication we report the detection by esr spectroscopy of such an arsanyl radical (**2**) during photolysis of di-*tert*-butyl peroxide with an Osram 250-W lamp in the presence of triphenylarsine. The photolyses were carried out in the cavity of a Varian E-12 spectrometer using a variety of solvents, including isopentane, dichlorodifluoromethane, and trichlorofluoromethane.

$$BOOB \xrightarrow{h\nu} 2BO\cdot \qquad (2)$$

$$BO\cdot + AsPh_3 \xrightarrow{k_3} \underset{\mathbf{2}}{BO\dot{A}sPh_3} \qquad (3)$$

The spin $I = {}^3/_2$ of ^{75}As results in a four-line spectrum for the radical $BO\dot{A}sPh_3$. In isopentane at $-90°$, with a microwave frequency of 9161.75 ± 0.02 MHz, the four lines occurred at the following values of the magnetic field: $M_I = +{}^3/_2$, 2138 ± 0.5 G; $M_I = +{}^1/_2$, 2664 ± 0.5 G; $M_I = -{}^1/_2$, 3337 ± 0.5G; $M_I = -{}^3/_2$, 4154 ± 0.5 G.

These data are indicative of an ^{75}As hyperfine interaction large enough to necessitate consideration of nonzero off-diagonal elements in the 8×8 matrix of M_S ($\pm{}^1/_2$) and $M_I(\pm{}^1/_2, \pm{}^3/_2)$. Terms in the sixth power of the ^{75}As hyperfine interaction constant (t) were retained in the diagonalization process. The values of t and g were determined using (i) the positions of the $M_I = \pm{}^3/_2$ lines and (ii) the positions of the $M_I = \pm{}^1/_2$ lines. The two independent solutions were: (i) $t = 1875$ MHz, $g = 2.0147$; (ii) $t = 1877$ MHz, $g = 2.0131$.

The value of the ^{75}As hyperfine interaction when compared to that of $(8\pi/3)\,\gamma_e\gamma_{As}\psi_{4s}^2(0)$ for ^{75}As (9525 MHz)[5] indicates a contribution of approximately 20% from the ^{75}As (4s) orbital to the orbital occupied by the unpaired electron. Such a contribution is consistent with an arsanyl radical of the type $BO\dot{A}sPh_3$. By analogy with the PF_4 radical,[6] arsanyl radicals would be expected to have a bipyramidal structure (C_s symmetry) with the unpaired electron occupying an (equatorial) a′ molecular orbital. Assuming that in such a radical the more electronegative OB ligand occupies an apical position,[7] and that, as in PF_4, the two apical bonds are virtually collinear, the equatorial Ph–As–Ph angle can be calculated[8] from the percentage As (4s) character in the a′ molecular orbital to be 130–135°.

Reaction of *tert*-butoxy radicals (generated by thermolysis of *tert*-butyl hyponitrite or by photolysis of di-*tert*-butyl peroxide) with triphenylarsine at 30° gave products[9] which showed that the intermediate arsanyl radical decomposed by α scission rather than β scission, *i.e.*

$$BO\dot{A}sPh_3 \longrightarrow BOAsPh_2 + Ph\cdot \qquad (4)$$

Competitive experiments suggested that triphenylarsine is about 400 times as reactive as isopentane toward *tert*-butoxy radicals and is about 100 times less reactive than triethyl phosphite. Davies, *et al.*,[10] have recently estimated that the rate constant for the reaction of triethyl phosphite with *tert*-butoxy radicals at 30° is $1.6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ which suggests that k_3 is approximately $10^6\ M^{-1}\ \text{sec}^{-1}$ at this temperature.

Rates of decay of $BO\dot{A}sPh_3$ in isopentane, dichlorodifluoromethane, or trichlorofluoromethane were measured by kinetic esr spectroscopy.[11] The rates were independent of the radical concentration and the triphenylarsine concentration and were proportional to the intensity of the initiating light. The following kinetic expression was therefore obeyed

$$\frac{-d[BO\dot{A}sPh_3]}{dt} = k_4[BO\dot{A}sPh_3]$$

where k_4 is the rate constant for reaction 4. Absolute values of k_4 in the three solvents were found to fit the equation

$$\log\,[k_4/\text{sec}^{-1}] = 10.7 - 8.0/\theta$$

where $\theta = 2.303RT$ kcal mol^{-1}. Extrapolation of this equation to 30° gave $k_4 = 8 \times 10^4\ \text{sec}^{-1}$. The arsanyl radical, $BO\dot{A}sPh_3$, is therefore more stable than phosphoranyl radicals of the structure $BO\dot{P}(OR)_3$ (where $R = CH_3$, C_2H_5, $(CH_3)_2CH$, or $(CH_3)_3C$) since it has been reported[12] that these radicals have rate constants for β scission of about $10^6\ \text{sec}^{-1}$ at 30°.

The quartet spectrum of the arsanyl radical was replaced by a singlet when di-*tert*-butyl peroxide was photolyzed in the presence of air-saturated triphenylarsine in isopentane. The new spectrum had a g value

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(1) Issued as NRCC No. 12756.

(2) K. U. Ingold and B. P. Roberts, "Free Radical Substiuttion Reactions," Wiley-Interscience, New York, N. Y., 1971, p 134.

(3) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); (b) A. G. Davies and B. P. Roberts, *J. Organometal. Chem.*, **19**, 17 (1969).

(4) A. G. Davies, D. Griller, and B. P. Roberts (*J. Organometal. Chem.*, **38**, C8 (1972)) have recently reported the detection of some arsanyl radicals of the structure $RS\dot{A}sMe_3$ (where $R = CH_3$, C_2H_5, $CH_3(CH_2)_3$, or $(CH_3)_3C$) during photolysis of dialkyl disulfides and trimethylarsine.

(5) Calculated from the data of C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966).

(6) J. Higuchi, *J. Chem. Phys.*, **50**, 1001 (1969).

(7) E. L. Meutterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(8) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967, p 257.

(9) For example, decomposition of *tert*-butyl hyponitrite (0.02 *M*) in triphenylarsine (0.05 *M*) and isopentane (8.6 *M*) gave benzene (0.025 *M*), *tert*-butyl alcohol (0.015 *M*), and *no* triphenylarsine oxide. A similar experiment substituting triphenylphosphine (0.1 *M*) for the triphenylarsine gave triphenylphosphine oxide and no benzene or *tert*-butyl alcohol.

(10) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int Ed. Engl.*, **10**, 738 (1971).

(11) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971).

(12) D. Griller, G. B. Watts, and K. U. Ingold, private communication.

of 2.0269, very similar to that of phosphoranyl peroxy radicals, $BO(RO)_3POO\cdot$,[14] and quite different from g values for carbon peroxy radicals (2.014 − 2.019).[15] The new radical has, therefore, been assigned the structure $BO(Ph)_3AsOO\cdot$.

The kinetics for the decay of $BO(Ph)_3AsOO\cdot$ proved to be complex. For example, the half-life at −40° was independent of the radical concentration and decreased by a factor of approximately 2 when the triphenylarsine concentration was increased by 20. A full discussion of the kinetics of the decomposition of this radical will be presented in a subsequent full paper.

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(14) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972).

(15) K. U. Ingold, *Accounts Chem. Res.*, 2, 1 (1969).

*Book Reviews**

Comprehensive Treatise on Inorganic and Theoretical Chemistry. Volume VIII. Supplement III. Phosphorus. By J. W. MELLOR. Senior Editor, A. A. ELDRIDGE. John Wiley-Interscience, New York, N. Y. 1971. x + 1467 pp. $79.95.

This monumental volume is very nearly a self-contained treatise on phosphorus chemistry. It is the sixth installment of supplements to Mellor's classic original work. The growth of inorganic chemistry can be judged by the fact that original Volumes II and VIII have both become three volumes in the Supplement. In addition to the enormous amount of information presented in text, tables, and graphs, one notices an improved organization and a better system of handling references. There are forty chapters, ranging in subject from the history and occurrence of phosphorus to the toxicity of phosphorus compounds. Notable among them is the chapter on the organic derivatives of phosphorus, which, with 250 pages and 2434 references, is a book in itself. The profession of chemistry is deeply indebted to the compilers of such an important volume as this, which must have required a small army of devoted workers.

The index of only ten pages is surprisingly short for a book so large and full of detail. The biggest shortcoming of this work, however, is the one that would have been most easily avoided: there is no indication whatsoever as to when the coverage of the literature ceased! The unsigned and undated preface enlightens us on the fascinating fact that Volume II, Supplement I, was originally called Supplement II, Part I, but gives no hint about how up-to-date the present volume is. Browsing in the long lists of references suggests that the cut-off date was the end of 1967, but whatever it may have been, it is hard to excuse hiding such information in a work of major reference value.

Third Conference on Industrial Carbons and Graphite. Edited by J. C. GREGORY. Society of Chemical Industry and Academic Press, London. 1971. viii + 565 pp. £15.

This volume contains about a hundred papers, all of which are reports of original research and are accompanied by transcripts of the discussions. The latter have undergone substantial editing and, apparently, amplification by the participants, and as a result are actually useful.

Cycloaddition Reactions. Edited by R. GOMPPER (University of Munich). Butterworths, London. 1972. v + 208 pp. $9.00.

Five of the specially invited lectures given at the Cycloaddition Symposium held in Munich in 1970 are reprinted from Volume 27 of *Pure and Applied Chemistry* in this book. Four are in English (P. D. Bartlett, C. S. Foote, G. M. J. Schmidt, N. J. Turro) and one is in German (H. Bestian).

Genetical, Functional, and Physical Studies of Hemoglobins. Edited by T. ARENDS, G. BEMSKI, and R. L. NAGEL. S. Karger, A. G., CH-4000 Basil, Switzerland. 1971. viii + 293 pp. $19.20.

This volume contains the Proceedings of the First International Symposium on Hemoglobins, held in Caracas in 1969. The papers are arranged in three groups: Geographical Distribution and Genetic Problems; Structure and Function; and Physical Studies of the Hemoglobin Molecule. They are well edited and well illustrated and are, in general, reports of original research. The book lacks an index.

XIIIth International Conference on Coordination Chemistry. Plenary Lectures. Edited by L. PAJDKOWSKI (University of Wroclaw). Butterworths, London. 1971. viii + 264 pp. $20.25.

This volume contains the texts of thirteen lectures, complete with illustrations, tables, and references, given in 1970 at Krakow-Zakopane. All are in English, although many of the lecturers came from non-English-speaking countries.

XXIIIrd International Congress of Pure and Applied Chemistry. Special Lectures. Volumes 1 to 4. Butterworths, London. 1971. Volume 1: vi + 417 pp. $15.00. Volume 2: vi + 337 pp. $12.00. Volume 3: v + 121 pp. $7.50: Volume 4: vi + 540 pp. $18.00.

These volumes contain the special lectures given at Boston in 1971; all are devoted to some aspect of organic chemistry. In Volume 1 there are three groups of lectures: Application of Quantum Mechanics to Organic Reaction Paths; Intramolecular Rearrangements, Valence Isomerization, and Cycloaddition; Photochemistry. Volume 2 contains the groups General Methods of Synthesis, New Natural Product Syntheses, and Small Rings. Volume 3 is devoted to Medicinal Chemistry and Insect Chemistry (a curious combination). Volume 4 covers Short-Lived Intermediates, Free Radicals and Homolytic Mechanisms, and Ion-pair Processes. All lectures are printed in English, and they contain tables, illustrations, and references; there are no indexes. The anonymous editors and the publishers are to be congratulated in making this material available so promptly.

Organic Solid State Chemistry. Edited by M. D. COHEN (Weizmann Institute for Science). Butterworths, London. 1972. vii + 526 pp. $17.25.

The plenary lectures of the 2nd International Symposium on Organic Solid-State Chemistry (Rehovot, 1970) are presented in this book. They are extensively illustrated and are accompanied by good bibliographies. There is no index.

Proceedings of the 2nd Conference on Applied Physical Chemistry. Edited by I. BUZAB (Technical University Budapest). Akademiai Kiado, Budapest. 1971. Volume 1, 759 pp. Volume 2, 738 pp. $28.00.

Volume 1 contains the papers of the 2nd Electroanalytical Symposium and of the 4th Symposium of Oscillometry; Volume 2 is devoted to Chemical Engineering and Pharmaceutical Technology. The reader is not told where and when the symposia were held, or under whose auspices, but the authors appear to be all Hungarian. The papers are reports of original research rather than reviews, and all are in English. There is an author index, but no subject index; the volumes are paperbound.

Selected Constants: Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution. By G. CHARLOT (Ecole de Phys-

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* Unsigned book reviews are by the Book Review Editor.