a decrease in the yield of the major product, digermane, in the variable pressure experiments above 80% moderator. In the constant pressure moderator experiments the digermane yield decreases slightly above 50% moderator but decreases nearly 50% between 0 and 20% moderator. Trigermane behaves similarly to digermane in the constant pressure experiments, up to 80% moderator, and then *increases*. In the variable pressure moderator experiments trigermane yield increases over the entire range. The only conclusion to be drawn at present from the moderator experiments is that there seems to be an effect of high moderator concentration suggestive of a true hot-atom reaction. The effect of *small* amounts of moderator indicates the importance of vibrational excitation in these reactions.

Acknowledgments. Valuable discussions with Dr. Alfred P. Wolf and Professor Michael J. Welch are much appreciated. These experiments were begun by Dr. S. Allan Bock and Dr. Carl A. Levy. Dr. Gerald A. Stewart and Mr. J. Dewey Holton, III, carried out the absolute yield determinations.

An Electron Spin Resonance Study of Some Arsanyl Radicals[1]

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Abstract: Arsanyl radicals of the structure $\mathrm{Ph_3\dot{A}sOB}$ and $\mathrm{Ph_2\dot{A}s(OR)OB}$ (where B = *tert*-butyl and R = methyl, ethyl, or *tert*-butyl) have been detected by esr spectroscopy during photolysis of di-*tert*-butyl peroxide in the presence of triphenylarsine or the appropriate alkoxydiphenylarsine ($\mathrm{Ph_2AsOR}$). Replacement of the apical phenyl group in $\mathrm{Ph_3\dot{A}sOB}$ by a more electrophilic alkoxy group increases the arsenic hyperfine interaction from 1876 to approximately 2200 MHz. On the other hand, replacing one or both of the *tert*-butoxy groups in $\mathrm{Ph\dot{A}s(OB)_2}$ by a more electronegative alkoxy group (OMe or OEt) produces a small decrease in t_{As}. The radicals $\mathrm{Ph_3\dot{A}sOB}$ and $\mathrm{Ph_2\dot{A}s(OR)OB}$ decompose principally by α scission to give a phenyl radical and a trivalent arsenic compound. At low temperatures (<0°) the rate constants for decomposition of $\mathrm{Ph_3\dot{A}sOB}$ (k_3) and $\mathrm{Ph_2\dot{A}s(OB)_2}$ (k_5) are given by the Arrhenius equations: $\log (k_3/\mathrm{sec}^{-1}) = (10 \pm 1.0) - (8 \pm 1)/\theta$ and $\log (k_5/\mathrm{sec}^{-1}) = (13 \pm 1.0) - (13 \pm 2)/\theta$, where $\theta = 2.303RT$ kcal mol^{-1}. At these temperatures $\mathrm{Ph_2\dot{A}s(OB)_2}$ is therefore considerably more stable than $\mathrm{Ph_3\dot{A}sOB}$. The stability of arsanyl radicals of the structure $\mathrm{Ph_2\dot{A}s(OR)OB}$ depends on the nature of R, with the stability increasing in the order $\mathrm{Ph_2\dot{A}s(OMe)OB} < \mathrm{Ph_2\dot{A}s(OEt)OB} < \mathrm{Ph_2\dot{A}s(OB)_2}$.

The reaction of organic and organometallic compounds with alkoxy radicals has proved very successful for generating free radicals in the liquid phase for electron spin resonance spectroscopic and kinetic studies.[2] Generally the radicals that have been detected were produced either by hydrogen-atom abstraction or displacement from the substrate. However, in a few cases, *e.g.*, with primary, secondary, and tertiary phosphines,[3] trialkyl phosphites,[2c,4] tertiary arsines,[5] $\mathrm{SF_4}$[6a] $\mathrm{OSF_2}$,[6b] and $\mathrm{SO_2}$,[6b,6c] the intermediate alkoxy-adduct radicals have been detected.

In this paper we report a more complete spectroscopic and kinetic study of the four coordinate arsenic radicals[7] formed by reaction of *tert*-butoxy radicals with triphenylarsine and some alkoxydiphenylarsines.

Results

Triphenylarsine. In a preliminary communication[5b] we reported the detection, by esr spectroscopy, of the arsanyl radical $\mathrm{Ph_3\dot{A}sOB}$ produced by photolysis of di-*tert*-butyl peroxide (BOOB) and triphenylarsine (*ca.* 0.02 *M*) in either isopentane or dichlorodifluoromethane.

$$\mathrm{BOOB} \xrightarrow{h\nu} \mathrm{2BO}\cdot \qquad (1)$$

$$\mathrm{BO}\cdot + \mathrm{Ph_3As} \longrightarrow \mathrm{Ph_3\dot{A}sOB} \qquad (2)$$

This radical was found to have an arsenic hyperfine interaction of 1876 ± 5 MHz and a g factor of 2.0140 ± 0.0005. A second arsanyl radical, with t_{As} = 2225 MHz and g = 2.0060, has since been detected in this system. This radical accumulated more slowly than $\mathrm{Ph_3\dot{A}sOB}$ and we believe it to be the secondary radical $\mathrm{Ph_2\dot{A}s(OB)_2}$ formed by reaction of *tert*-butoxy radicals

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[1] Issued as NRCC No. 13453.

[2] (a) J. K. Kochi and P. J. Krusic, *Chem. Soc. Spec. Publ.*, **No. 24**, 147 (1970); (b) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972), and preceding papers; (c) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972), and earlier papers by these authors; (d) D. Griller, *J. Magn. Resonance*, **6**, 402 (1972).

[3] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972).

[4] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 8784 (1972).

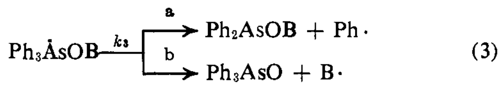
[5] (a) A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **38**, C8 (1972); (b) E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, **94**, 5932 (1972).

[6] (a) J. R. Morton and K. F. Preston, *Chem. Phys. Lett.*, **18**, 98 (1973); (b) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973); (c) T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Lett.*, 4075 (1972).

[7] Four coordinate arsenic radicals have previously been called *arsanyls*[5b] and *arsenanyls*.[5a] A more correct terminology would perhaps be *arsoranyls*.[8] However, for the present we prefer to use the shorter *arsanyl*.

[8] J. P. Casey and K. Mislow, *J. Chem. Soc. D*, 1410 (1970).

with the *tert*-butoxydiphenylarsine produced by α scission of $Ph_3\dot{A}sOB$.



$$Ph_3\dot{A}sOB \xrightarrow{k_3} \begin{cases} \xrightarrow{a} Ph_2AsOB + Ph\cdot \\ \xrightarrow{b} Ph_3AsO + B\cdot \end{cases} \qquad (3)$$

$$BO\cdot + Ph_2AsOB \xrightarrow{k_4} Ph_2\dot{A}s(OB)_2 \qquad (4)$$

The growth of the two arsanyl radicals after photolysis of a completely fresh sample of di-*tert*-butyl peroxide and triphenylarsine (0.01 *M*) in isopentane at $-100°$ is shown in Figure 1. The initial adduct, $Ph_3\dot{A}sOB$, was generated immediately, at an initial rate of 10^{-5} *M* sec^{-1}, and reached a steady-state concentration of 7.2×10^{-6} *M* after *ca.* 2 sec. The secondary radical accumulated more slowly and had not reached a steady-state concentration even after 100 sec of photolysis.

From -100 to $-50°$ the concentration of $Ph_3\dot{A}sOB$ always reached a steady state during photolysis and initial rates of radical production were equal to initial rates of radical decay when the initiating light was interrupted. Steady-state radical concentrations had an intensity exponent of 1.0 over a 50-fold change in light intensity. Rates of radical decay were exactly first order in the radical concentration and can, therefore, be described by the equation

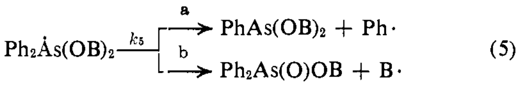
$$-d[Ph_3\dot{A}sOB]/dt = k_3[Ph_3\dot{A}sOB]$$

where k_3 is the unimolecular decay constant for $Ph_3\dot{A}sOB$.

Rates of decay of $Ph_2\dot{A}s(OB)_2$ were also first order with respect to the radical concentration, *i.e.*

$$-d[Ph_2\dot{A}s(OB)_2]/dt = k_5[Ph_2\dot{A}s(OB)_2]$$

where k_5 is the rate constant for the decomposition of $Ph_2\dot{A}s(OB)_2$.



$$Ph_2\dot{A}s(OB)_2 \xrightarrow{k_5} \begin{cases} \xrightarrow{a} PhAs(OB)_2 + Ph\cdot \\ \xrightarrow{b} Ph_2As(O)OB + B\cdot \end{cases} \qquad (5)$$

Above $-100°$, particularly with samples that had been subjected to short periods of photolysis, $Ph_2\dot{A}s(OB)_2$ reached a steady-state concentration during photolysis. Above *ca.* $-50°$ initial rates of radical accumulation were found to equal initial rates of radical decay and the intensity exponent for $[Ph_2\dot{A}s(OB)_2]_{ss}$ was 1.0. Below $-50°$, however, rates of radical accumulation were greater than rates of radical decay with the difference in these rates becoming larger as the temperature was decreased. Furthermore, the intensity exponent fell as the temperature was decreased until at $-90°$ it was only 0.2. The difference in the initial rates of production and decay of $Ph_2\dot{A}s(OB)_2$ was possibly due to reaction of this radical with *tert*-butoxy radicals during photolysis.

$$BO\cdot + Ph_2\dot{A}s(OB)_2 \longrightarrow \text{molecular products} \qquad (6)$$

Thus during photolysis (since $Ph_2\dot{A}s(OB)_2$ accumulated autocatalytically)

$$\frac{d[Ph_2\dot{A}s(OB)_2]}{dt} > \frac{-d[Ph_2\dot{A}s(OB)_2]}{dt} = k_5[Ph_2\dot{A}s(OB)_2] + k_6[BO\cdot][Ph_2\dot{A}s(OB)_2]$$

whereas during the dark

$$-d[Ph_2\dot{A}s(OB)_2]/dt = k_5[Ph_2\dot{A}s(OB)_2]$$

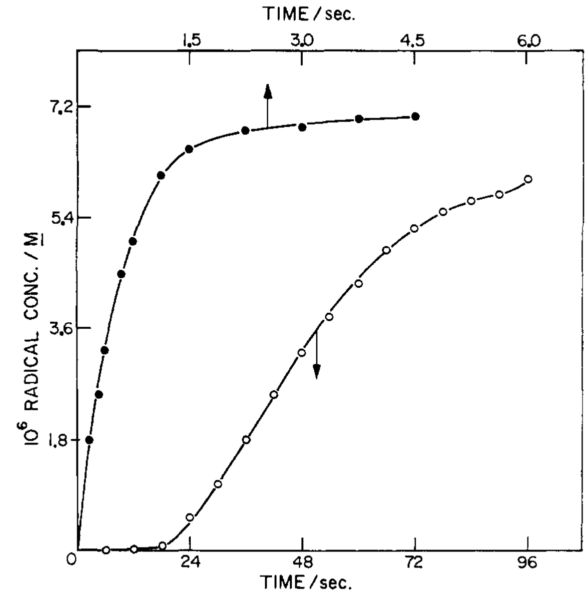


Figure 1. The variation of the concentration of $Ph_3\dot{A}sOB$ (●) and $Ph_2\dot{A}s(OB)_2$ (○) with the time of irradiation during photolysis of a fresh mixture of di-*tert*-butyl peroxide (1.0 *M*) and triphenylarsine (0.01 *M*) in isopentane at $-100°$.

Absolute values of k_3 (from -65 to $-115°$) and k_5 (from 0 to $-50°$) were determined. Plots of log k_3 and log k_5 against the reciprocal of the absolute temperature (Figure 2) afforded the Arrhenius equations

$$\log (k_3/sec^{-1}) = (10 \pm 1.0) - (8 \pm 1)/\theta$$

and

$$\log (k_5/sec^{-1}) = (13 \pm 1.0) - (13 \pm 2)/\theta$$

where $\theta = 2.303RT$ kcal mol^{-1}. At low temperatures, $Ph_2\dot{A}s(OB)_2$ is, therefore, considerably more stable than $Ph_3\dot{A}sOB$ (at $-65°$, for example, $k_3/k_5 \sim 2 \times 10^3$), apparently because of a larger activation energy for unimolecular decomposition. The preexponential factors for k_3 and k_5 are rather low for a simple unimolecular reaction and the entropies of activation are negative by 2–10 cal $°C^{-1}$ mol^{-1}.

A consequence of the difference in stability between these two radicals is that the primary radical becomes increasingly more difficult to detect as the reaction temperature is increased from $-100°$ until at *ca.* $-40°$ the secondary radical is the only species that can readily be detected.

Confirmation that the secondary radical formed during photolysis of BOOB and Ph_3As was indeed $Ph_2\dot{A}s(OB)_2$ was obtained from the reaction of *tert*-butoxy radicals with diphenyl-*tert*-butoxyarsine. The latter system gave only one arsanyl radical with $t_{As} =$ 2216 MHz and $g = 2.0079$, parameters very similar to the values for the secondary radical in the BOOB–Ph_3As system. Decay constants for $Ph_2\dot{A}s(OB)_2$ obtained in the two systems were identical within experimental error (see Figure 2).

Product studies revealed that the principal volatile products from the reaction of *tert*-butoxy radicals (produced by thermolysis of *tert*-butyl hyponitrite) with triphenylarsine, diphenylmethoxyarsine, diphenylethoxyarsine, and diphenyl-*tert*-butoxyarsine in a hydrogen-donor solvent at 50° were *tert*-butyl alcohol and benzene (see Experimental Section). It would, there-

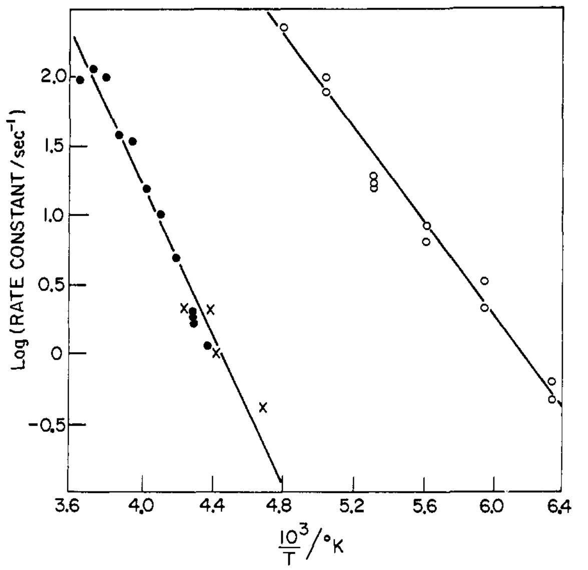
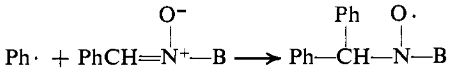


Figure 2. The variation of the logarithm of the rate constant for unimolecular decomposition of $\mathrm{Ph_3\dot{A}sOB}$ (○) and $\mathrm{Ph_2\dot{A}s(OB)_2}$ (●, ×) with the reciprocal of the absolute temperature. The filled circles and crosses refer to rate constants determined in the BOOB–$\mathrm{Ph_3As}$ system and BOOB–$\mathrm{Ph_2AsOB}$ system, respectively.

fore, appear that at this temperature $\mathrm{Ph_3\dot{A}sOB}$, $\mathrm{Ph_2\dot{A}s(OMe)OB}$, $\mathrm{Ph_2\dot{A}s(OEt)OB}$, and $\mathrm{Ph_2\dot{A}s(OB)_2}$ decompose principally by α scission to give a tertiary arsine and phenyl radicals (*i.e.*, reactions 3a and 5a).

The production of phenyl radicals was confirmed by photolyses of di-*tert*-butyl peroxide and triphenylarsine (or one of the alkoxydiphenylarsines) in the presence of phenyl *N*-*tert*-butyl nitrone. These systems gave esr spectra consisting of a triplet of doublets with t_N = 14.28 G and t_H = 2.16 G, parameters that are characteristic of diphenylmethyl *tert*-butyl nitroxide.[9]



$$\mathrm{Ph\cdot + PhCH{=}\overset{O^-}{\overset{|}{N^+}}{-}B \longrightarrow Ph{-}\overset{Ph}{\overset{|}{C}}H{-}\overset{O\cdot}{\overset{|}{N}}{-}B}$$

No other nitroxides could be detected in these systems which implies that *tert*-butoxy radicals add to tertiary arsines and that arsanyl radicals undergo α scission in preference to adding to phenyl *N*-*tert*-butyl nitrone or undergoing β scission.[10]

We have now found that triphenylarsine is approximately six times more reactive than triethyl phosphite toward *tert*-butoxy radicals at −96°. The rate constant for the latter reaction at −96° can be calculated to be $1.15 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ [2c] which implies that the rate constant for triphenylarsine is $\sim 7 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. This rate constant is higher than our previous estimate of $10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at 30° which we now believe to be in error.

Tris(para-substituted phenyl)arsines. Tris(*p*-methoxyphenyl)arsine and tris(*p*-methylphenyl)arsine both reacted with *tert*-butoxy radicals to give two arsanyl radicals, *i.e.*, $\mathrm{(C_6H_4X)_3\dot{A}sOB}$ and $\mathrm{(C_6H_4X)_2\dot{A}s(OB)_2}$, where X = $\mathrm{CH_3O}$ or $\mathrm{CH_3}$. Esr parameters and stabilities of these radicals were identical, within experimental error, to the analogous radicals produced from triphenylarsine. This implies that small changes in the electron withdrawing or donating capacity of the groups attached to arsenic have very little influence on the arsenic hyperfine interaction and on the stability of arsanyl radicals.

Alkoxydiphenylarsines. Only one type of arsanyl radical, $\mathrm{Ph_2\dot{A}s(OR)OB}$, where R = Me or Et, was produced by the reaction of *tert*-butoxy radicals with either diphenylmethoxyarsine or diphenylethoxyarsine. The esr parameters for these radicals together with the values obtained for $\mathrm{Ph_2\dot{A}s(OB)_2}$ are listed in Table I.

Table I. Esr Parameters for Some Arsanyl Radicals in Isopentane at −100°

Radical	t_{As},[a] MHz	g[a]
$\mathrm{Ph_3\dot{A}sOB}$	1876	2.0140
$\mathrm{Ph_2\dot{A}s(OMe)OB}$	2203	2.0069
$\mathrm{Ph_2\dot{A}s(OEt)_2}$	2185	2.0053
$\mathrm{Ph_2\dot{A}s(OEt)OB}$	2216	2.0059
$\mathrm{Ph_2\dot{A}s(OB)_2}$	2225	2.0060

[a] Exact analysis used; experimental error ±5 MHz in t_{As} and ±0.0005 in g.

Also included in this table are the parameters for diethoxydiphenylarsanyl, which was the only species that could be detected during photolysis of diethyl peroxide and triphenylarsine.

The radicals $\mathrm{Ph_2\dot{A}s(OMe)OB}$ and $\mathrm{Ph_2\dot{A}s(OEt)OB}$ both decayed by first-order kinetics. Unimolecular rate constants for these two species are listed in Table II together with the values for $\mathrm{Ph_2\dot{A}s(OB)_2}$. These three radicals increase in stability in the order $\mathrm{Ph_2\dot{A}s(OMe)OB} < \mathrm{Ph_2\dot{A}s(OEt)OB} < \mathrm{Ph_2\dot{A}s(OB)_2}$.

Table II. Unimolecular Rate Constants (in units of sec^{-1}) for the Decomposition of Some *tert*-Butoxy(alkoxy)diphenylarsanyl Radicals

	Radical		
Temp, °C	$\mathrm{Ph_2\dot{A}s}$-(OMe)OB	$\mathrm{Ph_2\dot{A}s}$-(OEt)OB	$\mathrm{Ph_2\dot{A}s(OB)_2}$
−117	0.75	0.04	
−112	1.4	0.1	
−100	3.5	0.2	0.005
−90		0.4	0.03
−80		0.7	0.075
−60		2.0	0.4

Discussion

Spectra. The arsanyl radicals observed in the present study can be regarded as derivatives of the prototype radical $\mathrm{AsF_4}$ which, to date, we have been unable to detect. However, by analogy with $\mathrm{PF_4}$,[11] arsanyl radicals would be expected to have a bipyramidal structure in which the OR ligand(s), being more electronegative than Ph, occupies the apical position(s).[12]

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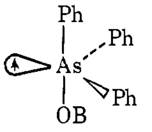
(9) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969).

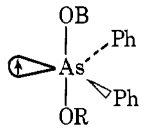
(10) We were unable to detect four coordinate antimony or bismuth radicals during photolysis of BOOB, triphenylantimony, or triphenylbismuth in isopentane. However, when these photolyses were carried out in the presence of phenyl *N*-*tert*-butyl nitrone the diphenylmethyl *tert*-butyl nitroxide radical was obtained. This implies that if four coordinate radicals analogous to $\mathrm{Ph_3\dot{A}sOB}$ were produced in these systems, they were too unstable to detect by esr spectroscopy.

(11) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966).

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

That is





where R = B, Et, or Me.

The value of t_{As} for the radical identified as $\mathrm{Ph_3\dot{A}sOB}$ (1876 MHz) is very similar to that recently reported for $\mathrm{Me_3\dot{A}sSB}$ (1835 MHz) and related species.[5a] It would, therefore, appear that an ^{75}As hyperfine interaction of *ca.* 1850 MHz is characteristic of arsanyl radicals with a single, apical RO or RS ligand. An increased ^{75}As hyperfine interaction (*ca.* 2200 MHz) appears to be characteristic of dialkoxyarsanyl radicals, confirming an earlier tentative identification of $\mathrm{Me_2\dot{A}s(OB)_2}$ (2157 MHz).[5a] An entirely analogous difference in the ^{31}P hyperfine interactions has been observed in the case of mono- and dialkoxyphosphoranyl radicals.[3] However, our data on different $\mathrm{Ph_2\dot{A}s(OR)_2}$ radicals suggest that t_{As} decreases with increasing electronegativity of the OR groups. Thus, in the series $\mathrm{Ph_2\dot{A}s(OR)OB}$ t_{As} changes from 2225 MHz (R = B), through 2216 MHz (R = Et), to 2204 MHz (R = Me). Also, t_{As} in $\mathrm{Ph_2\dot{A}s(OB)_2}$ (2225 MHz) is larger than, and in $\mathrm{Ph_2\dot{A}s(OEt)_2}$ (2185 MHz) smaller than, that in $\mathrm{Ph_2\dot{A}s(OEt)OB}$ (2216 MHz).

A possible explanation of these observations might be as follows: the substitution of a second (apical) BO ligand causes a large *increase* in t_{As} due to the combined effects of (a) the higher electronegativity of BO over Ph[13] and (b) an increased deviation from colinearity in the apical bonds. The small *decrease* in t_{As} on changing the second BO for OEt and OMe is probably due to the effects of the increased electronegativity being overcome by a tendency for the BO–As–OR bonds to become more nearly colinear as the size of R is decreased.

Radical Stabilities. Kinetic considerations alone would appear to eliminate the possibility that the arsanyl radicals studied in this work decomposed by β scission. Thus a rate constant difference of 2×10^4 at $-100°$ between $\mathrm{Ph_3\dot{A}sOB}$ and $\mathrm{Ph_2\dot{A}s(OB)_2}$ would not be expected if these radicals decomposed to give the arsine oxide and *tert*-butyl radicals. Moreover, $\mathrm{Ph_2\dot{A}s(OB)_2}$ would be expected to be less stable than $\mathrm{Ph_2\dot{A}s(OMe)OB}$ toward β scission, whereas it is more stable.

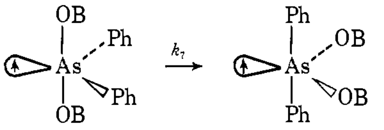
Apical bonds in trigonal bipyramidal molecules are expected to be weaker than equatorial bonds. It is, therefore, not surprising that $\mathrm{Ph_3\dot{A}sOB}$, which must have one apical As–Ph bond, undergoes α scission more readily than $\mathrm{Ph_2\dot{A}s(OB)_2}$, in which both phenyl groups can occupy equatorial positions. A comparison of the Arrhenius equations for the unimolecular decomposition of these two radicals implies that the difference in apical and equatorial bond strengths could be as large as 5 kcal mol^{-1}.

It is, however, conceivable that pseudo-rotation (reaction 7) is the rate-controlling reaction for decomposition of $\mathrm{Ph_2\dot{A}s(OB)_2}$. This explanation would imply that the energy barrier to pseudo-rotation is *ca.* 13 kcal mol^{-1}.

Table III. Yields of the Principal Volatile Reaction Products from the Decomposition of *tert*-Butyl Hyponitrite in the Presence of Some Tertiary Arsines in Either Isopentane (A) or Toluene (B) at 50°

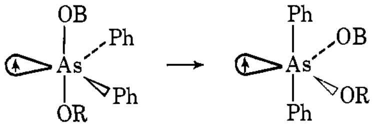
Arsine	Initial concn, *M*	$[\mathrm{BON_2OB}]_0$, *M*	Solvent	*tert*-Butyl alcohol, *M*	Benzene, *M*
$\mathrm{Ph_3As}$	0.025	0.012	A	0.0075	0.003
$\mathrm{Ph_3As}$	0.05	0.012	A	0.006	0.0075
$\mathrm{Ph_3As}$	0.083	0.012	A	0.0115	0.012
$\mathrm{Ph_3As}$	0.027	0.01	B	0.012	0.0035
$\mathrm{Ph_3As}$	0.067	0.01	B	0.0155	0.0055
$\mathrm{Ph_2AsOMe}$	0.025	0.01	B	0.01	0.0045
$\mathrm{Ph_2AsOEt}$	0.012	0.0067	B	0.0067	0.0035
$\mathrm{Ph_2AsOB}$	0.024	0.012	A	0.009	0.008
$\mathrm{Ph_2AsOB}$	0.048	0.012	A	0.0065	0.007
$\mathrm{Ph_2AsOB}$	0.068	0.012	A	0.0075	0.006
$\mathrm{Ph_2AsOB}$	0.019	0.01	B	0.0155	0.004
$\mathrm{Ph_2AsOB}$	0.038	0.008	B	0.0145	0.003

The radicals $\mathrm{Ph_2\dot{A}s(OMe)OB}$ and $\mathrm{Ph_2\dot{A}s(OEt)OB}$



(7)

can undergo α scission either by losing a phenyl group from an equatorial position or, if pseudo-rotation is rate-controlling, from an apical position.



(8)

The different stabilities of dialkoxyarsanyl radicals implies that either the rate constant for pseudo-rotation or the equatorial As–Ph bond strength depends on the nature of R.

Experimental Section

Materials. Triphenylarsine (Ventron Corporation, Alfa Products) was recrystallized from methanol. Chlorodiphenylarsine (PCR Inc., Gainesville, Fla.) was used without further purification. Tris(*p*-methylphenyl)arsine (mp 145–148°); *Anal.* Calcd for $\mathrm{C_{21}H_{21}As}$: C, 72.41; H, 6.08. Found: C, 72.43; H, 6.06) and tris(*p*-methoxyphenyl)arsine (mp 159–161°; *Anal.* Calcd for $\mathrm{C_{21}H_{21}O_3As}$: C, 63.64; H, 5.34. Found: C, 63.4; H, 5.31) were prepared from the appropriate arylmagnesium bromide and arsenic trichloride.[14] The alkoxydiphenylarsines were prepared from chlorodiphenylarsine and the appropriate alcohol in the presence of triethylamine. For example, methanol (0.024 mol) and triethylamine (0.024 mol) in dry pentane (10 cm^3) were added slowly to a stirred solution of chlorodiphenylarsine (0.024 mol) in dry pentane (20 cm^3) at 0°. After refluxing the mixture for 30 min, the solution was filtered and fractionated to give diphenylmethoxyarsine. Diphenylmethoxyarsine and diphenylethoxyarsine have previously been reported.[15] The purity of both these compounds by nmr and mass spectroscopic analysis was >90%. Diphenyl-*tert*-butoxyarsine gave a mass spectrum with only one parent ion (*m*/*e* 302) and one peak by glc. Integration of the nmr spectrum of this compound (two peaks, τ 8.69 (singlet), τ 2.62–2.86 (multiplet)) indicated that its purity was >90%. Di-*tert*-butyl peroxide was purified by passage through basic alumina followed by distillation. Di-*tert*-butyl hyponitrite was prepared by the method of Kiefer and Traylor.[16] Isopentane (Phillips Research Grade) and trichlorofluoromethane were used as received while toluene (Phillips Research Grade) was used after passage through basic alumina. Phenyl *N*-*tert*-butyl nitrone was a gift from Dr. E. G. Janzen.

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Radical Production and Kinetic Procedure. Arsanyl radicals were generated in the cavity of a Varian E-3 epr spectrometer by photolysis (using a 200-W Osram super pressure mercury lamp) of deoxygenated solutions of the appropriate tertiary arsine (0.01–0.1 *M*) and di-*tert*-butyl peroxide in a low-boiling solvent (typically isopentane, trichlorofluoromethane, or toluene). Some of the runs were carried out in the presence of phenyl *N*-*tert*-butyl nitrone (0.001 *M*). Reaction temperatures were varied between 0° and −120° with a Varian V-4557 variable-temperature accessory. Radical accumulations and decays were recorded with the *X*-*Y* recorder provided with the spectrometer or in a Fabri-Tek 1072 signal averager. The absolute concentration of an arsanyl radical was determined by comparing the double integration (×4) of one of the first derivative lines with the double integration (at the same temperature) given by a standard solution of 2,2-diphenyl-1-picrylhydrazyl.[17]

Decomposition of *tert*-Butyl Hyponitrite in the Presence of Some Tertiary Arsines. *tert*-Butyl hyponitrite and the appropriate arsine (either triphenylarsine, diphenylmethoxyarsine, diphenylethoxyarsine, or diphenyl-*tert*-butoxyarsine) were heated in deoxygenated isopentane or toluene at 50° for 10 half-lives of the hyponitrite. The volatile reaction products were analyzed by glc and mass spectroscopy, while the involatile products were analyzed by infrared spectroscopy. The principal volatile reaction products produced from these reactions are summarized in Table III.

Relative Reactivities of Triphenylarsine and Triethyl Phosphite to *tert*-Butoxy Radicals. A mixture of triphenylarsine (0.003 *M*) and triethyl phosphite (0.005 *M*) in deoxygenated trichlorofluoromethane containing di-*tert*-butyl peroxide was photolyzed *in situ* in the cavity of the spectrometer. Rates of accumulation and steady-state concentrations of $(EtO)_3\dot{P}OB$ and $Ph_3\dot{A}sOB$ were measured and gave the relative reactivities of the two substrates toward *tert*-butoxy radicals.

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Electronic Spectra of Ruthenium and Osmium Tetroxides

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Abstract: The electronic absorption spectra of gaseous ruthenium and osmium tetroxides have been measured in the energy region below 11 eV and the two lowest energy band systems of both materials have been investigated in SF_6 matrices at temperatures down to 20°K. It is shown that the substructure in the two initial band systems is vibronic, (*i.e.*, ν_2(e) activity). It is also shown that the electronic spectrum can be subdivided into valence and Rydberg bands and that much of the spectrum is interpretable using pes data. The relative energy of the virtual 2e-MO in RuO_4 and OsO_4 has been determined and it is the lesser antibonding energy of this MO in RuO_4 which is responsible for the lower energy of the valence transitions of this material.

The purpose of this work is to elaborate the electronic absorption spectra of gaseous RuO_4 and OsO_4 in the range 5000–1000 Å and to attempt an analysis of these spectra using photoelectron spectroscopic (pes) data recently generated in these laboratories.[1]

The pes data are tabulated in Figure 1 and provide the energies of the five highest energy filled MO's. The lowest energy virtual MO's are also shown in Figure 1. We believe, based on computational data[1] as well as on intensity considerations of the five lowest energy transitions of RuO_4 and OsO_4, that the two lowest energy virtual MO's, in order of increasing energy, are 2e and $4t_2$. We also maintain, based on the analysis which will be given, that the 2e-MO of RuO_4 is approximately 1 eV less energetic than the 2e-MO of OsO_4 and that it is this fact which is largely responsible for the lower electronic transition energies found in RuO_4. Finally, based on a fitting of spectroscopic data, a fitting which is probably quite suspect, we think that the $4t_2$-MO's of RuO_4 and OsO_4 are nearly isoenergetic and ∼3.5 eV higher than the 2e-MO of OsO_4. These prejudices are all elaborated in Figure 1 and will be discussed in the text. The only other virtual MO resulting from the basis set of AO's used in the computations (*i.e.*, the $3a_1$-MO) is situated in the continuum, is probably disruptive (if populated) of molecular integrity, and is not important to the discussion of spectroscopic characteristics; this MO is not shown in Figure 1.

The virtual AO's of metal and oxygen which were not included in the AO computational basis set are used in a discussion of the higher energy region of the spectrum. The virtual AO's of the metal are not needed for this purpose since they lie at considerably higher energies than the virtual AO's of the oxygens. In other words, all of the higher energy electronic spectroscopy can be rationalized in terms of Rydberg transitions from filled MO's of the ground state to virtual oxygen-like pseudo-AO's. Since these pseudo-AO's have approximately the same energy in both molecules and since the filled MO's of Figure 1 are also quite similar energetically, it follows that the Rydberg transitions, in contrast to the valence transitions, should be more or less isoenergetic. It is this premise, namely the dominance of Rydberg transitions, which is responsible for the energy coincidence of many features of both spectra in their high-energy regions.

Any discussion which attempts to discuss state energy differences, whether obtained from pes or simple electronic absorption spectroscopy data, in terms of MO energies is clearly dangerous. That course, without apology, is the tack which this discussion will adopt.

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