SO_2Cl has a distinctly different infrared spectrum from $Pt(PPh_3)_2CH_3I-SO_2$ (3, Table I). Comparison of the spectra of compounds 5 and 6, however, shows that it would not have been possible to eliminate from consideration the unknown five-coordinate platinum(II) species $O_2S-Pt(PPh_3)_2CH_3I$ on this basis.

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Phosphoranylperoxy Radicals[1]

Sir:

The existence of phosphoranylperoxy radicals, $X_4POO\cdot$, has been postulated to account for the products observed in the autoxidation of alkanes in the presence of phosphorus trichloride,[2] for the deoxygenation of pyridine *N*-oxide by trialkyl phosphites,[3] and for the photoinduced oxidation of benzenoid compounds by trialkyl phosphites.[4] The radical is assumed to be formed by reaction of a phosphoranyl radical with oxygen.

$$X_4P\cdot + O_2 \longrightarrow X_4POO\cdot \tag{1}$$

The epr spectra of phosphoranyl radicals, generated by the photolysis of di-*tert*-butyl peroxide in the presence of trialkyl phosphites or trialkylphosphines, have been observed recently.[5-7] The spectra are characterized by a doublet separated by 700–900 G.

We wish to report that *tert*-butoxy trialkoxyphosphoranyl radicals obtained in the above manner from trialkyl phosphites [$(R'O)_3P$, R′ = Me, Et, *i*-Pr, *tert*-Bu] in cyclopropane solution below −40°, will react with oxygen. The doublet due to the phosphoranyl radical disappears and is replaced by a doublet with a somewhat broader line width. The hyperfine coupling of the new doublet is ~9 G and there is no further resolvable fine structure. The radical has a *g* value of 2.022 which is between the value of 2.025 found for group IV trialkylmetalperoxy radicals[8] and the values of ~2.014–2.016 found for alkylperoxy radicals. Since the phosphoranyl radical reappears when the oxygen has been consumed (see below) we have assigned this new radical the structure *tert*-$BuO(R'O)_3POO\cdot$. We believe this to be the first direct observation of phosphoranylperoxy radicals. The coupling constants and *g* values are summarized in Table I.

Table I. Hyperfine Coupling Constants and *g* Values of Phosphoranylperoxy Radicals in Cyclopropane at −80°

Radical	a_P, G	g
tert-$BuO(MeO)_3POO\cdot$	9.2	2.022
tert-$BuO(EtO)_3POO\cdot$	9.5	2.022
tert-$BuO(i\text{-}PrO)_3POO\cdot$	8.9	2.022
(*tert*-$BuO)_4POO\cdot$[a]	9	2.02

[a] The doublet due to this peroxy radical is obtained together with a broad asymmetric unresolved signal (~400 G wide) so that measurements of its physical constants are imprecise. This signal may be due to impurities in the original phosphite since it can only be obtained in ~90% purity (V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964)).

Under continuous irradiation the phosphoranylperoxy radicals survived for several minutes at −90° but only for about 30 sec at −50°, after which they were, of course, replaced by phosphoranyl radicals. Clearly the dissolved oxygen is rapidly depleted by a chain reaction at the higher temperatures and the scheme suggested by Walling and Rabinowitz[9] seems not unreasonable. Reaction 4 is reasonably fast even

$$RO\dot{P}(OR')_3 \longrightarrow R\cdot + OP(OR')_3 \tag{2}$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \tag{3}$$

$$ROO\cdot + P(OR')_3 \longrightarrow ROO\dot{P}(OR')_3 \tag{4}$$

$$ROO\dot{P}(OR')_3 \longrightarrow RO\cdot + OP(OR')_3 \tag{5}$$

$$RO\cdot + P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \tag{6}$$

at low temperatures.[10] However, the scission of a *tert*-butyl radical from *tert*-$BuO\dot{P}(OEt)_3$ is not a particularly rapid reaction[11] and therefore at low temperatures and/or at high oxygen concentrations the Walling and Rabinowitz chain is probably replaced by

$$RO\dot{P}(OR')_3 + O_2 \longrightarrow RO(R'O)_3POO\cdot \tag{7}$$

$$RO(R'O)_3POO\cdot + P(OR')_3 \longrightarrow RO(R'O)_3POO\dot{P}(OR')_3 \tag{8}$$

$$RO(R'O)_3POO\dot{P}(OR')_3 \longrightarrow RO(R'O)_3PO\cdot + OP(OR')_3 \tag{9}$$

$$RO(R'O)_3PO\cdot \longrightarrow RO\cdot + (R'O)_3PO \tag{10}$$

$$RO\cdot + P(OR')_3 \longrightarrow RO\dot{P}(OR')_3 \tag{6}$$

The phosphoranylperoxy radicals from trimethyl, triethyl, and triisopropyl phosphite[12] decayed with second-order kinetics at temperatures below −85°.

$$2tert\text{-}BuO(R'O)_3POO\cdot \xrightarrow{2k_t} \text{nonradical products} \tag{11}$$

At peroxy radical concentrations in the range 0.5–1.0 × 10^{-5} *M* the measured values of $2k_t$ at −90° were 6 × 10^4 M^{-1} sec^{-1} for R′ = Me, 1 × 10^4 for Et, and 3 × 10^4 for *i*-Pr. These differences are within the probable experimental error. Over the temperature range from −89 to −116° $2k_t$ for R′ = Me is given by $2k_t = 10^{10} \exp(-4500/RT)\ M^{-1}\ \text{sec}^{-1}$.

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(10) The rate constant for the reaction of *tert*-butyl peroxy radicals with trimethyl phosphite is 1.0 M^{-1} sec^{-1} at −100°; J. A. Howard and G. B. Watts, unpublished results.

(11) For this radical,[7] $k_2 = 2.4 \times 10^{13} \exp(-9340/RT)$ sec^{-1}.

(12) The second radical obtained with tri-*tert*-butyl phosphite (footnote *a*, Table I) decayed slowly and prevented kinetic studies on the peroxy radical. A similar broad signal, but of much reduced intensity, was present in the other phosphoranylperoxy radicals and made kinetic studies rather difficult. The measurement of peroxy radical concentrations was also a problem because of the relatively short lifetime of the radical under continuous irradiation.

The phosphoranylperoxy radicals appear to exist in equilibrium with a diamagnetic dimer in this temperature range since a sudden increase in temperature from −100 to −60° during the course of a decay (in the dark) produces a temporary increase in the radical concentration. By analogy with the behavior of tertiary alkylperoxy radicals[13–15] it seems likely that this dimer is a tetroxide.

$$2\textit{tert}\text{-BuO(R'O)}_3\text{POO}\cdot \rightleftharpoons \textit{tert}\text{-BuO(R'O)}_3\text{POOOOP(OR')}_3\text{O-}\textit{tert}\text{-Bu} \quad (12)$$

At temperatures from −45 to −70° the phosphoranylperoxy radicals decay with first-order kinetics. The measured rate constants depend slightly on the phosphite concentration. Thus, a tenfold increase in phosphite almost doubled the first-order decay constant. With initial phosphite concentrations of 0.3 *M* the rate constants at −50, −60, and −70° were 2.6, 1.5, and 0.9 sec^{-1} for R′ = Me; 0.9, 0.4, and 0.2 sec^{-1} for R′ = Et; and 2.3, 0.8, and 0.2 sec^{-1} for R′ = *i*-Pr. The differences in rate constants between the three radicals are not significant, particularly as it is uncertain which process is being measured under conditions where a chain reaction is certainly occurring. Quite probably the rate-controlling step for chain termination involves some cross reaction such as

$$\text{RO(R'O)}_3\text{POO}\cdot + \text{RO}\dot{\text{P}}\text{(OR')}_3 \longrightarrow \text{RO(R'O)}_3\text{POOP(OR')}_3\text{OR} \quad (13)$$

so that the peroxy radicals decay with first-order kinetics. At lower temperatures the rate of attack of the phosphoranylperoxy radical on phosphite (reaction 8) will be reduced. In consequence, the concentration of phosphoranylperoxy radicals relative to that of the other radicals in the system will rise and hence the bimolecular self-reaction 11 will predominate.

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[16] NRCC Postdoctoral Fellow, 1970–1972.

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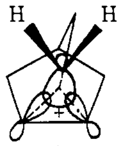
Electron Spectroscopy of Organic Ions. II.[1a] Carbon 1s Electron Binding Energies of the Norbornyl, 2-Methylnorbornyl, and Related Cations. Differentiation between "Nonclassical" Carbonium and "Classical" Carbenium Ions[1b]

Sir:

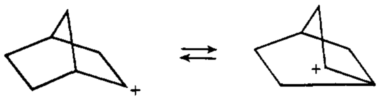
We have recently demonstrated in the case of the *tert*-butyl cation that in going from a neutral hydrocarbon to the corresponding trivalent carbocation (carbenium ion), intensive positive charge localization on the electron-deficient carbenium center increases the 1s electron binding energy of that atom by *ca.* 5 eV.[1,2] The less-affected methyl carbon atoms experience an increase of only 1.5 eV or less. Extensive charge delocalization, as in the trityl and tropylium cations, results only in a small and relatively uniform increase of the 1s orbital energy of all the carbon atoms which share the formal positive charge. Separate peaks cannot, therefore, be observed.

Since in electron spectroscopy the time scale of the measured ionization processes is on the order of 10^{-16} sec, definite ionic species are characterized, regardless of their possible intra- and intermolecular interactions (*e.g.*, Wagner–Meerwein rearrangements, hydride shifts, proton exchange, etc.). Thus, electron spectroscopy can give an unequivocal, direct answer to the long debated question of the "classical" or "nonclassical" nature of the norbornyl cation, independent of any possible equilibration process.

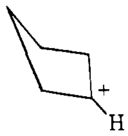
We wish to report new evidence for the nonclassical carbonium ion nature of the norbornyl cation **1**, as given by the electron spectroscopic study of this ion, compared to a series of related model ions with varying degrees of charge localization. These model ions are the cyclopentyl **2**, methylcyclopentyl **3**, and 2-methylnorbornyl **4** cations as well as the previously studied *tert*-butyl cation (see Table I). The carbon 1s electron spectra have been measured under similar conditions to those reported for the *tert*-butyl cation.[1a] However, we found that AsF_3 is, in many cases, a preferred solvent which, due to its higher freezing point, diminishes the probability of water condensation and ice formation on the surface of the samples. Thus, the probability of quenching of the ions in the surface layer during the measurement is greatly reduced. The carbon 1s spectrum of the cyclopentyl **2** and methylcyclopentyl **3** cations clearly exhibits two distinct carbon 1s electron lines with relative separations of electron binding energy ($\text{d}E_\text{b}$) values of 4.3 ± 0.5 and 4.2 ± 0.2 eV and approximate intensity ratios of 1:4 and 1:5, respectively.[3] These separations are characteristic of cationic species with intensive charge localization (*cf.* the relative chemical shift of 3.9 eV in *tert*-butyl cation[1a,2]). The 2-methylnorbornyl cation **4** (Figure 1, upper trace) shows a



1



1a **1b**



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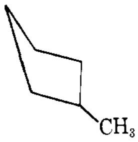

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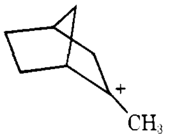

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[1] (a) Part I: G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970). (b) For the definition of carbocations differentiating trivalent *carbenium ions* from penta- or tetracoordinated *carbonium ions* see G. A. Olah, *ibid.*, **94**, 808 (1972).

[2] Corrected value in reference to methane. Spectrum measured in a frozen solution of $(\text{CH}_3)_3\text{C}^+\text{SbF}_6^-$ in AsF_3.

[3] The lower binding energy lines corresponding to four and five carbon atoms, respectively, are somewhat broadened, without showing any possibility of estimating the relative carbon 1s E_b values of these atoms.