Electron Spin Resonance Spectra of Organic Oxy Radicals. The Radical $(CH_3)_3CO_3$

Sir:

Although the hydroxyl radical has been studied extensively by esr in crystalline ice,[1-3] its spectrum has never been observed in rare-gas matrices, and it has never been detected in the liquid phase by esr. This is because, in the absence of any external perturbation, the unpaired electron is in an orbitally degenerate system, the ground state of which, being $^2\pi_{3/2}$, would have a g tensor ranging from 0 to 4. The strong, asymmetric hydrogen bonding to which OH is subjected in ice is sufficient to quench the orbital momentum very considerably, the g tensor now ranging between 2.06 and 2.002.[3] In the liquid phase, fluctuations in such perturbations would greatly modify the g value and hence would provide an efficient mechanism for spin relaxation. This would give very broad lines and hence $\cdot OH$ cannot be detected in fluid solution.

For these and other reasons it was predicted some time ago that the claim to have detected alkoxy radicals, $RO\cdot$, in the liquid state[4] was in error, and that the radicals were more probably peroxy radicals, $ROO\cdot$.[5] This prediction has since been confirmed.[6]

These same arguments can be applied to a recent study of a radical having a relatively narrow singlet, at $g_{av} = 2.004$, which was formed by *in situ* photolysis of di-*t*-butyl peroxide.[7] The purpose of this note is to suggest that the species being studied cannot be the simple alkoxy radical, but that it could well be the "ozonide" radical Me_3COOO, possibly formed by the reaction

$$Me_3C\dot{O} + O_2 \rightleftharpoons Me_3COOO \qquad (1)$$

When *t*-butyl hydroperoxide is present, the reaction

$$Me_3C\dot{O} + Me_3COOH \longrightarrow Me_3COH + Me_3COO \qquad (2)$$

occurs predominantly and the peroxy radical is detected by esr. Reaction 1 is probably reversible, but relatively slow.

Justification for this suggestion comes from the recent unambiguous detection of the ozonide radical, F_3COOO, which also has $g = 2.004$.[8] The g tensor for ROOO is governed largely by the shape of the oxygen framework (which is expected to be strongly bent) and should not be sensitive to the nature of R. These "ozonide" radicals are related to the very stable ozonide ion, O_3^-, which has been studied extensively by esr.

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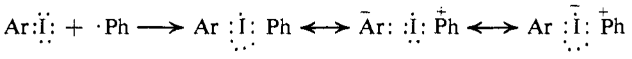
Halogen Abstraction Reactions. I. Free-Radical Abstraction of Iodine from Substituted Iodobenzenes[1]

Sir:

Although the free-radical abstraction of halogen atoms from various organic compounds is well documented, the abstraction of iodine from aryl iodides has only recently been reported.[2] We presently wish to report several interesting aspects of the abstraction of iodine from a series of substituted iodobenzenes by phenyl radicals generated by decomposition of phenylazotriphenylmethane (PAT) at 60°. The reactions were conducted in carbon tetrachloride solution, and the results are presented as relative reactivity of iodo compound per molecule of carbon tetrachloride.[3] Variation of the PAT concentration over a tenfold range and the ArI/CCl_4 ratio from 0.059 to 0.41 has a negligible effect on the k_I/k_{Cl} values.

It was found that the abstraction of an iodine bonded directly to an aromatic ring is an extremely facile process competing successfully with phenylation of the aromatic compounds under study since combined yields of iodobenzene and chlorobenzene typically average 75–90% based on PAT.

More interesting are the results depicted in Figure 1 where it is seen that a quite good Hammett correlation of relative reactivities is obtained with $\rho = +0.57$ (correlation coefficient = 0.946). This is the first reported example of an abstraction process by an organic free radical exhibiting a positive ρ value.[4] Many hydrogen abstraction reactions by various free radicals have been successfully correlated with σ or σ^+; all such reactions occur more readily if electron-donating substituents are present.[3,5] This indicates that there is a substantial difference in charge distribution in the transition state for homolytic cleavage of a carbon–iodine bond as contrasted to a carbon–hydrogen bond and that the phenyl radical is not insensitive to polar effects[3] for abstraction of iodine. Resonance structures II and III probably contribute significantly to the description of the transition state for iodine abstraction from aromatic iodo compounds (ArI) by phenyl radical (Ph·).



$$\mathrm{Ar}{:}\underset{\cdot\cdot}{\ddot{\mathrm{I}}}{:} + \cdot\mathrm{Ph} \longrightarrow \mathrm{Ar}\ {:}\underset{\cdot\cdot\cdot}{\dot{\mathrm{I}}}{:}\ \mathrm{Ph} \longleftrightarrow \overset{-}{\mathrm{Ar}}{:}\ {:}\underset{\cdot\cdot}{\dot{\mathrm{I}}}{:}\ \overset{+}{\mathrm{Ph}} \longleftrightarrow \mathrm{Ar}\ {:}\underset{\cdot\cdot\cdot}{\overset{-}{\mathrm{I}}}{:}\ \overset{+}{\mathrm{Ph}}$$

I II III

It is not possible to deduce from the present results whether the iodine abstraction reaction involves a concerted bond breaking and bond forming or if the reac-

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