

### Electron Spin Resonance Spectra of Organic Oxy Radicals. The Radical $(\text{CH}_3)_3\text{CO}_3$

Sir:

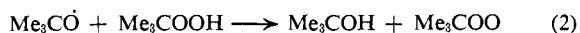
Although the hydroxyl radical has been studied extensively by esr in crystalline ice,<sup>1-3</sup> its spectrum has never been observed in rare-gas matrices, and it has never been detected in the liquid phase by esr. This is because, in the absence of any external perturbation, the unpaired electron 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.<sup>3</sup> 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  $\cdot\text{OH}$  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,  $\text{RO}\cdot$ , in the liquid state<sup>4</sup> was in error, and that the radicals were more probably peroxy radicals,  $\text{ROO}\cdot$ .<sup>5</sup> This prediction has since been confirmed.<sup>6</sup>

These same arguments can be applied to a recent study of a radical having a relatively narrow singlet, at  $g_{\text{av}} = 2.004$ , which was formed by *in situ* photolysis of di-*t*-butyl peroxide.<sup>7</sup> 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  $\text{Me}_3\text{COOO}\cdot$ , possibly formed by the reaction



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



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,  $\text{F}_3\text{C}\text{OOO}\cdot$ , which also has  $g = 2.004$ .<sup>8</sup> The  $g$  tensor for  $\text{ROOO}\cdot$  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,  $\text{O}_3^-$ , which has been studied extensively by esr.

(1) G. H. Dibdin, *Trans. Faraday Soc.*, **63**, 2098 (1967).

(2) J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, H. W. Wardale, and D. O. Williams, *ibid.*, **63**, 2112 (1967).

(3) J. A. Brivati, M. C. R. Symons, D. J. A. Tinling, and D. O. Williams, *J. Chem. Soc., A*, 719 (1969).

(4) L. H. Piette and W. C. Ladgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

(5) M. C. R. Symons "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press, New York, N. Y., 1963, p 283.

(6) K. H. Ingold and J. R. Morton, *J. Am. Chem. Soc.*, **86**, 3400 (1964).

(7) S. Weimer and G. S. Hammond, *ibid.*, **91**, 2182 (1969).

(8) R. W. Fessenden, *J. Chem. Phys.*, **48**, 3725 (1968).

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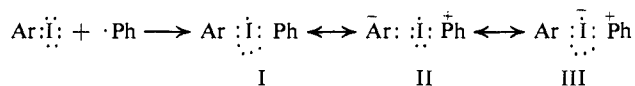
### Halogen Abstraction Reactions. I. Free-Radical Abstraction of Iodine from Substituted Iodobenzenes<sup>1</sup>

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.<sup>2</sup> 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.<sup>3</sup> Variation of the PAT concentration over a tenfold range and the  $\text{ArI}/\text{CCl}_4$  ratio from 0.059 to 0.41 has a negligible effect on the  $k_1/k_{\text{Cl}}$  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  $\rho$  value.<sup>4</sup> Many hydrogen abstraction reactions by various free radicals have been successfully correlated with  $\sigma$  or  $\sigma^+$ ; all such reactions occur more readily if electron-donating substituents are present.<sup>3,5</sup> 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<sup>3</sup> 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 ( $\text{ArI}$ ) by phenyl radical ( $\text{Ph}\cdot$ ).



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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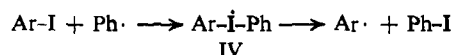
(2) J. F. Bunnett and C. C. Wamser, *J. Am. Chem. Soc.*, **88**, 5534 (1966); D. L. Brydon and J. I. G. Cadogan, *J. Chem. Soc., C*, 819 (1968).

(3) (a) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963); (b) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *ibid.*, **88**, 1189 (1966).

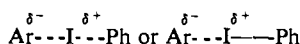
(4) The abstraction of chlorine from aromatic acid chlorides by the tri-*n*-butyltin radical exhibits a positive  $\rho$  value: H. G. Kuivila and E. J. Walsh, Jr., *ibid.*, **88**, 571 (1966).

(5) K. H. Lee, *Tetrahedron*, **24**, 4793 (1968); P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968); G. A. Russell and R. C. Williamson, *ibid.*, **86**, 2357 (1964); C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957); G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968); J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963), and references cited therein.

tion proceeds through two steps with the formation of a phenylaryliodine (IV) as an intermediate.<sup>6</sup> For the



present discussion, a distinction between the two possible processes is unnecessary, the significant observation being the apparent accumulation in the transition state of excess charge on the carbon from which the iodine is being abstracted.

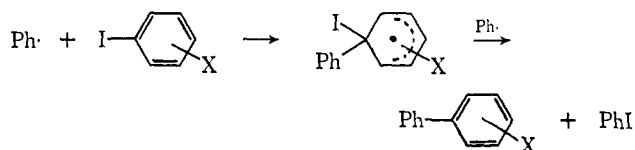


If it is assumed that the *meta* derivatives are well-behaved, it can be noted from Figure 1 that the *para*-substituted iodobenzenes appear somewhat less susceptible to iodine abstraction than expected. Although the data are by no means conclusive, this may reflect enhanced stability of the carbon-iodine bond of the substituted ring resulting from either substituent effects on the ground-state bond energies<sup>7</sup> or resonance stabilization of the presumed phenylaryliodine intermediate (e.g., for *p*-iodonitrobenzene). However, this stabilization effect



is small and is almost completely overwhelmed by the more important polar contributions to bond cleavage.

It has been conclusively demonstrated that the phenyl radical indeed attacks the iodine atom rather than the carbon to which it is attached to form a phenyliodocyclohexadienyl radical analogous to the mechanism for homolytic arylation<sup>8</sup> and the free-radical interchange of halogens in aromatic compounds.<sup>9</sup> In view of phen-



ylation studies on nitrobenzene which show enhanced reactivity of the *ortho* positions,<sup>10</sup> *o*-iodonitrobenzene would appear to be especially susceptible to attack by this process. In fact, less than 0.1% of *o*-nitrophenyl

(6) H. E. Bachofner, F. M. Beringer, and L. Meites, *J. Am. Chem. Soc.*, **80**, 4269, 4274 (1958). We have attempted to determine the stability of the proposed phenylaryliodine intermediates (IV) presumably formed by electroreduction of several phenyliodonium salts. The cyclic voltammetry results were complicated by adsorption processes and no conclusive results were obtained. It was noted, however, that different results were observed when the electrode was changed from mercury to platinum. The absence of a reduction wave in the -0.2-V (sce) region utilizing platinum suggests that electrochemical studies of iodonium salts with a mercury electrode are probably complicated by chemical reactions of the substrate (or a reduced form of the substrate) with the electrode: O. A. Ptitsyna, S. I. Orlov, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1947 (1966); *Chem. Abstr.*, **66**, 75433 (1967).

(7) E. M. Kosower and I. Schwager, *J. Am. Chem. Soc.*, **86**, 5528 (1964); N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., 1958, p 83.

(8) It has been suggested that abstraction of iodine from iodobenzene by the trifluoromethyl radical proceeds through such a mechanism: R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **62**, 128 (1966).

(9) B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *J. Am. Chem. Soc.*, **84**, 158 (1962); S. Levine and R. M. Noyes, *ibid.*, **80**, 2401 (1958).

(10) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, pp 57, 68.

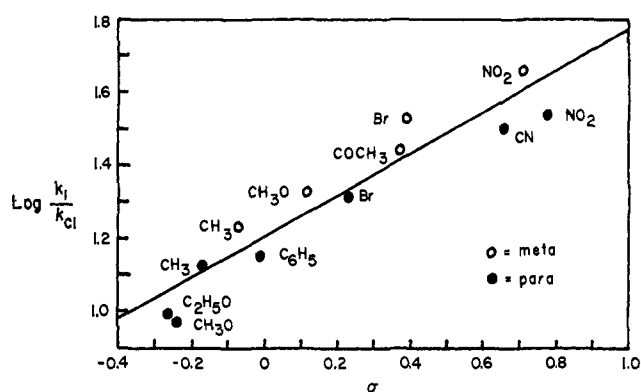


Figure 1. Plot of  $\log k_1/k_{Cl}$  at 60° vs. Hammett  $\sigma$  constants (from the compilation by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958)). Each point represents the average of at least three independent experiments.

and approximately 80% iodobenzene were formed when *o*-iodonitrobenzene was allowed to react with PAT; the above mechanism demands formation of equal amounts of iodobenzene and *o*-nitrophenyl. This result also eliminates a direct  $S_N2$  displacement of iodine on carbon as a mechanistic possibility.<sup>11</sup>

*o*-Iodonitrobenzene was found to be one of the more reactive compounds studied having  $k_1/k_{Cl} = 186$ .<sup>12</sup> An attempt to observe abstraction of bromine atom from *o*-bromonitrobenzene yielded less than 0.1% bromobenzene.

A series of *ortho*-substituted iodobenzenes were also studied, and an attempted Hammett correlation utilizing *ortho*  $\sigma$  constants specifically derived for such compounds<sup>13</sup> gave wide divergence. We believe that electrochemical reduction studies of such halogenated compounds are complicated by a rapid chemical reaction following electron transfer<sup>14</sup> and that the  $\sigma$  constants derived from such studies should not be applied to purely chemical processes.

Further work is in progress to learn more of the characteristics of the abstraction of halogen atoms from a variety of organic compounds.

(11) L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1753 (1967); *Chem. Commun.*, 754 (1968).

(12) This reactivity parallels the high reactivity of *o*-iodonitrobenzene in Ullmann coupling reactions: M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

(13) W. W. Hussey and A. J. Diefenderfer, *J. Am. Chem. Soc.*, **89**, 5359 (1967).

(14) W. C. Danen, T. T. Kensler, J. G. Lawless, and M. D. Hawley, *J. Phys. Chem.*, in press.

(15) National Science Foundation Undergraduate Research Participant, Summer 1968.

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## Ionic Dehydration of Aliphatic Alcohols in the Gas Phase

Sir:

The oxygen-proton-oxygen grouping is known to be important in the clustering of ions in the gas phase<sup>1-3</sup>

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(2) P. Kebarle, R. N. Haynes, and J. G. Collins, *ibid.*, **89**, 5793 (1967).

(3) G. R. A. Johnson and G. Scholes, Ed., "The Chemistry of Ionization and Excitation," Taylor and Francis, New York, N. Y., 1967.