The Simultaneous Detection of Gas Phase Atoms and Free Radicals Produced in a Microwave Discharge by ESR Spin Trapping Methods

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The simultaneous detection of gas phase atoms and free radicals produced in a 2450 MHz discharge is demonstrated by use of a previously described technique called spin trapping. The atoms or radicals are allowed to react with phenyl *N*-*t*-butyl nitrone to give relatively stable nitroxide radicals. The ESR spectra of these nitroxides provide the analytical data for identification of the atoms or radicals trapped.

In previous communications we have described a technique for the detection and identification of gas phase free radicals which depends on the rapid radical addition to phenyl *t*-butyl nitrone (PBN) to produce relatively stable nitroxyl radicals:[1,2)]

$$R\cdot + C_6H_5CH{=}N(O)C(CH_3)_3 \longrightarrow C_6H_5CH(R)\overset{O^-}{\underset{+}{\dot{N}}}C(CH_3)_3$$

The ESR spectra of the nitroxyl radicals recorded at room temperature in liquid solutions (*e.g.* in benzene) provide ideally an unique set of parameters for each radical (R·) trapped. We have called this technique spin trapping and the nitroxyl radicals produced spin adducts.[3,4)]

The previously reported gas phase work demonstrated the feasibility of detecting radicals at atmospheric pressures in a carrier gas (N_2) *e.g.* methyl, ethyl, and perfluoroethyl,[1)] or at total pressures as low as 0.1 Torr in the presence of the radical precursor *e.g.* methyl from acetone or azomethane, ethyl from 3-pentanone, tetraethyllead or diethylmercury.[2)] We now wish to report that hydrogen atoms can be detected simultaneously with radicals in the gas phase by spin trapping methods.

Experimental

A well established source of hydrogen atoms is the microwave discharge of hydrogen molecules. By placing powdered PBN in a 8 mm glass tube about 10—20 cm downstream from the microwave discharge of hydrogen in an apparatus similar to the one shown in Fig. 1, Ref. 2, benzyl *t*-butyl nitroxide, the hydrogen atom adduct of PBN is readily detected in a benzene solution of either the powdered PBN itself or the material collected in the liquid nitrogen trap downstream;

$$H_2 \longrightarrow H\cdot \xrightarrow{PBN} C_6H_5CH_2N(O\cdot)C(CH_3)_3$$

Results and Discussion

Deuterium molecules (D_2) gave the deuterium atom spin adduct in addition to some hydrogen atom addition product (see Table 1 for splitting constants). In some experiments with H_2 or D_2 an additional triplet of doublets was also observed which is tentatively assigned to the hydroxy radical spin adduct presumably produced from the discharge of water vapor inadvertently present in the system. Assignment of this structure is based on the results obtained from water vapor discharge which itself produces a strong hydrogen atom adduct signal and the same triplet of doublets. A previous spectral assignment to this spin adduct does not appear to be correct.[1)] Ammonia discharge has only given the hydrogen atom adduct (and the hydroxy radical adduct in some cases). No amino radicals have been detected to date but this result is not considered final.

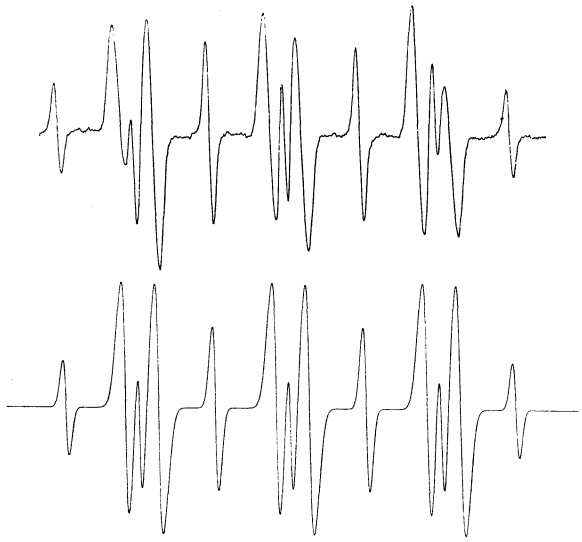

Fig. 1. ESR spectrum of hydrogen atom and methyl radical addition products of phenyl *N*-*t*-butyl nitrone (benzyl and α-methyl *t*-butyl nitroxides) in benzene at room temperature isolated from microwave discharge of methane (see Table 1); top: experimental result; bottom: computer simulated sum of the two spectra.

The nature of the products of microwave discharge of organic compounds has been the subject of some interest in the past.[5–7)] Hydrogen, acetylene, and

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1) E. G. Janzen and J. L. Gerlock, *Nature*, **222**, 867 (1969).

2) E. G. Janzen and I. G. Lopp, *J. Phys. Chem.*, **76**, 2056 (1972).

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

4) For reviews of this technique, see E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971); C. Lagercrantz, *J. Phys. Chem.*, **75**, 3466 (1971); M. J. Perkins, *Chem. Soc. Spec. Publ.*, No. 24, 97 (1970).

5) R. L. McCarthy, *J. Chem. Phys.*, **22**, 1360 (1954).

6) A. Streitwieser, *J. Amer. Chem. Soc.*, **84**, 1065 (1962); A. Streitwieser and H. R. Ward, *ibid.*, **85**, 539 (1963).

7) "Chemical Reactions in Electric Discharges," Advances in Chemistry Series, No. 80, American Chemical Society, Washington, D. C., 1969; see for example: J. P. Wightman and N. J. Johnston, p. 322; D. D. Neiswender, p. 338.

TABLE 1. HYPERFINE SPLITTING PARAMETERS OF NITROXYLS PRODUCED IN THE REACTION OF ATOMS AND RADICALS WITH PHENYL *N-t*-BUTYL NITRONE

$C_6H_5CH(R)N(O\cdot)C_4H_9$

R	Source	A_N	A_β^H	A_β^D	Reference
H·	$H_2 \rightsquigarrow H\cdot$ (2.5 Torr, 1 hr)	14.84	7.42		This work
H·	$(n\text{-Bu})_3SnH+PBN+h\nu$	14.88[a]	7.44[a]		3
D·	$D_2 \rightsquigarrow D\cdot$ (1 Torr, 2.5 hr)	15.10	7.67	1.15	This work
D·	$(n\text{-Bu})_3SnD+PBN+h\nu$	14.64	7.45	1.15	8
H·	$H_2O \rightsquigarrow H\cdot + HO\cdot$	14.98	7.50		This work
HO·	(0.55 Torr, 2 hr)	14.63	2.88		This work
D·	$D_2O \rightsquigarrow D\cdot + DO\cdot$	14.94	7.66	1.14	This work
DO·	(0.6 Torr, 1 hr)	14.70	2.61		This work
H·	$CH_4 \rightsquigarrow H\cdot + CH_3\cdot$	15.06	7.54		This work
$CH_3\cdot$	(0.8 Torr, 1.3 hr)	14.94	3.30		This work
$CH_3\cdot$	$CH_3COCH_3+h\nu$	14.82	3.47		2

a) Corrected values; see reference 3, p. 4483.

polymers are obtained from methane discharge but experimental evidence of methyl radical detection has not been reported. In our experiments hydrogen atoms and methyl radicals are readily detected (see Fig. 1) in the microwave discharge of methane. The ratio of these products varies from one experiment to another but the determining factors have not been ascertained.

From these preliminary experiments it can be seen that gas phase spin trapping techniques appear to be potentially useful in studies where simultaneous detection of atoms and radicals is desired. Further application of this technique are in progress.

The microwave discharge was operated at 2450 MHz by a 200 watt power supply. Either a rectangular or a cylindrical (Broida) type cavity was used.

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8) Unpublished results of Mr. Dale Nutter, Department of Chemistry, The University of Georgia, Athens, Georgia.