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TRAPPING EXPERIMENT OF RADICAL SPECIES PRODUCED BY GLOW DISCHARGE REACTION OF SOME AROMATIC COMPOUNDS

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The authors have described the successful application of spin trapping as a diagnosis of short-lived free radicals formed from the glow discharge reaction of aromatic compounds. For example, in the decomposition of toluene, benzyl radical was trapped by nitrosobenzene or phenyl-N-t-butylnitrone.

Based upon the study of the emission spectra resulting from the excitation of toluene vapor in electrode discharges, Schüler and Michel[1)] estimated the existence of benzyl radical as major reaction species. Kraaijveld and Waterman[2)] found the formation of bibenzyl as a major product by the electrodeless microwave excitation of toluene vapor, indicating that benzyl radical is the most probable intermediate. In spite of such extensive studies[3-5)] dealing with the behavior of organic compounds in glow discharges, there have been few reports on detection of organic radical species by esr.

The authors have tried to detect short-lived radicals produced by the radiofrequency glow discharge reaction of aromatic compounds such as toluene, benzene and chlorobenzene, using spin trapping agents such as phenyl-N-t-butylnitrone(PBN)[6)] and nitrosobenzene(NB).[7)]

The vapor of the aromatics excited at 28 MHz radiofrequency discharge was led to a cold trap(-195°C) containing 0.5 g of PBN or NB. Usually 50:1 dilutions with toluene were necessary to obtain good resolution. The esr spectrum recorded after decomposition of toluene using PBN showed triplet of doublets with coupling constants, A_N=14.3 and $A_{\beta-H}$=2.4 G. Since solvent effect exerts an unnegligible influence on the coupling constants, esr spectra of spin adducts of several radicals($C_6H_5\cdot$, o-, m-, p-$CH_3C_6H_4\cdot$, and $C_6H_5CH_2\cdot$) obtained by addition reaction between corresponding

Grignard reagents and PBN followed by air oxidation were measured for comparison by the use of toluene as a diluent(Table 1). As shown in Table 1, observed values are in good agreement with those of $C_6H_5(C_6H_5CH_2)CH(NO\cdot)C(CH_3)_3$. Thus PBN successfully trapped benzyl radical generated under the influence of r.f. discharge.

Table 1. Coupling Constants of t-Butyl α-Substituted Benzylnitroxides(gauss)

R	A_N	$A_{\beta\text{-H}}$	R	A_N	$A_{\beta\text{-H}}$
C_6H_5	14.2	2.2(2.1)$^{a)}$	m-$CH_3C_6H_4$	14.6	2.2
$C_6H_5CH_2$	14.3	2.4(2.4)	p-$CH_3C_6H_4$	14.1	2.1
o-$CH_3C_6H_4$	14.2	3.4			

a) Ref. 6).

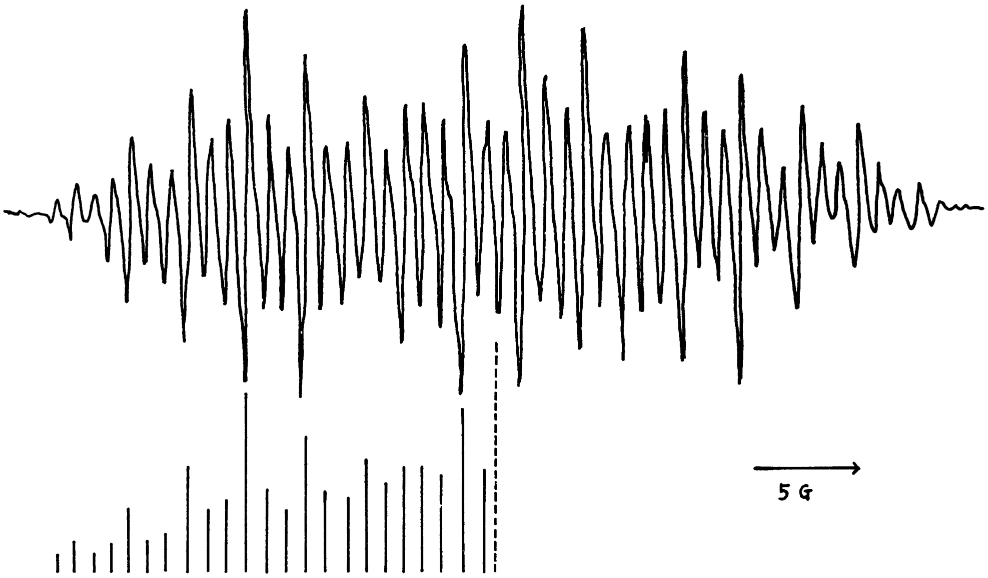

Figure 1. The esr spectrum obtained from toluene in the presence of NB.

The same trapping experiment was carried out using NB instead of PBN. This nitroxide(A_N=10.2, $A_{o,p-H}$=2.7, A_{m-H}=0.9, and $A_{\beta-H}$=6.3 G) was confirmed as benzyl spin adduct, since the pattern of the spectrum(Fig. 1) was completely the same as that (10.4, 2.8, 0.93, and 6.4 G) of the adduct reported by Ayscough et al.[8]

By the decomposition of chlorobenzene in the presence of NB in the cold trap, the formation of nitroxide spin adduct was observed by esr(Fig. 2). The comparison of this spectrum with an authentic esr spectrum showed the formation of $(C_6H_5)_2NO\cdot$, indicating the formation of phenyl radical by homolytic cleavage of the carbon-chlorine bond in chlorobenzene.

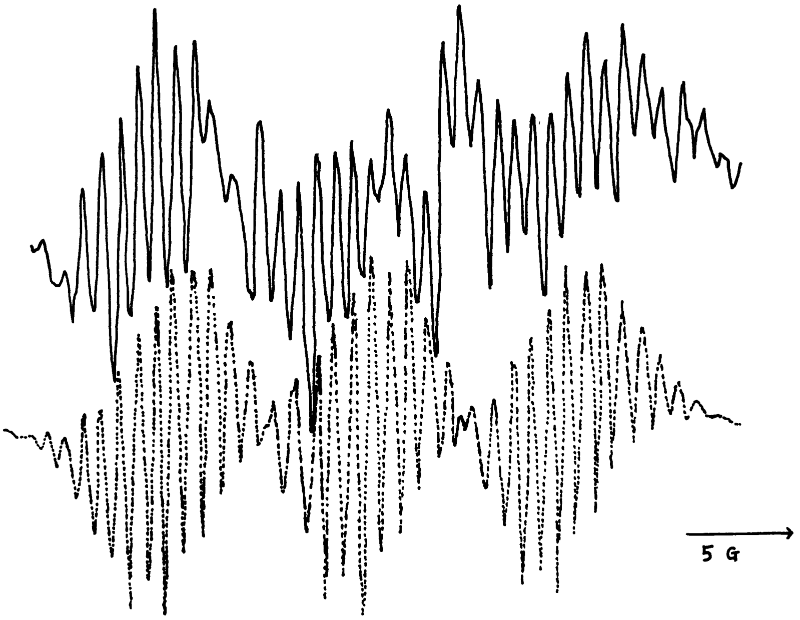

Figure 2. The esr spectrum obtained from chlorobenzene in the presence of NB (solid line). Dotted line indicates an authentic spectrum.

PBN(0.5 g) was located in a glass tube(between cold trap and discharge reactor) 5 cm from outlet of discharge reactor and the both ends of PBN were supported by glass wool. Benzene vapor, then, was introduced to the reactor under a reduced pressure and excited by r.f. glow discharge. After the passage of benzene vapor excited at 28 MHz r.f. discharge through this solid PBN, the PBN was immediately dissolved in toluene. The toluene solution indicated the spectra of nitroxides which contained two sets of three doublets, i.e., A_N=14.1, $A_{\beta-H}$=2.2 and A_N=14.4, $A_{\beta-H}$=2.4 G

Figure 3. The esr spectrum obtained from r.f. discharge reaction of benzene in the presence of PBN placed in a connecting glass tube between cold trap and discharge reactor.

(Fig. 3). These values are the same as those of spin adduct of phenyl and benzyl radicals, respectively(see Table 1). Accordingly, the former radical is considered produced in r.f. discharge reaction of benzene while the latter one may be derived from toluene which is one of primary products formed by r.f. discharge reaction3) of benzene.

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