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EVIDENCES FOR THE PHENYL-TRIPHENYLMETHYL RADICAL PAIR IN THE THERMOLYSIS OF PHENYLAZOTRIPHENYLMETHANES

Tadashi SUEHIRO, Ryuichi NAKAUSA, Seiichi MASUDA,
Michio KOBAYASHI, and Munehiro DATE*
Chemistry Department, Faculty of Sciences, Gakushuin University
Mejiro, Toshimaku, Tokyo 171
*The institute of Physical and Chemical Research, Wako, Saitama 351

Analyses of the emission signals in the CIDNP of phenylazotriphenylmethanes (PAT), of the e.s.r. spectra of phenyldiazenyl radicals, and of the calculated hfs constants of phenyl and phenyldiazenyl radicals, suppor the radical pair $\overline{\mathrm{Ph}\cdot\ \ \cdot\mathrm{CPh}_3}$ which determines the polarization of the phenyl group in the products derived from phenylazotriphenylmethanes.

Many investigations on the CIDNP phenomena of phenylazotriphenylmethanes in the thermolysis have presumed the radical pair $\overline{\mathrm{Ph{-}N{=}N}\cdot\ \ \cdot\mathrm{CPh}_3}$.[1,2] Seifert and Gerhart[2] ascribed the emission signals during the thermolysis of 3,5-dimethylphenylazotriphenylmethane in tetrachloromethane, for example, to the polarization of the 2- and 6-hydrogens in the dimethylphenyl group. This assignment does not accord with our findings obtained in the e.s.r. experiments on aryldiazenyl radicals if we assume that ^{1}H with high hfs constants gives rise to strong CIDNP: the 3,5-hydrogens of the phenyldiazenyl radicals have hfs constants of ca. 1.2 gauss, but the 2-, 4-, and 6-hydrogens do not show any measurable coupling constants.[3] To solve the problem on this matter we have conducted again the CIDNP experiments using arylazotriphenylmethanes.

The ^{1}H and ^{13}C CIDNP experiments were performed using phenylazotriphenylmethane in dimethyl sulfoxide-d_6 and tetrachloromethane, and using 3,5-dimethylphenylazotriphenylmethane in dimethyl sulfoxide-d_6. We confined us to the studies of the emission signals in order to attain to the definitive assignment of the polarized atoms of the reaction products. The enhanced absorption signals of the aromatic hydrogens were overlapped by hydrogen signals of several compounds, so that the assignment of the relevant compound was uncertain.

It was established that the emissions of aromatic hydrogens stemmed from the ortho hydrogens of arylazo group, and the emission of ^{13}C originated from the C-1, or C-3 and -5 carbons of the phenyl group. The signals due to the C-2 and -6 ,however, were not detected. Because the relaxation rates of the nuclear polarization of the C-2 and -3 of chlorobenzene do not differ so much from each other, we should be able to observe the emission signals due to the C-2 and -6, if the carbons C-2,6 had the same sign of the coupling constant as the C-3, if the C-2,6 were polarized so much as the C-3, and if the polarized radicals reacted with substrates sufficiently rapidly.

Table 1. Emission Signals of CIDNP of PATs

PAT	Solvent	Product	Atoms of Emission	Chem. Shift(TMS) found	ref.
Ph-N=N-CPh$_3$	CD$_3$SOCD$_3$	Ph-D	H-2,6	7.31	7.37
	CCl$_4$	Ph-Cl	H-2,6	7.19	7.24
			C-1	134.6	134.4
			C-3,5	129.4	129.3
		Ph-CCl$_3$	C-1	142.6	142.8
3,5-Me$_2$C$_6$H$_3$-N=N-CPh$_3$	CD$_3$SOCD$_3$	3,5-Me$_2$C$_6$H$_3$D	H-2,6	6.96	6.99

The emission signals of the ortho hydrogens of deuteriobenzenes and of chlorobenzene were not consistent with the observed hfs constants of the meta hydrogens of phenyldiazenyl radicals.$^{3)}$ The emissions of ^{1}H and ^{13}C in the thermolysis of PATs, however, are consistent with the calculated hfs constants of phenyl radicals (vide infra). Phenyl radical has the g value of 2.00234$^{4)}$ which is lower than the g value of triphenylmethyl, 2.00266. Because both the g values of phenyl and phenyldiazenyl radicals$^{3)}$ are lower than that of triphenylmethyl, the radical pair hypothesis should lead to the conclusion that the same sign of the coupling constants in phenyl and phenyldiazenyl radicals gives the same mode of nuclear polarization.

We have calculated hfs constants of ^{1}H and ^{13}C of phenyldiazenyl radicals by the use of INDO program$^{5)}$ and the results are listed in the Table 2, together with the calculated hfs constants of phenyl radical.$^{5a)}$

Based on the hfs constants of phenyl radical and on the radical pair model,$^{6)}$ $\overline{Ph\cdot \ \cdot CPh_3}$, we can expect the emissions of the 2,6-hydrogens of deuteriobenzene, and chlorobenzene, and the emissions of the C-1, C-3, and C-5 of chlorobenzene and trichloromethylbenzene. For the latter compound we assume the radical-radical combination reaction,

$$\text{Ph}^{*}\cdot \quad + \quad \cdot\text{CCl}_3 \longrightarrow \text{Ph}^{*}\text{-CCl}_3,$$

where * denotes the polarized species. The experimental results accord very well with this expectation, although the nuclear polarization in the phenyl radicals in the radical-radical combination reactions should have decreased a little.

Table 2. Hfs Constants of ^{1}H and ^{13}C of Phenyl and Phenyldiazenyl Radicals (calculated in gauss)

Radical	H-2,6	H-3,5	H-4	C-1	C-2,6	C-3,5	C-4
Phenyldiazenyl	+0.46	+0.82	-0.34	+12.1	+1.19	-0.07	+0.73
Phenyl$^{5a)}$	+18.7	+6.1	+3.9	+151.3	-4.8	+10.7	-2.6

On the contrary, the radical pair model, $\overline{\text{Ph-N=N}\cdot \ \cdot\text{CPh}_3}$, suggests the emission signals due to the 3,5-hydrogens of deuteriobenzene and chlorobenzene, and also no emission in the case of 3,5-dimethyldeuteriobenzene. This model should lead to the emission due to the C-1 and C-2,6 carbons. These suggestions were not proved by the experiments.

The radical pair, $\overline{\text{Ph-N=N}\cdot \ \cdot\text{CPh}_3}$, can not be excluded from the mechanism of the thermolysis of phenylazotriphenylmethanes, because the paired radicals recombine back to the azo compounds.$^{1)}$ But the effects of the nuclear polarization in the phenyldiazenyl radicals could not be confirmed in the escape reaction products except for the ^{15}N-polarized products.$^{7)}$ This situation can be explained partly by supposing the by far the lower degree of nuclear polarization in the 3,5-hydrogens and the C-2,6 carbons because of the low hfs constants (ca. 1 gauss) compared to that of the 2,6-hydrogens (18.7 gauss) and of the C-3,5 (10.7 gauss) in the phenyl radical, and by supposing that the intersystem crossing in the radical pair $\overline{\text{Ph-N=N}\cdot \ \cdot\text{CPh}_3}$ is controlled mainly by the Δg value (0.0020). Another factor which would effect the negative CIDNP of phenyldiazenyl radicals is their long life-time.

The rate constant of the decay of phenyldiazenyl radicals was calculated as $1.6\cdot10^{5}$ s^{-1} at 60 °C.$^{8)}$ The nuclear spin-lattice relaxation rates of the radical estimated (10^{4}-10^{5} s^{-1}), are comparable to the decay rate of the phenyldiazenyl radicals. It is therefore plausible to assume that the nuclear polarization of the phenyldiazenyl radicals escaped from the radical pair, is settled down considerably to the thermal equilibrium before they go to reactions.

The reaction processes of the thermolysis of PATs can be illustrated as shown in the Scheme.

Scheme

$$\begin{tikzcd}
\text{Ph-N=N-CPh}_3 \arrow[d, shift left, "\text{in CCl}_4"] & \\
\overline{\text{Ph-N=N}^{*}\cdot\ \cdot\text{CPh}_3^{*}} \arrow[u, shift left] \arrow[r] \arrow[d, "k_{dif}"] & \overline{\text{Ph}^{*}\cdot\ \cdot\text{CPh}_3^{*}} \arrow[dd, "\substack{k_{dif}\\ k_{react}}"] \\
\text{Ph-N=N}^{*}\cdot\ +\ \cdot\text{CPh}_3^{*} \arrow[d, "k_{relax}"] & \\
\text{Ph-N=N}\cdot\ +\ \cdot\text{CPh}_3 \arrow[d, "k_{react}"] & \text{Ph}^{*}\cdot\ +\ \text{CCl}_4 \longrightarrow \text{Ph}^{*}\text{-Cl}\ +\ \cdot\text{CCl}_3 \\
\text{Products} & \text{Ph}^{*}\cdot\ +\ \cdot\text{CCl}_3 \longrightarrow \text{Ph}^{*}\text{-CCl}_3
\end{tikzcd}$$

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