THE PHENYLDIAZENYL RADICAL: AN INTERMEDIATE DURING THE
DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE [1]
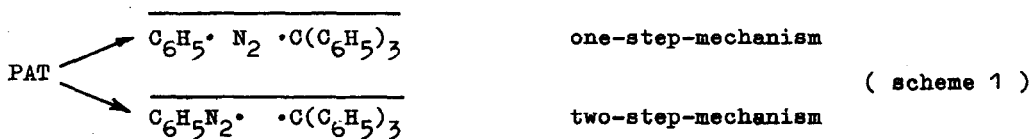
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The occurence of the phenyldiazenyl radical (I) during the decomposition of
phenylazotriphenylmethane (PAT) has been suggested by Wieland [2], but no
products derived from I could be found among the reaction products. The ESR
parameters of I are not known yet, since I seems to be too unstable to be
detectable by means of ESR [3,4]. Recently, I has been characterized by the
method of 'Chemically Induced Dynamic Nuclear Polarization' (CIDNP) [5]
during the thermolysis of phenylazo alkanes and phenyl triazenes [6]. Closs
and coworkers have estimated the g-value of I to be smaller than 2.0012 [7].

We have reinvestigated the decomposition of PAT using the CIDNP method. This
method allows to distinguish between a one-step-mechanism or a two-step-
mechanism of decomposition via the phenyldiazenyl radical (scheme 1) .

$$\text{PAT} \quad \begin{array}{l} \overline{C_6H_5 \cdot \quad N_2 \quad \cdot C(C_6H_5)_3} \\[1em] \overline{C_6H_5N_2 \cdot \quad \cdot C(C_6H_5)_3} \end{array} \qquad \begin{array}{l} \text{one-step-mechanism} \\[1em] \text{two-step-mechanism} \end{array} \qquad (\text{ scheme 1 })$$

According to the rules of CIDNP [8] the diamagnetic product derived from the
phenyl radical in a one-step mechanism should show the multiplet effect,
while the product derived from I should give rise to an energy polarization
under the condition that the difference of the g-values of the primary
radical pair is larger than 10^{-3} . Using the estimated g-value of I and the
measured g-value of the trityl radical, g = 2.00266 [9], this condition is
satisfied. Therefore, the nature of the reactive intermediate, phenyl radical
or I , can easily be deduced from the pattern of the polarization of the

corresponding reaction product.

We have thermolyzed PAT inside the preheated probe of an A 60 Varian nmr
spectrometer at 80° using carbontetrachloride or cyclohexanone as solvents.
In both cases the reaction products, chlorobenzene or benzene, respectively ,
appeared in emission and no multiplet effect was observed at this temperature.
As it is shown above, the net emission is caused by a radical pair with
different g-values and therefore, we can conclude that PAT decomposes via a
two-step-mechanism which is convincingly demonstrated by these experiments.
The sign of the polarization (emission or enhanced absorption) is the product
of four parameters: difference of the g-values of the primary radical pair,
kind of product formation, multiplicity of the precursor, and the signs of the
hyperfine coupling constants. If three of these parameters are known, the
fourth may be deduced from the sign of the observed polarization. In this
case, the g-values are measured or estimated, and if we assume decomposition
from a singlet state and product formation via a transfer step, the polari-
zation (emission) is in agreement only with positive hyperfine coupling
constants of I .

Because of the unknown ESR parameters of I, we have tried to estimate the
relative magnitude of the hyperfine coupling constants at the various
positions. For this purpose we inverstigated the decomposition of some sub-
stituted phenylazotriphenylmethanes. During thermolysis in CCl_4 , p-bromo-
phenylazotriphenylmethane yielded p-bromochlorobenzene; in this product only
the ortho protons were polarized (emission), indicating a small electron
density at the meta position of I . 3,5-dimethyl-chlorobenzene, generated
from 3,5-dimethyl-phenylazotriphenylmethane in CCl_4 , showed no polarization
of the para proton; we only observed a strong emission of the ortho protons.
From these two experiments we can derive the electron distribution in I;
apparently, the hyperfine coupling constant of the ortho position is much
larger than those of the meta and the para positions:

$$A_o \gg A_m \approx A_p$$

To check our experimental results and for completion we have performed a
SCF INDO calculation for I [10] on an IBM 360/195 computer by the unrestricted
Hartree-Fock method of Pople [11] using the program written by Dobosh [12].
The criterion for self-consistency was a variation of less than 10^{-6} a.u. in
the energy. The geometry was taken from an X-ray analysis of azobenzene [13]
using C-C bond lengths of 1.4 Å and a C-H bond length of 1.08 Å . The C-N
bond length was taken to be 1.41 Å and the bond length of the azo group was
1.23 Å . For all calculations, we held the bond lengths and angles constant
and varied only the angle between the phenyl ring and the azo group. It
turned out that the most stable conformation (E = 67.003134 a.u.) is such
that the azo group is perpendicular to the phenyl ring with a CNN bond angle
of 135° . The calculated averaged hyperfine coupling constants for the bent
orthogonal conformation are given in table 1 .

atom	N_1	N_2	C	C_o	C_m	C_p	H_o	H_m	H_p
hfs (G)	6.5	13.8	19.5	-1.8	1.3	-0.6	1.5	0.3	0.4

table 1

These calculations demonstrate that the radical center of I is not at N_1 ;
highest spin density is localized in the C-N bond. Obviously, the CIDNP
observations and the calculations are in good agreement and they confirm
that the phenyldiazenyl radical is a bent σ-radical with positive hyperfine
coupling constants which decrease in their magnitude from the ortho to the
para position.

A detailed desciption of the mechanism of the decomposition of PAT in
dependence of the temperature will be given elsewhere [14].

References

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