ON THE STABILITY AND DECOMPOSITION OF PHENYL(PHENYLAZO)METHYL HYDROPEROXIDE

Júlia Vágó* and Júlia Paál-Lukács
Central Research Institute for Chemistry of the Hungarian Academy
of Sciences, H-1025 Budapest, Pusztaszeri út 59-67, Hungary

Abstract: Protons, even in trace amounts decrease the stability of
phenyl(phenylazo)methyl hydroperoxide ($\underline{1}$). The decomposition of $\underline{1}$ is
more rapid in CCl_4 than in CH_3CN, owing to an additional reaction
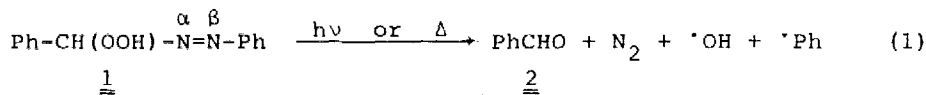route in the former solvent. A mechanistic suggestion is presented.

α-Azohydroperoxides have recently been reported as being sources
of hydroxyl radical[1,2] and oxidizing agents[3,4]. However, their
application is often limited by their poor stability, especially in
solvents like $CHCl_3$, $CDCl_3$ or CCl_4.[3,5-10] Some aromatic α-azohydro-
peroxides (among them phenyl(phenylazo)methyl hydroperoxide, $\underline{1}$) could
only be isolated in the form of a molecular complex with the solvent
(preferably in a ratio $\underline{1}$:solvent=1:5).[5,9]

Our aim is to use $\underline{1}$ as hydroxyl radical source in non-aqueous
medium which is inert toward the attack of ˙OH radicals (CH_3CN,
carbon tetrachloride).

According to our experience, after the preparation[11] of $\underline{1}$, the
evaporation of the solvent resulted in instantaneous decomposition of
$\underline{1}$, as described earlier by Tezuka and Ando.[5,9] However, when the
vessels used had been conditioned by boiling them in alkaline baths
(pH=9-10) improved stability of $\underline{1}$ has been observed. Under such
conditions $\underline{1}$ could be dried almost completely: according to NMR
measurements[12] it contained only about 3% solvent and no detectable
amounts of decomposition products were present. As a result of the
improved stability, the decomposition of $\underline{1}$ becomes reproducible and
suitable for kinetic measurements if the solvent is properly chosen
(see below). It can be concluded that even traces of protons
accelerate the decomposition rate of $\underline{1}$.[13]

Further, we found that the stability of $\underline{1}$ in solutions is affected
by its concentration: the more concentrated the solution of $\underline{1}$ the
lower its stability.

If $\underline{1}$ is intended to be used as hydroxyl radical source, the
following decomposition[1] is expected to occur:

$$\text{Ph-CH(OOH)} \overset{\alpha}{-} \overset{\beta}{\text{N=N-Ph}} \xrightarrow{\quad h\nu \quad \text{or} \quad \Delta \quad} \text{PhCHO} + \text{N}_2 + \text{'OH} + \text{'Ph} \qquad (1)$$
$$\underline{\underline{1}} \qquad\qquad\qquad\qquad\qquad \underline{\underline{2}}$$

Our results[15] obtained in acetonitrile as solvent are in good
agreement with the above mechanism: benzaldehyde[16] ($\underline{2}$) is formed
almost quantitatively, phenol[16] formation takes place (in about 15%
of $\underline{1}$ decomposed)[17] and hydroxyl radical[18] can be detected. Moreover,
at -40 °C alkoxyl radical[18] can also be trapped, indicating that the
first step of reaction (1) is the homolytic cleavage of the O-O bond
yielding Ph-CH-N=N-Ph and 'OH radicals. At room temperature this
$\quad\quad\quad\underset{\underset{\displaystyle O\cdot}{|}}{}$
step is presumably followed by the instantaneous decomposition of the
alkoxyl radical to give $\underline{2}$, N_2 and 'Ph, since at these conditions
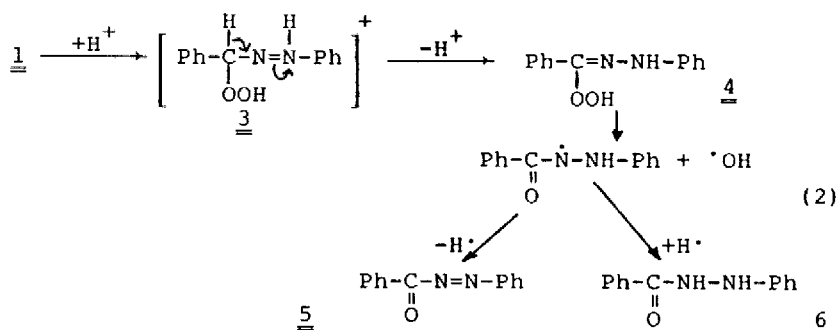alkoxyl radicals could not be detected.

In carbon tetrachloride, however, the decomposition is faster. A
new intermediate and new products are observed, namely an N-centered
radical[18], benzoylphenyldiazene[16] ($\underline{5}$) and N-benzoyl-N'-phenylhydra-
zine[16] ($\underline{6}$).

In order to explain these results it has been assumed that protons
present in the system interact with the lone pair of electrons of any
of the four heteroatoms of $\underline{1}$. However, the attack on the β-nitrogen
is most likely to result in formation of new products, as will be
discussed below. According to literature data[21], α-azohydroperoxides
exist predominantly in intramolecular hydrogen-bonded structure. In
the case of acyclic α-azohydroperoxides the evidence of the six-
membered ring was shown.[22] In such a chelate of $\underline{1}$ the β-nitrogen
contains no lone pair of electrons and hence $\underline{1}$ becomes less reactive
toward protons. Consequently, six-membered intramolecular H-bondings
are expected to stabilize the α-azohydroperoxides. The concentration
dependence of the stability of $\underline{1}$ in solution is due to the increase
in the number of the intermolecular H-bondings at the expense of
intramolecular ones. Since intermolecular H-bondings can be formed
with any of the four heteroatoms the ratio of $\underline{1}$ with lone pair of
electrons on the β-N increases, decreasing thus the stability of $\underline{1}$.

The enhanced decomposition rate and the additional products in
solvents containing Cl-atom may as well be explained by the presence

of protons. (Upon exposure to light, Cl atoms are formed and yield hydrochloric acid.[23]) Protons reacting with the β-nitrogen form intermediate 3 the aliphatic carbon atom of which may lose a proton yielding the corresponding hydrazone hydroperoxide (4). The isomerization of azocompounds (analogues to 1) to give the corresponding hydrazones (analogues to 4) in solvents containing chlorine has been described earlier.[23] However, α-azohydroperoxides containing no H atom on their aliphatic carbon atom can not undergo this type of isomerization, thus they are expected to be more stable. This may be the explanation for the experience of Baumstark and Vasquez[3,6,8] concerning the stability of different α-azohydroperoxides in $CDCl_3$.

Being rather unstable, 4 readily decomposes into a Ph-CO-Ṅ-NH-Ph radical which, in turn, produces 5 and 6 by losing or gaining one hydrogen atom, according to eq.2.

$$
1 \xrightarrow{+H^+} \left[\begin{array}{c} \overset{H}{\underset{|}{}} \overset{H}{\underset{|}{}} \\ Ph-\overset{|}{\underset{|}{C}}-N{=}N-Ph \\ OOH \end{array} \right]^+ \xrightarrow{-H^+} \begin{array}{c} Ph-C{=}N-NH-Ph \\ | \\ OOH \end{array} \quad 4
$$

$$
Ph-\overset{\cdot}{C}-\overset{\cdot}{N}-NH-Ph + \ ^{\cdot}OH
$$

$$
\overset{\|}{O} \tag{2}
$$

$$
\underset{-H\cdot}{\swarrow} \qquad \underset{+H\cdot}{\searrow}
$$

$$
\begin{array}{c} Ph-C-N{=}N-Ph \\ \| \\ O \end{array} \qquad \begin{array}{c} Ph-C-NH-NH-Ph \\ \| \\ O \end{array}
$$

5   6

The significant amount of 2 formed during the decomposition indicates that reaction (1) and (2) proceed simultaneously in carbon tetrachloride.

As a consequence, the presence of protons and the decrease in the number of the six-membered intramolecular hydrogen bondings result in an enhanced decomposition rate of α-azohydroperoxides of type 1. Therefore, the authors suggest to apply solvents containing no chlorine atom and to avoid high concentrations when these α-azohydroperoxides are used.

References_and_notes

1. T. Tezuka, and N. Narita, J.Am.Chem.Soc., 101 (1979) 7413.
2. T. Tezuka, N. Narita, W. Ando, and Sh. Oae, J.Am.Chem.Soc., 103 (1981) 3045.
3. A.L. Baumstark, and P.C. Vasquez, Tetrahedron Lett., 24, (1983) 123.
4. E.Y. Osei-Twum, D. McCallion, A.S. Nazran, R. Panicucci, P.A. Pisbood, and J. Warkentin, J.Org.Chem., 49, (1984) 336.
5. T. Tezuka, and S. Ando, Chem.Lett., 1985, 1621.
6. A.L. Baumstark, Bioorganic Chemistry, 14, (1986) 326.
7. H.C. Yao, and P. Resnick, J.Org.Chem., 30, (1965) 2832.
8. A.L. Baumstark, and P.C. Vasquez, J.Org.Chem., 48, (1983) 65.
9. T. Tezuka, and S. Ando, Chem.Lett., 1986, 1671.
10. K.H. Pausacker, J.Chem.Soc., 1950, 3478.
11. 1 was prepared by autoxidation of benzaldehyde phenylhydrazone in benzene at 30 °C and 10^6 Pa, according to Pausacker.[10]
12. ^1H NMR spectrum of 1 was recorded in $CDCl_3$ solution on a Varian XL-400 instrument. ^1H NMR $(CDCl_3)$:δ=6.37(s, 1H,CH-O), 7.41-7.82(m,10H,aromatic H), 9.43(s,1H,OOH).
13. The decomposition of 1-phenylazo-1-hydroperoxycyclohexane under mildly acidic conditions was described by Utaka et al.[14] However, that mechanism can be excluded in the case of aromatic hydroperoxides.
14. M. Utaka, Y. Fujita, and A. Takeda, Chem.Lett., 1982, 1607.
15. 1 was decomposed by photoirradiation with a 250 W medium pressure mercury arc lamp. Two filters were applied: an UG 1/3.5g glass filter of 3 mm thickness and a 2 M KNO_3/water filter of 2 cm thickness to isolate the 366 nm band.
16. Stable products were analyzed by HPLC: column RP-18, eluent 50% methanol – 50% water, UV detection at 224 nm. The retention times increased in order: phenol, 2, 6, 5, 1.
17. Presumably, phenol is formed from Ph· and ·OH in the cage when 1 decomposes, in accordance with the experience of Tezuka and Narita who found that a considerable amount of p-Br-phenol was formed when Ph-CH(OOH)-N=N-Ph-Br is decomposed in benzene.[1]
18. The identification of the radicals was carried out by a JEOL JES-FE3X ESR spectrometer. Hydroxyl radicals were trapped with dimethyl pyrrolidonoxide[19], alkoxyl radicals with 2,6-dichloro-nitrosobenzene[20]. The N-centered radicals could be detected without trap.
19. G.M. Rosen, and E.J. Rauckman, Proc.Natl.Acad.Sci.USA, 78 (1981) 7346.
20. F.P. Sargent, and E.M. Gardy, Canad.J.Chem., 52 (1974) 3645.
21. W.H. Richardson in "The chemistry of functional groups", Peroxides, Ed.:S. Patai, Wiley, New York, 1983, Chapter 5.
22. S. Bozzini, S. Grattan, A. Risalti, A. Stener, M. Calligaris, and G. Nadin, J.Chem.Soc.,Perkin.Trans.1, 1977, 1377.
23. R.C. Corley, and M.J. Gibian, J.Org.Chem., 37, (1972) 2910.