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RESONANCE PARTICIPATION OF SULFUR AND OXYGEN IN RADICALS
DECOMPOSITION OF AZOBIS(2-PROPANE) DERIVATIVES.

A. Ohno and Y. Ohnishi
Sagami Chemical Research Center
3100 Onuma, Sagamihara-shi, Kanagawa, 229, Japan

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Qualitatively, it is known that hetero atoms such as oxygen and sulfur can stabilize a radical center by resonance. The ease of abstracting an α-hydrogen in ethers has been interpreted in terms of the stability of the resulting radical by an electron transfer from the oxygen to the carbon(1). Although this effect

is smaller for sulfides than for their oxygen analogs, the electron-sharing conjugation of a sulfur has been proposed to explain larger Q-values for vinyl sulfides than for their corresponding oxygen analogs(2). Recent studies also

support this idea(3 - 5). However, it is still ambiguous whether these results reflect truely the stabilities of radicals produced, because the processes of polymerization, decomposition of peroxides, or abstraction of hydrogens include fairly complex phenomena.

Meanwhile, it is well established that the rate of unimolecular decomposition of a symmetric azo compound dramatically exemplifies the stability of the forming radical(6). Furthermore, the reaction has an advantage over others in being able to give both enthalpy and entropy of activation, from which one can obtain useful information.

In this communication, we wish to report the activation parameters for decompositions of azobis(2-propane)s substituted by hetero atoms at the 2-position and to discuss the ability of α-hetero atoms to stabilize a radical center

Table I

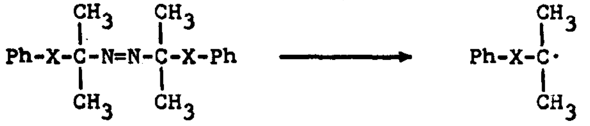
Compd.	Condition	Yield,%[a]			
		Dimer	$PhXCHMe_2$	$PhXCMe{=}CH_2$	Others
Ia	120° in PhOPh	15	37	10	PhSSPh (8)
Ib	160° in PhOPh	4	16	4	PhCOMe (52), CH_4
Ic	160° in PhOPh	-[b]	43	4	$PhCH{=}CMe_2$ (2)

a. Yields were determined by vpc except for dimers, for which nmr was employed. Similar results were obtained in tetralin as solvent.

b. Very small amount.

on a carbon atom.

Azobis(2-phenylthio-2-propane), Ia(mp 86.5 - 87°, λ_{max} = 371 mμ in CCl_4), and its oxygen analog, Ib(mp 90 - 91°, λ_{max} = 385 mμ in CCl_4), were prepared by the reaction of azobis(2-chloro-2-propane) with thiophenol and phenol, respectively(7). As a reference material, azobis(2-benzyl-2-propane), Ic(mp 68 - 70°, λ_{max} = 374 mμ in CCl_4), was synthesized from the corresponding amine according to Stevens(8).



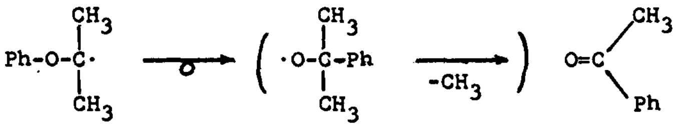
$$\mathrm{Ph{-}X{-}\underset{CH_3}{\overset{CH_3}{C}}{-}N{=}N{-}\underset{CH_3}{\overset{CH_3}{C}}{-}X{-}Ph} \longrightarrow \mathrm{Ph{-}X{-}\underset{CH_3}{\overset{CH_3}{C}}\cdot}$$

Ia, X = S   IIa, X = S

Ib, X = O   IIb, X = O

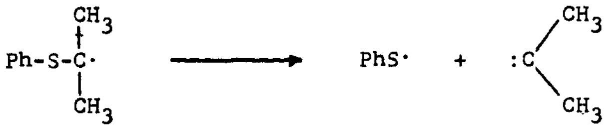
Ic, X = CH_2 IIc, X = CH_2

The preliminary results on the analyses of the reaction products are listed in Table I. It is interesting to note that the formation of methane and acetophenone was resulted from the reaction of Ib together with the migration of a phenyl group in IIb(9), while the formation of diphenyldisulfide from Ia was



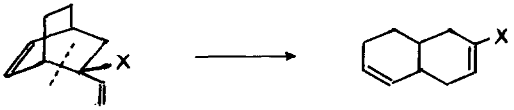
$$\mathrm{Ph{-}O{-}\underset{CH_3}{\overset{CH_3}{C}}\cdot} \longrightarrow \left(\mathrm{\cdot O{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Ph} \xrightarrow[-CH_3]{}\right) \mathrm{O{=}C(CH_3)(Ph)}$$

observed suggesting the formation of a dimethylcarbene(10).



$$\text{Ph-S-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\cdot \longrightarrow \text{PhS}\cdot + :C(CH_3)_2$$

Kinetics of decompositions in tetralin were followed by observing the volume of nitrogen evolved. The reactions were first-order for all runs. The activation parameters calculated (at 150°), by least-squares method, from at least seven kinetic points are listed in Table II, where the results with azobisisobutyronitrile(AIBN) are also listed for comparison. The difference in enthalpies of activation between Ib and Ic ($\delta \Delta H^{\ddagger}_{bc}$) is 3.3 kcal/mole which could be compared to the difference in energies of activation between IIIa and IIIb ($\delta E_a^{H,OH} = 2.4$ kcal/mole)(11) and could be attributed to the stabilizing effect of the oxygen as claimed by Berson and Walsh. However, we believe that such a small difference cannot imply the resonance participation from the oxygen to the radical center. Severn and Kosower have proposed that the difference in λ_{max} of $n \rightarrow \pi^*$ transition in azo compounds is due to the difference in the steric hindrance in their ground states(12). According to them, $\delta\lambda_{max}$ between Ib and Ic (11 mμ) predicts 2.2 kcal/mole higher energy for Ib than for Ic and this value, therefore, when combined with the inductive effect,



IIIa, X = H

IIIb, X = OH

Table II

Compd.	E_a, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Ia	25.7 ± 0.5	24.9 ± 0.5	-12.6 ± 2
Ib	33.2 ± 0.5	32.3 ± 0.5	- 2.5 ± 2
Ic	36.4 ± 0.5	35.6 ± 0.5	+ 4.1 ± 2
AIBN	28.4 ± 0.5	27.5 ± 0.5	+ 1.9 ± 2
AIBN(13)	31.3	—	—

these entire energy difference can explain nearly whole the value of $\delta\Delta H^{\ddagger}_{bc}$ observed. Thus, we might conclude that the contribution, if any, of an oxygen to stabilization of a neutral radical is negligibly small. The entropies of activation of these compounds also support the conclusion.

On the other hand, Ia has a very small enthalpy of activation ($\delta\Delta H^{\ddagger}_{ac}$ = 10.7 kcal/mole), apparently indicating participation by the sulfur. The entropy of activation for this compound is also small in comparison to those for Ib and Ic. Thus, there remains no doubt that a sulfur atom, in contrast to an oxygen atom, stabilizes a radical center at the α-position by electron-sharing conjugation, which is as effective as the stabilization by a cyano group (cf. $\Delta H^{\ddagger}$ for AIBN).

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