AZO COMPOUNDS AS SPIN TRAPS IN THEIR PHOTOCHEMICAL DECOMPOSITION

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Summary: In their photochemical decomposition, azo compounds of the type PhN=NSO₃Na trap radicals R'and form RPhN-NSO₃Na, where R' is NaSO₃' in water at 275 K and ^{*}H' in C₂H₈O^{*}H at 320 K. The ESR parameters of the radicals observed are reported and the mechanism of their formation is discussed.

Previously we described the photochemical decomposition¹ of azosulfonates of structures I and their application in polymer chemistry to synthesize water-soluble photo resins². Now additionally the photochemical behaviour of the following compounds is investigated by ESR spectroscopy.

Compounds I were prepared according to the literature¹. Saturated solutions of I in polar solvents like H_2O , CH_3OH or C_2H_5OH were irradiated with a high pressure mercury lamp directly in the spectrometer cavity at various temperatures. ESR spectra were recorded and simulated on a Bruker SRC 200D spectrometer equipped with an Aspect 2000 computer.

In polar solvents at low temperature (water, 275 K) radicals II and in the less polar solvents at higher temperature (C_2H_5OH , 320 K) radicals III were observed (see Table 1). The radicals were unstable and vanished after the irradiation was stopped with half-life time between 0.1-2 sec. Fig.1 and Fig.2 show the basic ESR spectra of II and III. Their splitting constants obtained by simulation are summarized in Table 1. The subnumbering of II and III corresponds to I. Both types of radicals (II, III) possess two nitrogen nuclei with a relatively high spin density ($a_n \approx 1$ mT). This is compatible with hydrazyl radicals³. Their formation in the system investigated here can be well understood assuming that the azo compounds trap free radicals R according to the Scheme 1.



Scheme 1



Fig.1: The low field half of the ESR spectra observed at 275 K in the photochemical decomposition of IIa and IIa-¹⁶N in water (identical spectra were found in D₂O and in H₂O) (ΔB: peak-to-peak width; Y_m: maximal difference between line amplitudes)



Fig.2: ESR spectra obtained at 320 K in the photochemical decomposition of Ia in C2H5OH (IIIa) and in C2H5OD (IIIa-D)

Table 1: Splitting constants and their assignment to radicals II and III

	1	NaO32				*	,y`X		
	II	2'N1-	- N ²	1	1	ш 5' (С	∑ ^{2'} .		
		3' 🖉 🤞	SU31	NG		6' F	<u> </u> -'N	2 SO3Na	
Structure >					Splitting con	nstants (in mT)			g-Values
			a _n (1)	a _№ (2)	а _н (2´, 6´)	a _H (3´,5´)	а _н (4 ^)	a _{rr} (1)	
IIa	X =	н	1.024	1.125	0.063 0.063	0.061 0.061	0.032	-	2.0037
IIa- ¹⁶ N	X = N(1) =	H ¹⁵ N	1.44	1.125	0.063 0.063	0.061 0.061	0.032	-	2.0037
ΙΙЬ	X(2´) =	осн3	1.05	1.125	0.064	0.064 < 0.064	0.02	-	2.0037
IIc	X(3 [^]) =	OCH3	1.028	1.115	0.064 0.064	0.064	0.02 9	-	2.0038
IId	X(4') =	OCH3	1.028	1.12 k	ow radical co	ncentration -	pure res	olution of	the spectra
IIIa	X =	н	0.738	0.976	0.23 0.24	0.077 0.077	0.25	0.805	2.0037
IIIa– ¹⁶ N	X = N(1) =	H ¹⁵ N	1.032	0.976	0.23 0.24	0.077 0.077	0.25	0.805	2.0037
III a-D	X = H(1) =	H D	0.738	0.976	0.23 0.24	0.077 0.077	0.25	0.123	2.0037
IIIb	X(2') =	OCH₃	0.715	0.965	0.264	0.073 0.073	0.274	0.80	2.0038
IIIc	X(3´) =	OCH3	0.731	0.965	0.228 0.238	0.078	0.247	0.797	2.0036

Two questions are to be considered: What is R' and which nitrogen of the azo compound $(N^1 \text{ or } N^2)$ traps the radical R'(Scheme 1, structure A or B)?

By the photolysis of I in water the following radicals are expected: mainly X-Ph^{*}, NaSO₃^{*} and less likely H^{*}, OH^{*}. We confirmed this in spin trap experiments⁴. X-Ph^{*}, H^{*} and OH^{*} should contribute to the hyperfine structure of the ESR spectra of II. No contribution is expected from NaSO₃^{*}. Structures II in Table 1 show only interactions resulting from the nuclei of azo compound I, i.e. $a_n(1,2)$ and $a_n(2^*,3^*,4^*,5^*,6^*)$. Consequently, the trapped radical R^{*} had to be NaSO₃^{*}. In ethanol solution structure III is found probably formed by H-abstraction from the solvent which may proceed via a photochemically activated complex of I with ethanol. In the ESR spectra of III (Table 1) an additional splitting constant $\overline{a}_n(1)\approx 0.8$ mT is found. Experiments in C₂H₅OD, C₂D₅OD, and C₂D₅OH indicate that the proton added to ¹N originates from the hydroxylgroup of the solvent. Only in the case of the deuterated hydroxylgroups (C₂D₅OD and C₂H₅OD) the splitting constant $a_n(1)$ changes from 0.805 mT in IIIa to 0.123 mT in IIIa-D (Table 1, Fig.2, IIIa and IIIa-D).

To get information about the position of the trapped radical R¹, in addition to Ia, we also prepared compound Ia-¹⁵N from ¹⁵N-aniline. Upon irradiating Ia and Ia-¹⁵N, spectra IIa and IIa-¹⁵N in Fig.1 were observed. From their simulation (Table 1) it is obvious that the splitting constant a_n (1)=1.024 mT in IIa changes to 1.44 mT in IIa-¹⁵N. Consequently, the lower values \overline{a}_n (1)≈1.03 mT were assigned to N¹. An analogous result was found

for III. Employing ¹N with ¹⁵N marked nitrogen the splitting constant a_N (1)=0.738 mT in IIIa changes to 1.032 mT in IIIa-¹⁵N (Table 1).



Fig.3: ESR spectra observed in the photochemical decomposition of Ia in MeOH at various temperatures

Therefore, the lower values with $\overline{a}_{N}(1)\approx 0.73$ mT have to be assigned to N¹. This is evidence in favour of structure type **A** in Scheme 1, since, according to the literature³, the higher splitting constant a_{N} in hydrazyl radicals is attributed to the nitrogen with free valence.

The most suitable conditions for generating type-II radicals were low temperature and high solvent polarity (275 K, H_2O), and for type – III radicals, high temperature and lower solvent polarity (320 K, C_2H_5OH) were favourable. In CH_3OH both products were obtained as shown in Fig.3. At 200 K only II was found; at 225 K and 250 K, II and III; and at 300 K only III was observed.

Further results worth mentioning are: IIc and IIe give identical ESR spectra. The concentration of II and III decreases for $X = OCH_3$ going from the ortho via the meta towards the para position. This is possibly due to the increasing ionic pathway of azo decomposition¹. Radicals II show a non-homogeneous line broadening towards the outer lines of the spec-

trum in the high and low ranges of the field (Fig.1) indicating the hindered rotation around the ${}^{1}N - {}^{2}N$ axis. The spectrum of IIIa was approximately simulated with homogeneous $\Delta B_{pp} = 0.022$ mT. The spectrum of IIa- ${}^{16}N$ was already simulated with inhomogeneous ΔB_{pp} as given in Fig.1.

Our investigations showed that the azosulfonates function in their photochemical decomposition as spin traps under the formation of hydrazyl radicals as reactive intermediates. This brings new aspects for understanding and interpreting of the mechanism and the radical products formed in those systems, especially in their applications e.g. in polymerisation reactions and photo resin processes.

Literature

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