Reference Data

ESR Parameters of 5,5-Dimethylpyrrolidine 1-oxide (DMPO) Spin Adducts in the Photochemical Decomposition of Azo Compounds

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Splitting constants and g values are reported for 5,5-dimethylpyrrolidine 1-oxide spin adducts with radicals such as substituted-Ph', NaSO₃', PhSO₂' and others observed in the photochemical decomposition of azo compounds in various solvents.

KEY WORDS Photochemical decomposition Azo compounds ESR 5,5-Dimethylpyrrolidine 1-oxide Spin adducts Solvents

INTRODUCTION

Two routes are generally considered in the decomposition of azo compounds,¹ as shown in Scheme 1

 $R_1 N = N R_2$ $R_1 + N_2 + R_2$ (synchron) $R_1 N = N R_2$ $[R_1 N = N R_2$ $R_1 + N_2 + R_2$ (asynchron)Scheme 1

Generally, the formation of R_1^{*} and R_2^{*} is well established, but a direct verification of the presence of $R_1 N_2^{*}$ is so far questionable.² Because of the limited stability of R_1^{*} and R_2^{*} , and presumably also of $R_1 N_2^{*}$, we have investigated the photochemical decomposition of azo compounds in various solvents in the presence of 5,5-dimethylpyrrolidine 1-oxide (DMPO); these compounds are listed in Table 1.

EXPERIMENTAL

Compounds 1-3 were prepared as described previously.³ The ESR spectra were recorded

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Fable	1. Structures of $R_1 N = NR_2$	f compounds
Compound	R,	R ₂
1a	C ₆ H ₅	$SO_{3}Na$
1b	2-CH ₃ OC ₆ H ₄	$SO_{3}Na$
1c	3-CH ₃ OC ₆ H ₄	$SO_{3}Na$
1d	4-CH ₃ OC ₆ H ₄	$C(CH_{3})_{2}CN$
2a	2,6-Cl ₂ C ₆ H ₃	$C(CH_{3})_{2}CN$
2b	4-BrC ₆ H ₄	$C(CH_{3})_{2}CN$
2c	4-NO ₂ C ₆ H ₄	$C(CH_{3})_{2}CN$
3a	C ₆ H ₅	$C_{6}H_{5}SO_{2}$
3b	3-CH ₃ C ₆ H ₄	C ₆ H ₅ SO ₂
3c	4-CH ₃ C ₆ H ₄	C ₆ H ₅ SO ₂
3d	4-CIC ₆ H ₄	C ₆ H ₅ SO ₂
3e	4-NO ₂ C ₆ H ₄	C ₆ H ₅ SO ₂

using a Bruker 200D SRC spectrometer operating in the X-band region, equipped with an Aspect 2000 computer. The sample tube of 0.8 mm diameter was filled with 0.05 M azo compound and 0.1 M DMPO solution and irradiated for 1–20 min at 295 K until the best resolved spectra were found. The irradiation source was a xenon lamp, selecting the 200–400 nm region. A typical spectrum is shown in Fig. 1. Splitting constants were evaluated by computer simulation.

RESULTS AND DISCUSSSION

The ESR parameters obtained are summarized in Table 2. In the main, two types of





Figure 1. Typical ESR spectra observed in the photochemical decomposition of azo compounds in the presence of DMPO. Their simulation parameters $(A_N, A_H \text{ in mT})$ are as follows: $(A_N, A_N = 1.592; A_H = 2.466; g = 2.0061, *, A_N = 1.445, A_H = 1.602; g = 2.0053 \text{ and} +, A_N = 1.44; g = 2.0064.$

experiment

Reference Data

			R			
∕ N∕ H						
Trapped					Generated	
radical	Solvent	A _N (mT)	А _н (mT)	g value	from	
C ₆ H ₅	H ₂ O	1.54	2.46	2.0062	1a	
C ₆ H ₅	СН₃ОН	1.50	2.22	2.0062	1a, 3a	
C ₆ H ₅	C₂H₅OH	1.49	2.16	2.0062	1a, 3a	
C ₆ H ₅	C _e H _e	1.395	1.985	2.0062	3a	
C ₆ H₅	С₃Н₂ОН	1.509	2.14	2.0061	1b	
2-CH₃OC₅H₄	H₂O	1.59	2.407	2.0060	1b	
2-CH₃OC₅H₄	СН₃ОН	1.50	2.14	2.0062	1b	
2-CH₃OC₅H₄	C₂H₅OH	1.509	2.14	2.0061	1b	
3-CH₃OC ₆ H₄	H₂O	1.587	2.43	2.0056	1c	
3-CH ₃ OC ₆ H ₅	СН₃ОН	1.494	2.17	2.0061	1c	
3-CH ₃ OC ₆ H ₅	C₂H₅OH	1.484	2.124	2.0057	10	
4-CH ₃ OC ₆ H ₅	H₂O	1.592	2.495	2.0058	1d	
$4-CH_3OC_6H_5$	CH ₃ OH	1.514	2.246	2.0058	10	
$4 - CH_3 OC_6 H_5$	C₂H₅OH	1.50	2.20	2.0058	10	
2,6-Cl ₂ C ₆ H ₄		1.504	2.124	2.0061	28	
		1.501	2.22	2.0061	2a 2a	
		1.30	2.93	2.0001	20	
		1.30	1.90	2.0002	20	
2,0-Cl ₂ C ₆ Π ₄		1.350	1.903	2.0003	2a 2a	
2,0-01206114 3,0H C H		1.507	2.22	2.0001	20 3h	
3-CH C H		1 48	2.16	2.0061	3b	
3-CH C H	C H	1 395	1 975	2 0062	3b	
3-CH_C_H_	C.H.CH.	1.392	1.955	2.0061	3b	
4-CH_C_H_	CH_OH	1.50	2.22	2.0060	3c	
4-CH_C_H_	C.H.OH	1.49	2.18	2.0061	3c	
4-CH ₃ C _e H _e	C _e H _e	1.40	1.99	2.0061	3c	
4-CH ₃ C ₆ H ₅	Ҁҝ҄Ӊҝ҇ҀӉҙ	1.392	1.9 95	2.0061	3c	
4-CIC ₆ H ₅	СН _а ОН	1.49	2.19	2.0060	3d	
4-CIC ₆ H ₅	С₂н₅он	1.49	2.195	2.0060	3d	
4-CIC ₆ H ₅	C ₆ H ₆	1.387	2.026	2.0062	3d	
4-CIC ₆ H ₅	C ₆ H ₅ CH ₃	1.375	1.965	2.0062	3d	
4-BrC ₆ H ₅	СН₃ОН	1.50	2.19	2.0061	2b	
4-BrC ₆ H ₅	C₂H₅OH	1.504	2.205	2.0061	2b	
4-BrC ₆ H ₅	CHCl ₃	1.45	2.06	2.0061	2b	
4-BrC ₆ H₅	CCI4	1.392	1.95	2.0063	2b	
4-BrC ₆ H₅	C ₆ H ₆	1.39	1.95	2.0062	2b	
4-BrC ₆ H ₅	$C_6H_5CH_3$	1.39	1.96	2.0062	2b	
$4-NO_2C_6H_5$	CH₃OH	1.485	2.16	2.0059	2c, 3e	
$4 - NO_2C_6H_5$	C₂H₅OH	1.48	2.115	2.0062	2C, 3e	
4-NO ₂ C ₆ H ₅	CHCI ₃	1.43	2.03	2.0061	20	
$4 - NO_2C_6H_5$		1.38	1.95	2.0063	2C 2a	
$4 - NO_2 C_6 H_5$		1.37	1.90	2.0062	20	
$4 - 100_2 U_6 \Pi_5$		1.37	1.900	2.0002	120 12 h c d	
		1.40	1.0	2.0058	1a, b, c, u 1a b c d	
NaSO.=	C.H OH	1 41	1.51	2 0058	1a, b, c, d	
4-SO_C_H_	CHCL	1.37	1.60	2.0065	3a, b, c, d	
4-SO_C_H_	C.H.	1.26	1.31	2.0064	3a, b. c. d	
4-SO_C_H_	C H-CH-	1.255	1.31	2.0063	3a, b, c, d	
X-1	H ₂ O	1.44		2.0055	1a	
X-1	сн_он	1.44		2.0055	1a, 1c	
X-1	С₂нँ₅он	1.42		2.0058	1c	
X-2	H₂O	1.665	2.84	2.0056	1b	

Table 2. DMPO spin adduct parameters obtained in the photochemical decomposition of azo compounds in various solvents

Reference Data

DMPO adducts with R_1 and R_2 were found, in accord with a synchronous decomposition (Scheme 1). The first adduct has $A_{\rm N} = 1.4-1.6$ mT and $A_{\rm H} = 2.0-2.5$ mT. Based on the data in the literature on similar structures,4 radical R is evidently a carboncentred radical and we assigned it to the phenyl group (R₁) of azo compounds 1-3. The second adduct with $A_N = 1.2-1.5$ mT and $A_{\rm H} = 1.4-1.6$ mT was assigned to the DMPO adducts with NaSO₃ and C₆H₅SO₂ radicals. The dependence of A_N and of A_H on the solvent polarity, e.g. on the molar ratio of water in ethanol, $\gamma(H_2O)$, by compound 1a, is described by the relationships $A_{\rm H} = 21.31$ + 3.35 γ (H₂O) and $A_{N} = 14.85 + 1.11\gamma$ (H₂O) with correlation coefficients $r_{\rm H} = 0.989$ and $r_{\rm N} = 0.982.$

A third type of radical (X-1, Table 2) with $A_{\rm N} = 1.4$ mT was observed in a few cases. This may be a secondary adduct which is formed after free radicals abstract hydrogen from the primary adduct with the formation of the corresponding nitron. This nitron then traps free radicals and forms secondary adducts. Additionally, in the case of substrate 1b in water, a further adduct is found with an unusually high $A_{\rm H}$ value of 2.84 mT (X-2, Table 2); this has so far not been assigned. The expected formation of R₁N₂-DMPO adducts was not observed. Numerous spin adducts were detected, and their data are summarized. The ability of azo compounds **1a-d** to trap R_2 or H and to form $R_1R_2N - NR_2$ or $R_1HN - NR_2$, as described in Ref. 5, is noteworthy.

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