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RADICAL MECHANISM IN THE PHOTOREACTION OF ORGANIC N-OXIDES: SOME PARADIAZINE N,N-DIOXIDES

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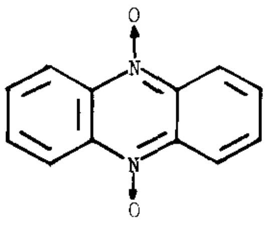
Abstract - Based on the e.s.r. identified nitroxyl radicals 4, 5, and 6 produced in organic solvent, a radical mechanism in the photoreaction of some paradiazine N,N-dioxides was suggested. The intermediate radicals 8 were produced , in the photoreduction process such as deoxygenation and hydrogen abstraction, from either triplet excited state or from diradicals 7.

The photochemical properties of heteroaromatic compound containing N-oxide functions have been studied extensively[1]. Among the intermediates suggested to explain the photochemical processes of these compounds, the three-membered ring oxaziridine is well-known for photorearrangement that started from excited singlet state, while the excited triplet species is responsible for deoxygenation[1,2,3]. Only a few reported cases involve radicals, usually radical ions[4]. It is strange that no valid experimental evidence, such as that from e.s.r. studies, for the radical mechanisms has been ever reported.

The detection of intermediate radicals is important in the deduction of a radical mechanism of a chemical process. In our electron spin resonance studies at room temperature on the in situ photolyzed solution of phenazine N,N-dioxide 1[5], quinoxaline N,N-dioxides 2[5,6], and pyrazine N,N-dioxide 3[5], we identified three novel nitroxyl radicals 4, 5, and 6 respectivelly which gave well-resolved e.s.r. spectra. Based on these results of e.s.r. studies shown in Table 1, we rationalize a radical mechanism for the photoreaction of the benzo- or dibenzoparadiazine N,N-dioxides as shown in Scheme 1. Monoradical 8, which is rather stable in the liquid phase, is formed through hydrogen abstraction from the solvent molecule HR from either triplet state of the parent compound or diradical 7. The latter two species cannot be observed



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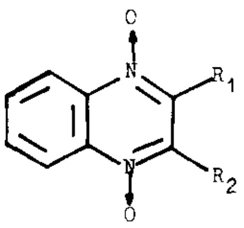

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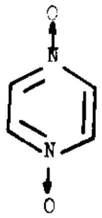

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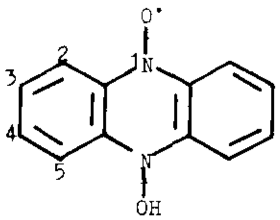

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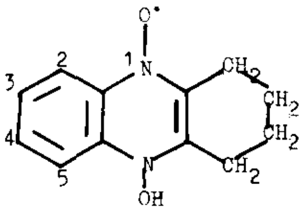

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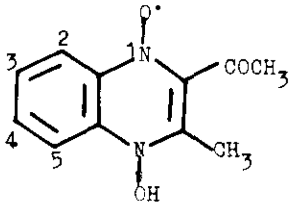

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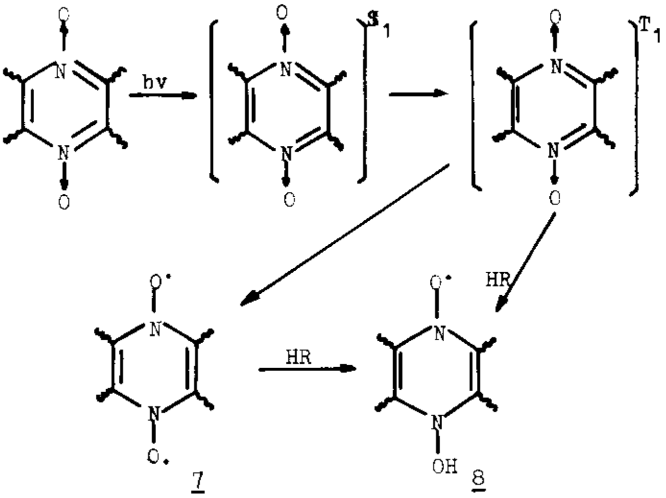
Table 1. E.s.r. spectral data for 4, 5, and 6[a]

Radical	g value	a_1^N	$a_{2,4}^H$	$a_{3,5}^H$	Ref.
4	2.0048	9.39	2.43	0.52	5
5	2.0035	9.69	3.56	1.01	5
6	2.0053	9.20	3.40	1.00	6

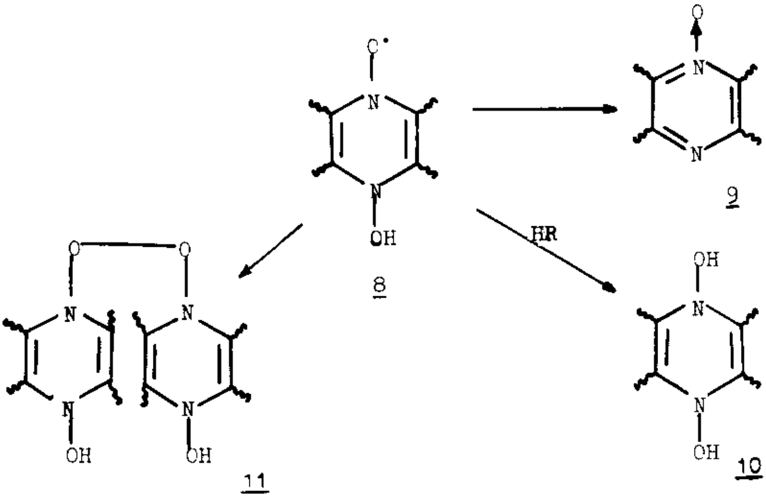
a Coupling constants are given in gauss, the solvent is deaerated chloroform.

by e.s.r. method, for they are usually relatively short-lived[7]. A major kind of photoreaction of these N-oxides is deoxygenation[1]. The possible deoxygenation process can occur from the intermediate radical 8 by removal of a hydroxyl group, with the homolysis of N-OH bond in 8, leading to the formation of the deoxygenation product 9 (see Scheme 2). We suppose that further deoxygenation[8] takes place only in the subsequent photoreaction with 9 as starting compounds. The decay of 8 can also be achieved by further hydrogen abstraction[7] and consequently N,N-dihydroxyl compounds 10 is formed. The dimerization can be resulted in the decaying process, giving the dimerized compounds 11.

Scheme 1



Scheme 2



In the experiment, a purified substrate N,N-dioxide compound was dissolved in solvent with concentration of about 10^{-3}M. Solution was introduced into a 4mm O.D. quartz tube, which was degassed and sealed under argon atmosphere. E.s.r. spectra were recorded at room temperature on a Varian E-115 X band spectrometer. Irradiation of samples was achieved with a Varian 150W xenon lamp.

It is necessary that the solution be deaerated before the photolysis and the e.s.r. measurement, in order to record e.s.r. signals. This shows that the dissolved oxygen will quench the excited triplet state, i.e., the precursor of nitroxyl radical.

As an example, the e.s.r. spectrum of 5-hydroxylphenazine-10-nitroxyl radical (4) is shown in Fig. 1. It is interesting that the same pattern of e.s.r.

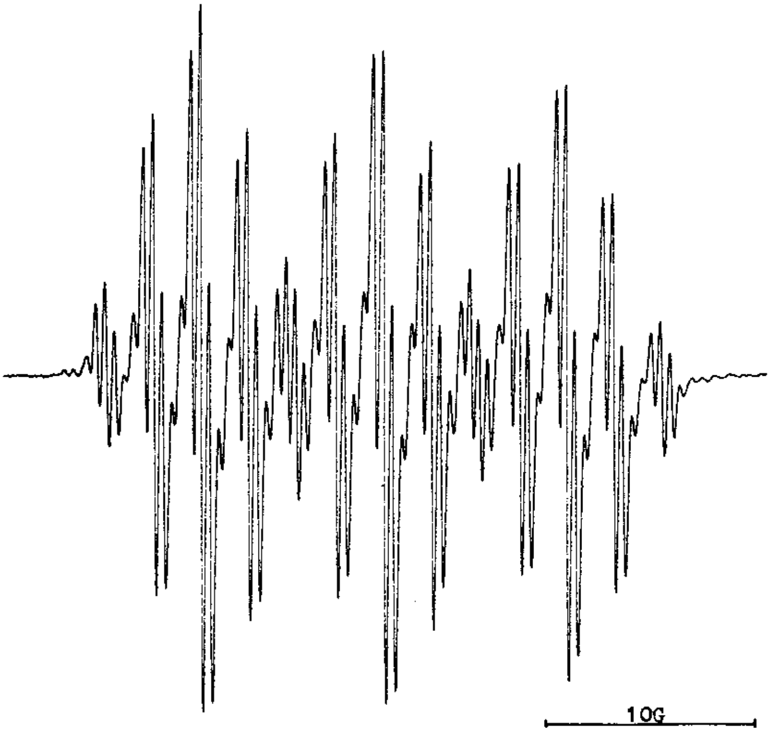


Fig. 1 E.s.r. spectrum of 5-hydroxylphenazine-10-nitroxyl radical (4) recorded at room temperature, with chloroform as solvent. The data were shown in Table 1.

spectra of 4 also can be easily recorded with various solvents such as dichloromethane, benzene, toluene and cyclohexane. The INDO MO calculation and the comparison of the e.s.r. parameters of these radical with those of structurally similar nitroxyl radicals support the assignment of hyperfine coupling constants shown in Table 1[5].

No e.s.r. signals were recorded for cpd. 3 in various solvents at room temperature. We believe, from the experiment, that quinoxaline N,N-dioxide (2, $R_1=R_2=H$), and all the 2,3-disubstituted quinoxaline N,N-dioxides(2, $R_1=H$, $R_2=CH_3$; $R_1=R_2=CH_3$; $R_1=H$, $R_2=C_6H_5$; $R_1=C_6H_5$, $R_2=COC_6H_5$; $R_1=CH_3$, $R_2=COOC_2H_5$) which produce poorly-resolved e.s.r. spectra, upon photolysis in suitable solvents, also produce nitroxyl radicals and take the same mechanism shown in Schemes 1 and 2. Fig. 2 shows spectra of the nitroxyl radicals produced from quinoxaline N,N-

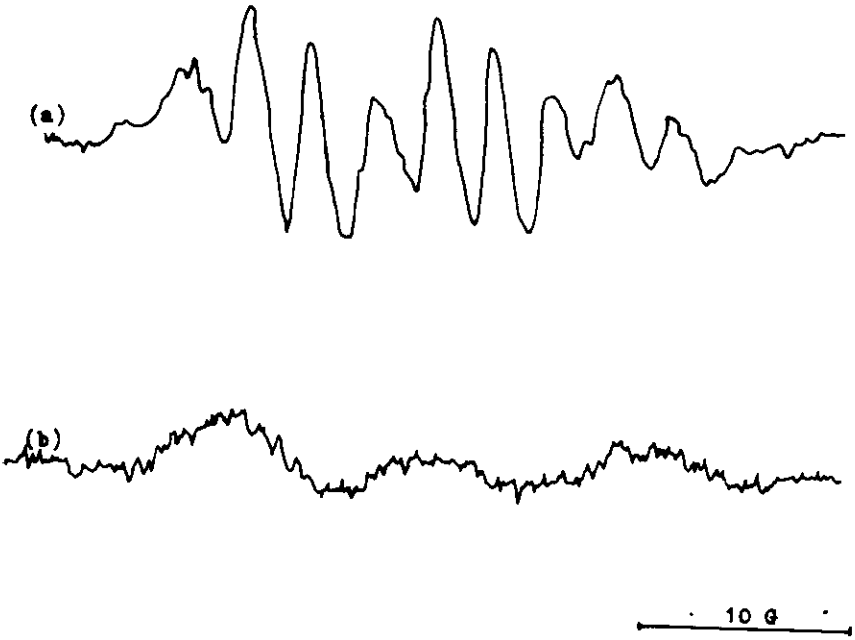


Fig. 2 E.s.r. spectra of the nitroxyl radical produced from quinoxaline N,N-dioxide(2, $R_1=R_2$), in (a) benzene and (b) methanol, at room temperature. The three main peaks are due to the splitting of ^{14}N of N-O$^{\bullet}$ group.

dioxide in benzene and in methanol. Therefore, the case that the photoexcited solvent molecules reacting with the substrate to form radicals should be excluded, for the same radical had been produced in solvent as methanol, which is not photoactive here.

The present mechanism seems most reasonable at the stage of these preliminary e.s.r. investigations. Because of the physicochemical importance in photochemistry and radical chemistry etc., these photolysis systems will be studied in more details.

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