Mem. Fac. Educ., Shimane Univ. (Nat. Sci.)Vol. 18, pp. 1–6, (1984).

ESR Spectra of Iminoxy Radicals produced in Nitroso Naphthols and Nitroso phenols

Kunihisa SOGABE*

ABSTRACT : ESR spectra of iminoxy radicals chemically produced in 1-nitroso 2-naphthol, 1-nitroso 2-naphthol 3, 6-disulfonic acid, 2-nitroso 1-naphthol, 2-nitroso 5-dimethylaminoaphenol, and 4-nitroso phenol were observed. These radicals were assigned to be produced *via* less stable nitroso naphtho or nitroso benzo semiquinone radicals, which were first derived in nitroso compounds by oxidations. Two isomers, Z type having nitrogen hyperfine coupling constants of *ca.* 2.7 mT and less stable E type with those of *ca* 3.1 mT were involved in 1-nitroso naphthol, 1-nitroso 2-naphthol 3.6-disulfonic acid, and 2-nitroso 5-dimethyl amino phenol while the E type in 2-nitroso 1-naphthol was too weak to be detected. The only one iminoxy radical was detected in 4-nitroso phenol. On UV irradiations of 1-nitroso 2-naphthol at −100°C, the less stable E type was detected in almost same intensity as the Z type. The structures and stability of the iminoxy radicals were concluded to be affected by the carbonyl group adjacent to the iminoxy one.

Introdution

Forrester *at al* [1]. and Miller and Miller [2] have reproted that a key step on an activation for carcinogenic metabolities such as 2-hydroxyl acetyl aminofluorene or 2-naphthyl amine is probably a production of a nitroxide radical. Many investigators have been working to find correlations between carcinogenic activities and nitroxide radicals chemically derived in N-hydroxylamines [3] or N-nitroso amines [4]. Present author have recently obtained interesting results which two pathways of active and deoxicate process are included in oxidative reaction of nitroxide radicals derived in N-hydroxyl amines and N-nitroso amines [5].

On the other hand, no discussion on carcinogenic activities of radicals formed in aromatic C-nitroso compounds being possibly carcinogenic. Two different nitroxide radicals were odserved in oxidized carcinogenic nitroso benzene [6]. Nothing but iminoxy radicals were, however, detected in 1-nitroso 2-naphthol or 2-nitroso 1-naphthol in spite of their percarcinogen [7,8]. It is very interesting to discuss on carcinogenic activities of iminoxy radicals derived in nitroso naphthol or nitroso phenol, and of nitroxide radicals created in nitroso benzene. To find behaviors of iminoxy radicals, 1-nitroso 2-naphthol, 2-nitroso 1-naphthol, and 4-nitroso phenol as carcinogenic compounds and 1-nitroso 2-naphthol 3, 6-disulfonic acid and 2-nitroso 5-dimethylamino phenol as noncarcinogenic C-nitroso compounds were oxidized by UV light, metal ions, and oxidants.

Experimental

Sample used here were purcharsed from Tokyo kasei Co., and used without further

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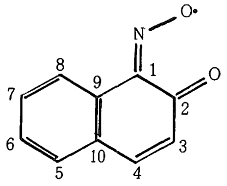
* Fac. of Educ., Univ. of Shimane, 1060, Nishikawatsu Matsue 690

purification. Dioxane, water, toluene, and dichloro methane solutions by *ca.* 10^{-2} mol were prepared. $VOCl_2$, $CuCl_2$, and $FeCl_3$ were used as metal ion, and cerium sulfate, lead tetra acetate, and silver oxide as oxidant. ESR spectra were recorded by JEOL FEIX at room temperature except toluene solution at −100°C. A frozen spectrum was recorded at 77 K. 500 W Xe lamp made by WACON was used as UV source and UV light was directly irradiated on the sample tube in the ESR cavity. *g* Values and hyperfine coupling constants were measured utilizing the mangane standard sample.

Results and Discussion

ESR spectra of iminoxy radicals chemically produced in (a) 1-nitroso 2-naphthol, (b) 1-nitroso 2-naphthol 3,6-disulfonic acid and (c) 2-nitroso 1-naphthol by metal ions and oxidants are shown in Figure 1 (a) - (c), respectively. ESR parameters derived from these spectra are summerized in Table 1 and are in good agreement with those reported in literatures[7,8]. It is well known two isomers are involved in iminoxy radicals. These spectra seen in Figure 1 may be attributed to an Z type as illustrated below :

Z type :



(I)

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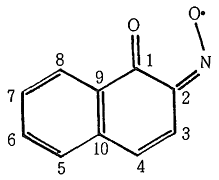
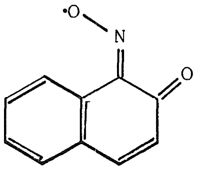


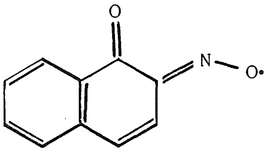
(II)

E type :



(I′)

,



(II′)

Three triplet doublets are demonstrated in Figure 1 (a). The doublet having 0.21 mT coupling constants is assigned to be a proton at 3-position of (I) since it is no longer observed in Figure 1 (b) when the proton at the same position in 1-nitroso 2-naphthol 3, 6-disulfonic acid is substituted. No triplet doublet but triplet is detected in Figure 1 (c) because of two equivalent protons at 3-and 8 positions. Spin density on the proton of 3-position in (I) is considerablly larger than that in (II). This fact is assumed to be resulted in their radical structures.

A spectrum of a less stable E type (I′) could be obtained although very difficult to detect. The spectrum is shown in Figure 2, together with satellites due to ^{13}C and ^{15}N isotopes. A spectrum in 2-nitroso 1-naphthol is too weak to detect in spite of many attempts. UV irradiation on 1-nitroso 2-naphthol toluene solution at −100°C produced two isomers of (I) and (I′) in equall strength, although a prolonged UV irradiation caused in the decay of the isomers. UV irradiation might enhance a possiblity of the less stable isomer. A specrum of a less stable isomer expected in 2-nitroso 1-naphthol was too weak to detect in spite of

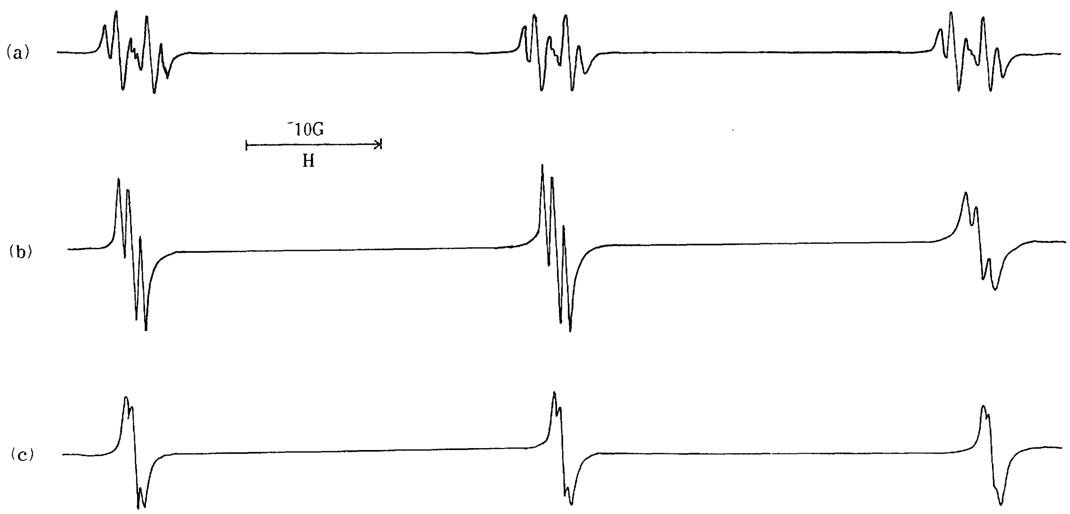


Figure 1 ESR spectra of imonoxy radicals produced in (a) 1-nitroso 2-naphthol, (b) 1-nitroso 2-naphthol 3, 6-dimethyl amino sulfonic acid and (c) 2-nitroso 1-naphthol under oxidations.

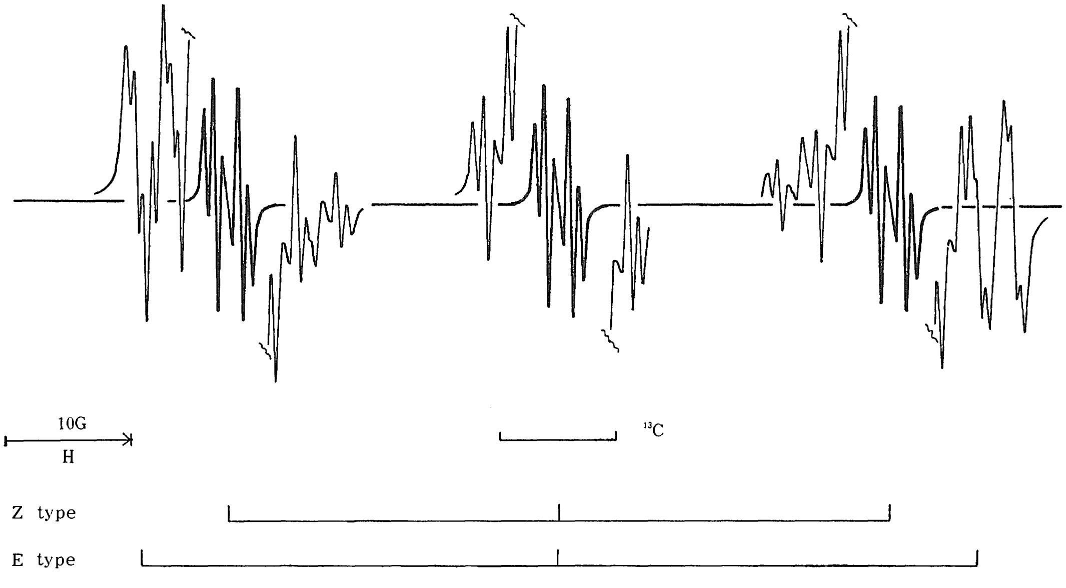
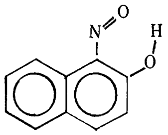
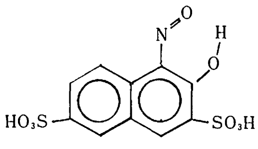
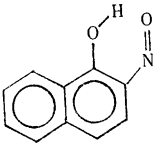
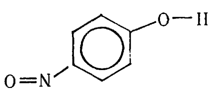
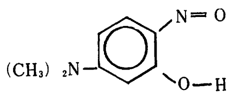


Figure 2 ESR spectra of iminoxy radicals produced in UV irradiated 1-nitroso 2-naphthol toluene solution at −100°C.

many attempts.

These ESR parameters of (I′) determined from the spectrum are summerized in Tablel, together with those of (I). As can be seen from Table 1, Nitrogen hyperfine coupling constants in (I′) are slightly larger than those in (I). It is understood that a decrease in an interaction of a carbonyl group with an iminoxy one in (I′) rather than (I) gives rise to an increase in spin density on iminoxy group. A CNO bond angle in 1-nitroso 2-naphthol is expected to ca. 134° because of a hydrogen bond between a nitroso group and a hydroxyl one $^{7)}$. On preparation of iminoxy radical, the CNO bond angle is expected to be broadened

Table 1 ESR Parameters of iminoxy radicals produced in nitroso naphthols and nitroso phenols

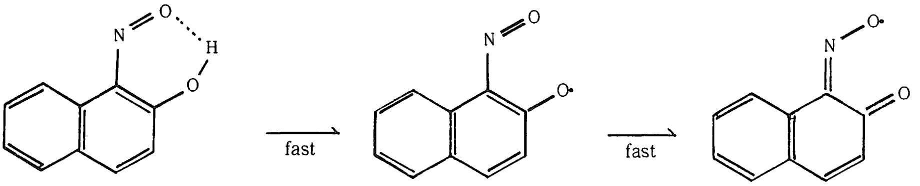
Radical (as parent compound)	Metal ion, oxidant, or UV [1]	Soluvent [2]	g-Value	Hyperfine Coupling Constant (mT)			
				A_N	A_H	A_H	$A^{13}C$
	P	D	2.0054	2.78	0.20	0.08	0.94
			2.0048	3.30	0.30	0.07	
		W	2.0053	2.83	0.21	0.07	
			2.0049	3.29	0.31	0.07	
	C	D	2.0054	2.76	0.20	0.07	0.94
			2.0048	3.31	0.28	0.07	
		W	2.0053	2.83	0.21	0.07	
			2.0049	3.29	0.30	0.08	
	VO	D	2.0053	2.82	0.21	0.08	
	UV	T	2.0054	2.78	0.20	0.08	0.95
			2.0048	3.31	0.30	0.08	
	P	W	2.0052	2.85		0.07	
			2.0045	3.36	0.28	0.07	0.95
	C	W	2.0052	2.85		0.07	
			2.0045	3.38	0.28	0.07	
	A	W	2.0052	2.83		0.07	
			2.0045	3.38	0.28	0.07	
	Cu	W	2.0052	2.85		0.08	
			2.0045	3.39	0.28	0.08	
	P	D	2.0055	2.74		0.05	
		W	2.0055	2.75		0.05	
	C	D	2.0055	2.74		0.05	0.95
		W	2.0055	2.74		0.05	
	Fe	W	2.0055	2.75		0.05	
	P	D	2.0055	3.30	0.39	0.14	
	C	D	2.0055	3.31	0.40	0.13	
	VO	D	2.0055	3.30	0.39	0.14	
	P	D	2.0055	2.55		0.17	
			2.0053	3.49		0.17	
	C	D	2.0055	2.56		0.17	1.09
			2.0053	3.48		0.17	
	A	D	2.0055	2.56		0.17	1.09
			2.0053	3.49		0.17	
	Cu	D	2.0055	2.56		0.17	

1) P ; $Pb(CH_3COO)_4$, C ; $Ce(SO_4)_2$, A ; Ag_2O, VO ; $VOCl_2$, Fe ; $FeCl_3$, Cu ; $CuCl_2$ and UV ; UV light.

2) D ; dioxane, W ; water, and T ; toluene.

considerably because of cleavation of the hydrogen bond. The CNO bond angle was determined as 140° from a frozen spectrum using the equations 7). Spin densities on a_s^2 and a_p^2 are 0.049 and 0.315 respectively. Unpaired electron of 36% are distributed on the nitrogen nucleus.

A steep variation of 134° to 140° in the CNO bond angle might be resulted from the two step reaction via a semiquinoid type radical as illustrated below :

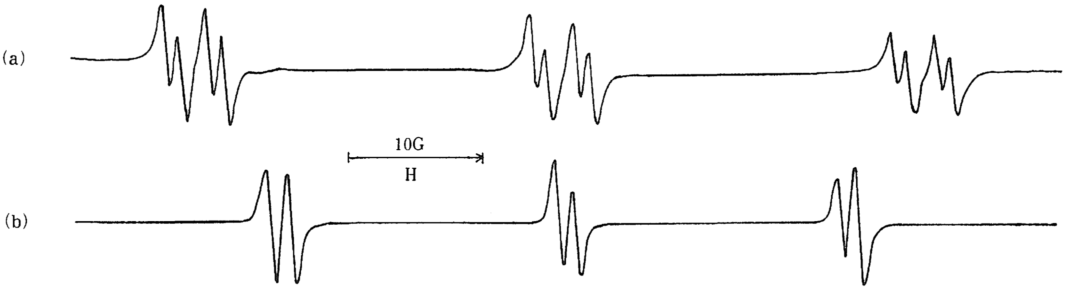


1-nitroso 2-naphthol 1-nitroso 2-naphtho semiquinone radical 2-naphtho 1-iminoxy radical (I)

Namely, the 1-nitroso 2-naphtho semiquinone radical was formed by oxidation of 1-nitroso 2-naphthol, changing instantly into 2-naphtho 1-iminoxy radical. A CNO bond angle of (I′) may be expected to 140° or more, but it is very difficult to determine a frozen spectrum of (I′).

ESR spectra of iminoxy radicals obtained in oxidized 4-nitroso phenol and 2-nitroso 5-dimethyl amino phenol are shown in Figure 3 (a) and (b), and these parameter are summerized in Table 1. As can be seen from Figure 3 (b), an unsymmetric spectum is understood to be resulted from overlapping of a triplet and a doublet triplet. The observation of the triplet was readily controlled by experimental conditions. The doublet triplet was determined to be due to Z type although nitrogen hyperfine coupling constants were shightly smaller than those in naphhto iminoxy radicals mentioned above. The triplet may be assumed to be a iminoxy radical with similar structure as Z type. A less stable E type was detected in very low concentration with satellites due to ^{13}C and ^{15}N isotopes. A doublet due to a proton at 3-position was noticeble in E type while in Z type, the hyperfine of the doublet due to 6-position was observed.

The spectrum shown in figure 3 (a) was obtained on oxidation of 4-nitroso phenol since no isomer in 4-benzo iminoxy radical was detected, The doublet doublet due to unequvalent protons, 3- and 5-positions, and the largest nitrogen hyperfine coupling constants were



Figuree 3 ESR spectra of iminoxy radicals produced in (a) 4-nitroso phenol, and (b) 2-nitroso 5-dimethyl amino phenol under oxidations.

observed from the spectrum. The largest hyperfine coupling constants is considered to be caused by a decrease in an interaction between a carbonyl and iminoxy groups.

In oxidation of such C-nitroso compounds as nitroso naphthols and nitroso phenols, nothing but the iminoxy radicals were observed in spite of the carcinogenic sample or not. On the other hand, two nitroxide radicals were produced in carcinogenic nitroso benzene. Differences in these results may be depended on structures of C-nitroso compounds. The nitroso group in nitroso benzene is very easy to react with oxidants, while in nitroso naphthols or nitroso phenols, hydroxyl group is marked for attack of oxidants in preference to the nitroso group.

The obsevations of the iminoxy radicals in oxidative C-nitroso compounds provided many interesting informations on precarcinogen. Further studies on behaviors of the iminoxy radicals derived in carcinogenic compounds.

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