Mechanisms and structures of free radicals in the photoreaction processes of o-substituted nitrobenzaldehydes

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Abstract

The photoreaction mechanisms of o-nitro- and 2,4- dinitrobenzaldehyde have been studied by the ESR technique. Results indicate that, totally different from other aromatic aldehydes, the photochemical processes of o-substituted nitro benzaldehydes are rather complicated and unusual. The observed ESR spectra show overlapping signals consisting of three and two types of free radicals for o-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde respectively. In photoreaction processes, not only did the reaction of photorearrangement to o-nitrosobenzoic acid take place, but also the photolysis reactions as well as the addition reactions simultaneously. The photorearrangement product o-nitrosobenzoic acid could act as a spin trap to react with active radicals in photolysis to form the stable nitroxyl radicals. It is certain that the ESR signals in the photochemical reaction did stem from the products of secondary reaction processes via post-photoisomerization. An entirely new type of reaction is proposed.

Keywords: o-Nitrobenzaldehyde; Photoreaction; ESR; Nitroxyl free radical

1. Introduction

The unusual photochemical behavior of o-nitrobenzaldehyde, which is one of the standard scintillators and the reference material in quantum efficiency measurements of photochemistry, has attracted much attention from chemists. Up to date, however, its photoreaction mechanism has not been known. Bowen and others [1–3] who investigated the photorearrangement of o-nitrobenzaldehyde to o-nitrosobenzoic acid considered that the photorearrangement was an irreversible process and there was no side-reaction in the whole process. Tench and Coppens [4] observed the ESR spectrum produced in an ethyl alcohol solution of o-nitrobenzaldehyde after UV radiation; they considered the ESR spectrum was the signal of a radical ion, and supposed that the photoradical probably arose from a side-reaction. But whatever was the side reaction they guessed? So far it has not been answered.

In this paper, photochemical reaction processes of o-nitrobenzaldehyde and 2,4-dinitrobenzaldehyde were studied in detail by means of the ESR method. Extremely interesting results were obtained, and the reaction mechanisms are proposed and discussed.

2. Experimental details

2.1. Materials

Aromatic aldehydes (Aldrich), recrystallized from water/ethyl alcohol (5:1), benzene and ethyl alcohol were of G.R. grade. Spin-trap PBN was synthesized according to the literature [5].

2.2. ESR measurements

A high-pressure mercury lamp with a main wavelength of 320 nm was used as radiation source. Concentrations of the sample solutions were 2×10^{-2} to 8×10^{-2} mol l^{-1}. All the measured solutions were bubbled by highly pure N_2 to remove O_2 for 10 min before and during UV radiation, as well as during ESR detection processes.

ESR spectra were measured by a Bruker Model ESP-300 spectrometer with X band. The *EPRCALC* program was used for the simulation of ESR spectra.

No ESR signal was observed in the benzene solution of aromatic aldehydes before being irradiated. But after being

Table 1
The ESR parameters of spin-adducts formed in photoreactions of o-substituted nitrobenzaldehydes/benzene system

Free radical	Splitting constant (in G)				g value	Number of lines	Life time (h)
	a_N^{α}	$a_{H(N)}$	$a_H^{o,p}$	a_H^m			
$\langle A \rangle$ [a]	8.12	11.93	2.99	1.06	2.0061	50–52	20–40
	8.04	11.84	2.99	0.98	2.0061	50–52	20–40
	8.1	11.2	2.90	1.00			
$\langle B \rangle$	6.93	–	2.30	0.61	2.0055	27	50–70
$\langle C \rangle$	6.82	–	2.27	0.62	2.0055	45	100–150
$\langle D \rangle$	7.52	10.04	2.76	0.85	2.0058	30	30–50
$\langle E \rangle$	6.68	–	2.02	0.52	2.0053	18	60–80
$[PBN\text{-}R_1]$ [b]	12.60	–	$a_H^{\beta} = 2.61$			6	

[a] Second line: in the presence of PBN. Third line: the value of "radical ion" measured by Tench and Coppens.
[b] R_1 is aryl radical $NO_2C_6H_4CO$.

irradiated, clear, strong and complicated ESR signals were detected immediately.

3. Results and discussion

The experimental results are shown in the figures; some simulated spectra concerned with the nitroxyl radicals are also shown. In all figures, the scales of the gauss coordinate are the same, but not the scales of the intensity. All the superfine coupling constants and g values of free radicals detected are listed in Table 1.

It was observed during the ESR measurements that o-substituted nitrobenzaldehydes were highly photosensitive to UV radiation. After UV radiation for only 1 min, clear signals could be detected readily; when irradiated for 3 min, considerable strong and stable ESR spectra could be observed (Fig. 1), and when irradiated for 6 min the intensity of ESR signals increased greatly – about twice as much – especially in the central part of the signals, where the increment of intensity was about three- or fourfold. After irradiation for 10 min, complex overlapping spectra were detectable (Fig. 2(a)). It means obviously that the observed ESR signals were overlapping spectra of mixed radicals, not the spectrum of a single radical.

Whether it was a single signal or not, it was further distinguished by way of the decay of the ESR signals based on the different lifetimes of free radicals generated in reaction systems.

In experiments it was observed that the overlapping ESR spectra gradually changed with time at a slow rate, and both
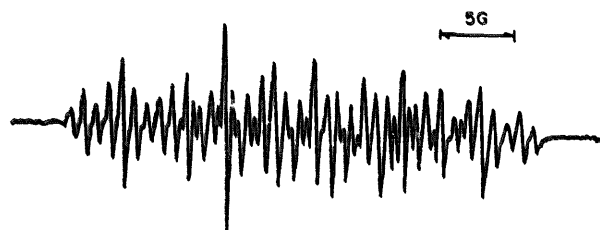

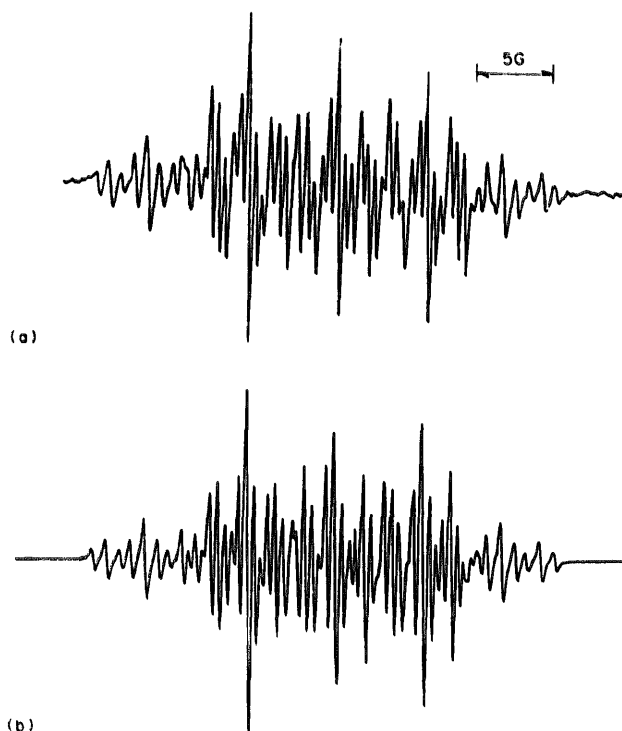Fig. 1. ESR spectra of benzene solution of o-nitrobenzaldehyde irradiated by UV for 3 min.

Fig. 2. (a) ESR spectra of benzene solution of o-nitrobenzaldehyde irradiated by UV for 10 min. (b) Simulated ESR spectra of three kinds of nitroxyl radicals overlapped according to $\langle A \rangle : \langle B \rangle : \langle C \rangle = 1:1:2$.

sides of spectral lines weakened at a very fast rate; the half-time was about 5–10 h. After 15 h from the first detection, the widest spectrum with 50 or 52 lines (total width is 35.60 G) weakened greatly (Fig. 3(a)), and the widest ESR spectrum disappeared entirely after 20–30 h from the first detection; thus the observed ESR signals had only 45 lines and its width (25.30 G) became narrower than the original observed spectra; 60–80 h afterwards, the central peaks with 27 lines, which were overlapped with the 45-line spectrum, weakened greatly so that the central stable ESR spectrum with 45 lines was entirely projected at the end (Fig. 3(b)). The relative intensity ratios of spectrum lines were no longer changed with time, and the ratio numbers were 1:4:6:4:5:16:24:16:
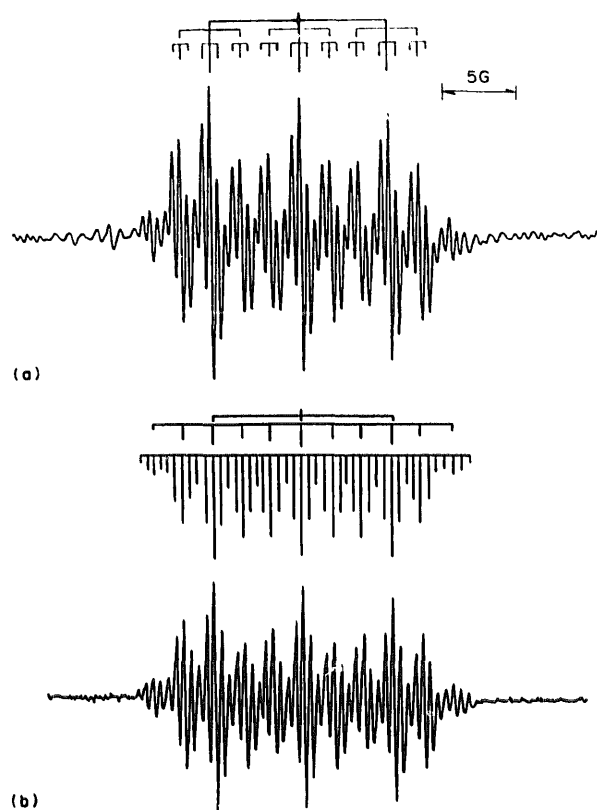
Fig. 3. (a) ESR spectra detected 15 h later from *o*-nitrobenzaldehyde/ benzene system irradiated for 10 min. (b) ESR spectrum detected 90 h later from *o*-nitrobenzaldehyde/benzene system irradiated for 10 min.

10:24:36:24:11:20:30:20:10:20:30:20:11:24:36:24:11:20:
30:20:10:20:30:20:11:24:36:24:10:16:24:16:5:4:6:4:1.

Therefore it was shown from the above results that there were three kinds of free radicals in the photoreaction of *o*-nitrobenzaldehyde; the observed ESR signals might be over $_n$ lapping spectra consisting of three types of radicals. This result is very different from that obtained by Tench and Coppens [4], who concluded that there was only one kind of radical ion in the photoreaction.

Let us now discuss the exact "ownership" of the overlapping signals of three types of free radicals.

It is well known that, when irradiated by UV, *o*-nitrobenzaldehyde is immediately isomerized to *o*-nitrosobenzoic acid [2], as shown in reaction (1). The quantum efficency of reaction (1) is 0.5 constantly. The necessary time for the completion of reaction (1) is only about 10^{-12} s. It is evident that the transient intermediate formed during reaction (1) cannot be detected by the conventional ESR method.

Tench and Coppens [4], according to their experimental results, proposed one of the following structures for the observed radical:


<i>   <ii>
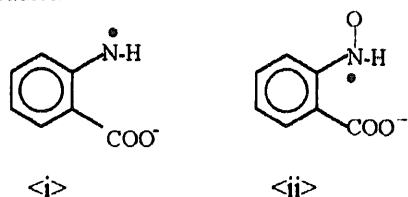
It is apparent that in the photoreaction system of *o*-nitrobenzaldehyde, the above asumption of the two radical ion is inadequate. In general, most of the nitrogen-centered free radicals are very unstable; their ESR signals cannot be detected at room temperature. In alcohol, especially in benzene solution, ionization of *o*-nitrosobenzoic acid to radical ions is quite difficult. Therefore, according to our research results, the appearance of the free-radical signals implies that photorearrangement was not the sole process in the reaction system, and there might be other parallel or secondary reactions which produced free radicals at the same time.

It is well known that some nitroso compounds usually are able to act as a spin trap to react with short-lived free radicals and form stable nitroxyl radicals which can be detected by the conventional ESR method. Therefore it is suggested that, except for photorearrangement reaction (1), the following photolysis processes also took place simultaneously:
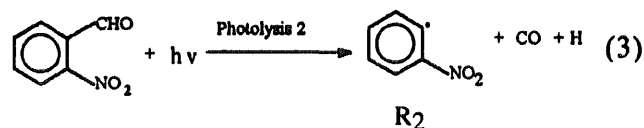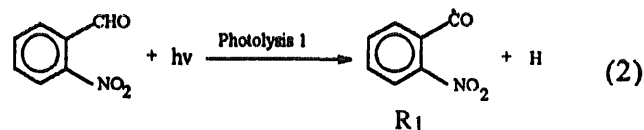
As a consequence, the following secondary reactions-addition processes took place next:
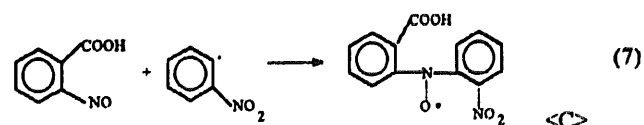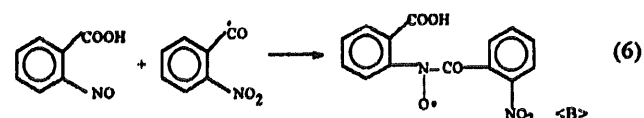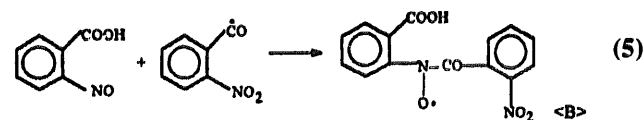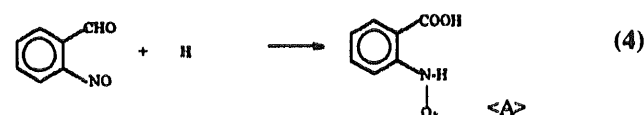
As can be seen from reactions (1) to (7), at first, when *o*-nitrobenzaldehyde was irradiated by UV, *o*-nitrosobenzoic acid was produced via oxygen transfer from the nitro group to the aldehydic group; at the same time, *o*-nitrobenzaldehyde was photolyzed by UV to form the acyl radical *o*-NO$_2$-(C$_6$H$_4$)CO· (R$_1$ radical) and aromatic radical *o*-NO$_2$C$_6$H$_4$·
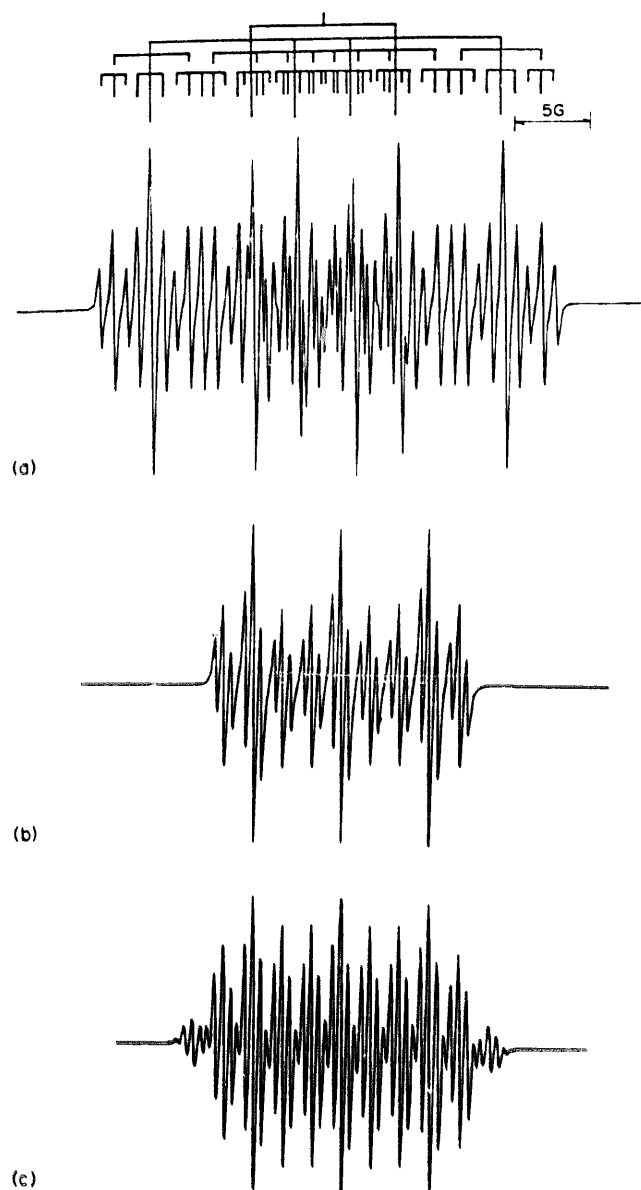
(a)

(b)

(c)

Fig. 4. (a) Simulated ESR spectrum of nitroxyl radical ⟨A⟩. (b) Simulated ESR spectrum of nitroxyl radical ⟨B⟩ (c) Simulated ESR spectrum of nitroxyl radical ⟨C⟩.

(R_2 radical); and then, the photochemical hydrogen-abstracting reaction between o-nitrosobenzoic acid and o-nitrobenzaldehyde, as well as the addition of o-nitrosobenzoic acid with a free hydrogen atom led to the formation of spin-adduct ⟨A⟩; in the meantime, the addition reaction of o-nitrosobenzoic acid with the active radicals $R_1 \cdot$ and $R_2 \cdot$ resulted in the generation of spin adducts ⟨B⟩ and ⟨C⟩ respectively. Thereupon, a series of secondary reactions led to the formation of three kinds of spin-adducts, namely, nitroxyl free radicals ⟨A⟩, ⟨B⟩ and ⟨C⟩.

In free radical ⟨A⟩, the unpaired electron could couple with an α-N, an α-H(N), two o,p-protons and two m-protons in the benzene ring, and should give 54 lines, but only 50 lines (sometimes 52 lines) were detected by virtue of the

overlap of the lines. The ESR spectrum of ⟨A⟩ is the widest in the detected overlapping spectra (Figs. 1 and 2). The simulated spectrum is shown in Fig. 4(a).

Lemaire et al. observed the ESR spectrum of the monophenyl nitroxyl radical C_6H_5–HN–O · produced in the reduction process of nitrobenzene with lithium aluminum hydride in diethylene glycol medium [6]. The free radical C_6H_5-NH-O · should give an ESR spectrum with 72 lines, but only 43 lines were obtained owing to the overlap of lines as well the poor resolution. The measured superfine coupling constants ($a_N = 9.1$ G, $a_H = 12.1$ G, $a_H^{o,p} = 3.0$ G, and $a_H^m = 1.0$ G) are quite identical with the nitroxyl radical ⟨A⟩ measured in our experiment (Table 1), even though one H atom of the benzene ring is replaced by a carboxyl group in radical ⟨A⟩. Therefore, the research result on nitrobenzene obtained by Lemaire et al. may be regarded as collateral evidence for the structure of adduct ⟨A⟩ proposed in our research.

In spin-adduct ⟨B⟩, the unpaired electron has an α-N, two o,p-H and two m-H, so it could give an ESR spectrum with 27 lines, which is consistent with our observed spectrum. The simulated spectrum of ⟨B⟩ is shown in Fig. 4(b).

As for radical ⟨C⟩, the unpaired electron could couple with an α-N, four o,p-H and four m-H (in both benzene rings), and ought to give 75 lines, but owing to the overlap of lines the detected spectrum only gave 45 lines, i.e. $(3 \times 5 - 4) \times 5 - 10 \times 1 = 45$. The measured intensity ratio showed no difference from the calculated one. The g factor (2.0058) is the same as that of radical ⟨B⟩. The observed spectrum of nitroxyl radical ⟨C⟩ (Fig. 3(b)) is identical with the simulated spectrum shown in Fig. 4(c). It must be noted that, in accordance with the decay and change of 27 lines, the existence of nitroxyl radical ⟨B⟩ may be confirmed without doubt.

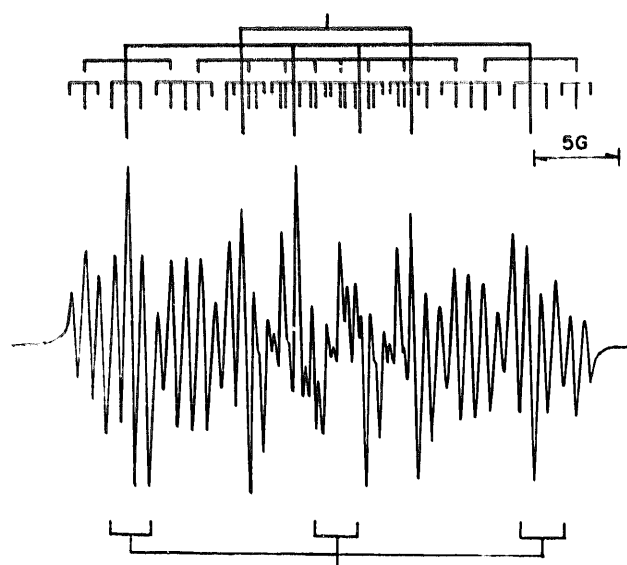When spin-trap PBN was used in the photoreaction system, the strong ESR signals shown in Fig. 5 were observed after

Fig. 5. ESR spectra of o-NO$_2$C$_6$H$_4$CHO/C$_6$H$_6$ system in the presence of PBN irradiated by UV for 6 min.

irradiation by UV for only 6 min. It is noted that, owing to the presence of PBN, the active acyl radical (R_1) produced from photolysis process 1 was easily trapped, and brought about generation of the rather stable spin-adduct [PBN-R_1] · with six ESR lines. In Fig. 5, the stick spectrum with six lines indicates the position of the PBN adduct signal. It is apparent that the trapping ability of PBN for the R_1 radical is larger than that of o-nitrosobenzoic acid for R_1, and thus PBN could avoid the formation of free radicals $\langle B \rangle$ or $\langle C \rangle$, so as to prevent the overlapping and interference of complicated signals and to make the spectrum lines of $\langle A \rangle$ clear and project. As in the presence of PBN, the splitting constants of $\langle A \rangle$ are: $a_N = 8.04$ G, $a_{H(N)} = 11.83$ G, $a_H{}^{o,p} = 2.99$ G and $a_H{}^m = 0.98$ G, which are identical with those in the case without PBN (see Table 1). The splitting constants of [PBN-R_1] · are $a_N = 12.60$ G and $a_H = 2.61$ G, which are close to the the values for other aromatic aryl radicals [7]. Here, there was no signal of R_2 radical in photoreaction system as a result of the short duration of the UV radiation.

In the detected overlapping spectra, the difference of the central field for $\langle A \rangle$ to $\langle B \rangle$ and $\langle C \rangle$ is 0.93 G. By using the *EPRCALC* program, we made a simulation of the ESR spectra of $\langle A \rangle + \langle B \rangle + \langle C \rangle$ according to the intensity ratio A:B:C = 1:1:2; the resultant simulated spectrum (Fig. 2(b)) is completely identical with the observed spectra obtained from the experimental measurement. Therefore, it is shown that the structures of the free radicals, including the active intermediates, stable spin-adducts and the reaction mechanisms agree well with the experiment facts, so the reaction mechanisms proposed by the authors are able to give a very rational and satisfactory explanation for the origin of the ESR signals, as well as the exact structures of various intermediates.

The order of the lifetimes and stability for the three radicals is $\langle A \rangle < \langle B \rangle < \langle C \rangle$.

Usually, the lifetime of nitroxyl radical $\langle A \rangle$ was about 20–40 h, $\langle B \rangle$ was about 50–70 h and $\langle C \rangle$ was about 100–150 h. Because the unpaired electron of radical $\langle C \rangle$ is delocalized in two benzene rings, $\langle C \rangle$ is the relatively most stable radical among these three nitroxyl radicals.

With respect to 2,4-dinitrobenzaldehyde, similar results were also obtained (Fig. 6), and the following nitroxyl radicals $\langle D \rangle$ and $\langle E \rangle$ were detected:
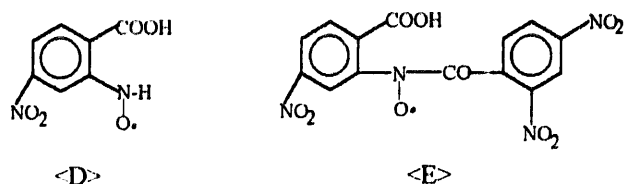
For nitroxyl radical $\langle D \rangle$, the unpaired electron has an α-N, α-H(N), two o,p-H and one m-H, and should give 36 lines, but only 30 lines were observed as a result of the overlap of lines, i.e. $(3 \times 3 \times 3)2 - 6 = 30$. In free radical $\langle E \rangle$, the unpaired electron could couple with an α-N, two o,p-H and one m-H, so it gave an ESR spectrum with 18 lines, but the
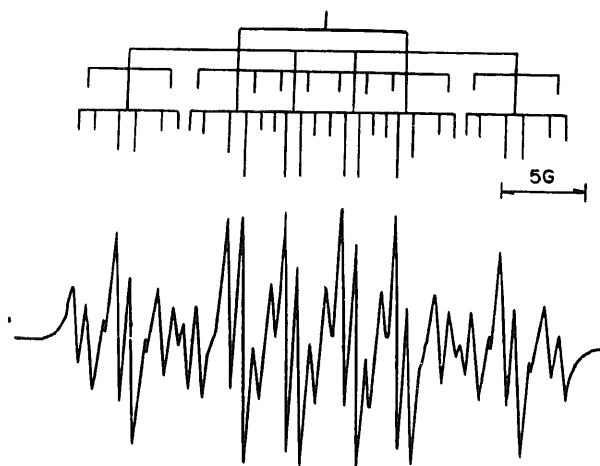

Fig. 6. ESR spectra of benzene solution of 2,4-dinitrobenzaldehyde irradiated by UV for 10 min.

observed signal of $\langle E \rangle$ was very weak. The lifetime of free radical $\langle D \rangle$ was about 30–50 h; $\langle E \rangle$ was about 60–80 h. The splitting constants and g values of $\langle D \rangle$ and $\langle E \rangle$ are listed in Table 1. The formation of $\langle D \rangle$ and $\langle E \rangle$ were relatively more difficult than that of $\langle A \rangle$ and $\langle B \rangle$, so stronger radiation intensity or longer radiation duration is necessary to obtain clear ESR signals. In the meanwhile, no signal of an aromatic radical adduct was observed. Perhaps it is because of the difficulty in taking off the aldehydic group –CHO in 2,4-dinitrobenzaldehyde.

Although the stability of nitroxyl radicals $\langle A \rangle$ and $\langle D \rangle$ was not very good, they were still able to exist for a considerable period, possibly owing to the form of intramolecular hydrogen bond increasing the stability of the spin-adducts.

In view of the fact that the photoreaction behavior of o-substituted nitrobenzaldehyde possesses an extremely particular feature which is entirely different from any other reaction model, such as reversible reaction, parallel reaction, consecutive reaction, cross-linking reaction or chain reaction, etc., so the photochemical reaction behavior may be regarded as a new type of reaction.

4. Conclusion

From the above, definite conclusions can be obtained.

(1) In photoreaction processes of o-substituted nitrobenzaldehydes, not only the reaction of photorearrangement to o-nitrosobenzoic acid took place, but also photolysis reactions to active free radicals.

(2) The photoisomerization product, o-nitrosobenzoic acid, could immediately act as a spin trap to add to the active radicals produced in photolysis leading to the form of the stable neutral nitroxyl radicals, not the radical ions. So did the photoisomerizatian product of 2,4-dinitrobenzaldehyde.

(3) In photoreaction, three or two kinds of nitroxyl radicals could be formed, not one kind only.

(4) The ESR signals in photoreaction did stem from the products of the secondary reaction processes via post-photoisomerization, not from the transient intermediates of the photoisomerization processes.

Acknowledgements

References

[1] E.J. Bowen, H. Hartley, W.D. Scott and H.G. Watts, *J. Chem. Soc., 125* (1924) 1218.

[2] J.G. Calvert and J.N. Pitts Jr., *Photochemistry*, Wiley, New York, 1966, p. 477.

[3] P.A. Leighton and F.A. Lucy, *J. Chem. Phys, 2* (1934) 757, 760.

[4] A.J. Tench and P. Coppens, *J. Phys. Chem., 67* (1963) 1378.

[5] L.I. Smith and F.L. Taylor, *J. Am. Chem. Soc., 57* (1935) 2370, 2460.

[6] H. Lemaire, A. Rassat and J.P. Ravet, *Tetrahedron Lett., 47* (1964) 3507.

[7] D.W. Chen, J.W. Zhou and G.Z. Xu, *Chin. J. Magn. Reson., 3* (1986) 339 (in Chinese).