JOURNAL OF PHYSICAL ORGANIC CHEMISTRY. VOL. 1. 191–195 (1988)

ESR STUDIES OF PHOTOCHEMICAL REACTION OF 2-METHYL-3-ACETYLQUINOXALINE N,N′-DIOXIDE(MAQO)

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ABSTRACT

The photochemical reaction of MAQO with various aromatic amines were studied by ESR. The results show that nitroxide radicals are stable productrs of the photooxidation of both diphenylamines and phenylamines. The photolyzed phenothiazine does not yield nitroxide as the final product, instead it gives the neutral radical as the stable final product.

INTRODUCTION

We have reported[1,2] the result of the ESR studies of nitroxide radicals generated photolytically from heterocyclic N,N′-dioxides.

It is shown that two $\rangle C{=}N-$ double bond in the excited triplet N,N′-dioxides undergo a photochemical transfer, leading to the formation of nitroxide biradicals from binitrones, and the biradicals so formed may abstract hydrogen from the solvent chloroform giving monoradicals. We also reported[3] that the photolysis of chloroform solutions containing MAQO and dialkyl aminines leads to the observation of ESR spectra of the corresponding dialkyl nitroxides. Oxygen transfer exciplex which derived from the triplet state of MAQO is suggested as an intermediate to give nitroxide through N—H bond cleavage in the secondary amine within exciplex.

In a recent spectroscopic investigation of aromatic amine, Lin and Retsky[4] have observed some photochemical behavior of diphenylamines and phenothiazines. Both diphenylamines and phenothiazines yield nitroxide radicals as the final products upon photolysis in the presence of air as evidenced from the observed ESR spectra.

In this paper, we wish to report the photochemical behavior of MAQO in the presence of aromatic amines. Our results show that nitroxide radicals are the stable products of the photooxidation of both diphenlyamines and phenylmethylamines, while neutral radicals are the stable product of the photolyzed phenothiazines in the presence of MAQO.

0894–3230/88/040191–05$05.00

Received 18 November 1987
Revised 10 January 1988

EXPERIMENTAL

Materials

MAQO was prepared according to the procedures described in literature.[5] Diphenylamines, phenylmethylamines and phenothiazines were purchased from Aldrich Chemical Co. Chloroform as solvent was dried and distilled under argon prior to use.

Preparation of Sample

Samples (concentration $\sim 10^{-3}$M) were carefully introduced into 4 mm O.D. quartz tubes, which were sealed under vacuum after several freeze–thaw-degassing cycles.

ESR Spectral Measurements:

ESR spectra were recorded on a Varian E-115 X-band spectrometer in our studies. The sample was placed in the cavity of ESR apparatus. Irradiation of samples *in situ* was achieved with a 150W xenon lamp. All experiments were performed at room temperature. Magnetic parameters were derived by simulating the spectrum using a computer program on Varian E-936 computer.

RESULTS AND DISCUSSION

No ESR signal was detected from the deoxygenated MAQO in chloroform before photoirradiation. Figure 1 shows the ESR signal of MAQO in chloroform after photoirradiation. When MAQO and aromatic amines were mixed in the chloroform, no ESR signal was obtained before the commencement of photoirradiation. The experimental results obtained from photolysis of the mixed solution by UV irradiation are now presented in detail.

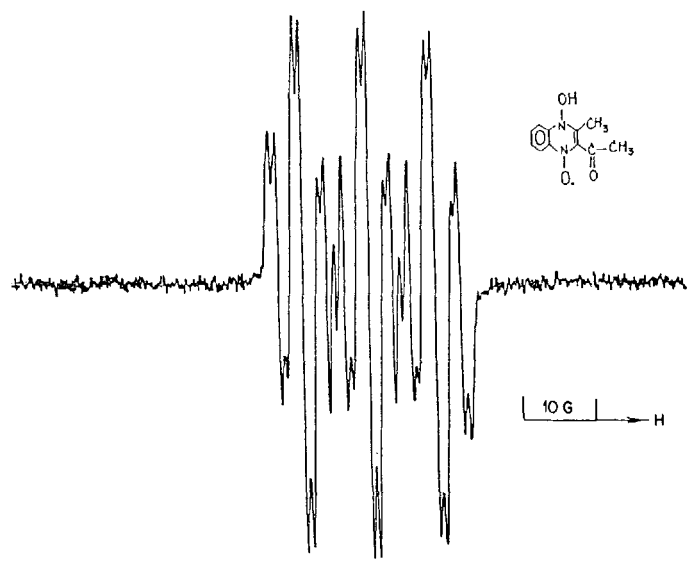


Figure 1. ESR specrum of MAQO in chloroform after irradiation at room temperature

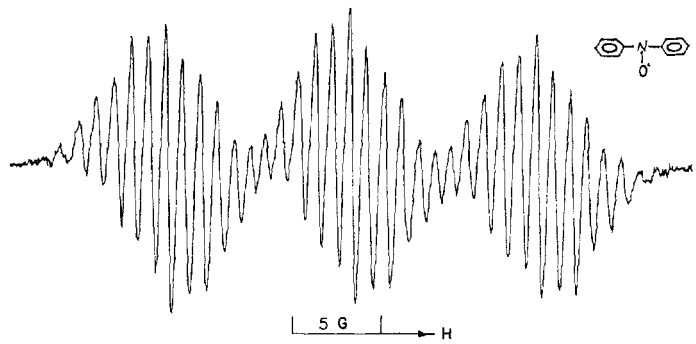


Figure 2. ESR spectrum of MAQO-diphenylamines in chloroform, after irradiation at room temperature.

The spectrum obtained from the photoreaction of MAQO-diphenylamines system, when a degassed solution of MAQO-diphenylamines was irradiated, is given in Figure 2. This spectrum is identical with that of diphenylnitroxide in benzophenone reported in Reference 4. We therefore assign this spectrum to diphenylnitroxide radical. ESR magnetic parameters with $g = 2{\cdot}0057$, $a^{N} = 9{\cdot}80$, $a^{H}_{o,p} = 1{\cdot}80$, a^{H}_{m} 0·80G have been obtained.

Photoreaction of MAQO-phenylmethylamines system. The photolysis of a mixture of MAQO and phenylmethylamines in chloroform led to the observation of a well-resolved ESR spectrum shown in Figure 3. This spectrum is very similar to the reported spectrum of phenylmethylamines[6] derived from the oxidation of corresponding amine with *p*-nitroperbenzoic acid. The spectrum can fit with the following paremeters $a^{N} = 11{\cdot}00$, $a^{H}_{CH_3} = 10{\cdot}40$, $a^{H}_{o,p} = 2{\cdot}90$, $a^{H}_{m} = 1{\cdot}00$G.

A direct conclusion from our experimental results is that the oxygen in the diphenylnitroxide and phenylmethylnitroxide come from the MAQO, and the nitroxides are formed in the process of photooxidiation of the diphenylamines and phenylmethylamines with the photoexcited MAQO as the oxidizer.

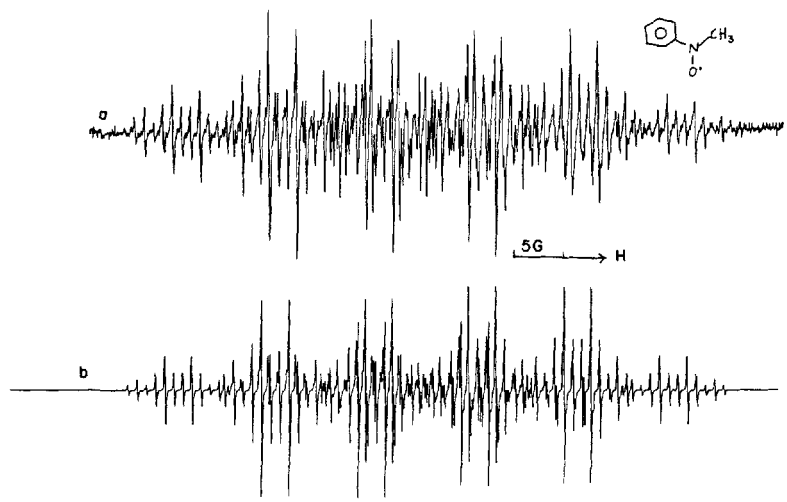


Figure 3. ESR spectrum of MAQO-phenylmethylamines in chloroform after irradiation at room temperature. a. Experimental Spectrum; b. Simulated Spectrum.

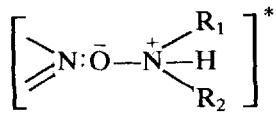
We suppose that similar to the case involving secondary amines the intermediate responsible for the formation of a stable nitroxide radical is also the oxygen transfer exciplex which was produced according to the following scheme:

$$MAQO(S_0) \xrightarrow{h\nu} MAQO(S_1)$$

$$MAQO(S_1) \xrightarrow{I.S.C.} MAQO(T_1)$$

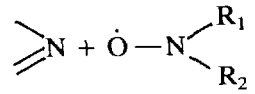
$$MAQO(T_1) + A \longrightarrow \text{Exciplex}$$

Exciplex —



E

E —



The homolysis of α-bond of N—H in the amine part of the transient species *E* leads to the formation of stable diphenylnitroxide(phenylmethylnitroxide), the leaving H atom can be scavenged by environmental molecules or decay through dimerization.

However, photolysis of the MAQO-phenothiazines system produced an ESR spectrum shown in Figure 4a. This spectrum cannot be assigned to the nitroxide radical, but it can be satisfactorily computer-simulated (Figure 4b) on the basis of $a^{N} = 7{\cdot}07$, $a^{H}_{3,7} = 3{\cdot}75$, $a^{H}_{1,9} = 2{\cdot}75$, $a^{H}_{2,8} = 1{\cdot}00$, $a^{H}_{4,6} = 0{\cdot}80$G and we therefore assign the spectrum to phenothiazine neutral radicals.

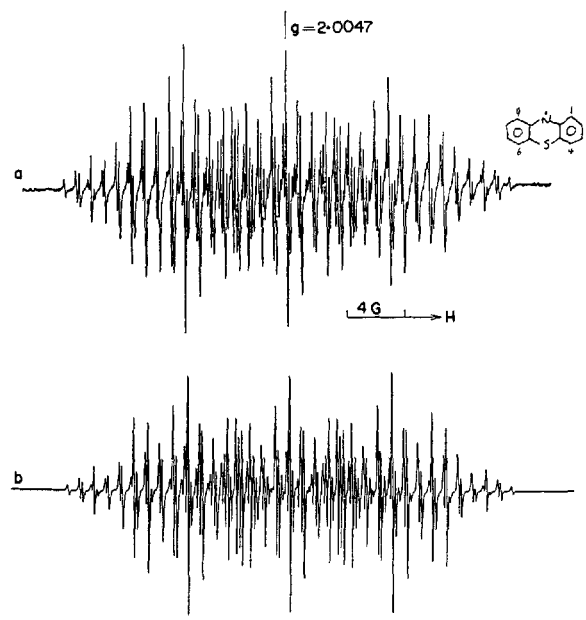


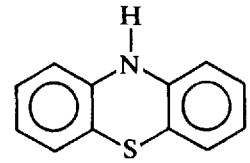
Figure 4. ESR spectrum of MAQO-phenothiazines in chloroform, after irradiation at room temperature. a. Experimental Spectrum; b. Simulated Spectrum.

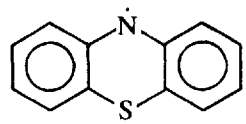
In contrast to diphenylamines and phenylmethylamines, the photolyzed phenothiazines does not yield nitroxide as the final product.

The possible photochemical processes of phenothiazines are:

$$MAQO(T_1) + RNH \longrightarrow MAQO^{-} + RNH^{+}$$

$$\longrightarrow MAQOH + RN\cdot$$

RNH = 

where RN· =  is phenothiazine neutral radical.

It is clear that MAQO is an effective hydrogen abstractor via its photoexcited triplet state. The excited triplet species might abstract a hydrogen atom from nitrogen in phenothiazine molecule to give a phenothiazine neutral radical. The phenothiazine is a good hydrogen donor. We have shown previously[7] that the photolysis of CO_2 $(CO)_6$ $(PBu_3)_2$ with phenothiazine in toluene yield phenothiazine neutral radicals. According to this result we suggest that photogenerated $Co(CO)_3$ (PBu_3) might abstract a hydrogen atom from nitrogen in phenothiazine to give a neutral radical.

We conclude that excited triplet species of MAQO can act either as a good oxygen donor, or as a good hydrogen acceptor.

ACKNOWLEDGEMENTS

This research was supported by National Science Foundation.

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