# PHOTOCHEMISTRY OF α-PHENOXYACETOPHENONE: AN INTERESTING CASE OF INTRAMOLECULAR TRIPLET DEACTIVATION

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## Summary

α-Phenoxyacetophenone undergoes efficient intramolecular triplet deactivation involving quenching by the β-phenyl ring. The process is about an order of magnitude faster than in the case of the all-carbon analogue β-phenylpropiophenone. The difference in the rates of intramolecular quenching is attributed to a reduction of the hydrogen eclipsing interactions in the case of the heteroatom-containing backbone. α-Phenoxyacetophenone photodecomposes with a quantum yield of about 0.004 to yield $C_6H_5CO\overset{\cdot}{C}H_2$ and $C_6H_5\overset{\cdot}{O}$; in spite of its low quantum yield the process is quite rapid, occurring with an estimated rate constant of $3 \times 10^7 \, s^{-1}$.

## 1. Introduction

β-Phenylpropiophenone (I) is essentially photostable, even in good hydrogen donor solvents [1 - 6]. This photostability contrasts with the reactivity of other photoexcited ketones such as benzophenone and acetophenone [7]. Work from this and other laboratories has demonstrated that the photostability of β-phenylpropiophenone and a wide range of closely related substrates [1, 2, 4 - 6, 8] is due to their short triplet lifetime which prevents other frequently slower modes of triplet decay from making a significant contribution. The short triplet lifetime of β-phenylpropiophenone can be attributed to efficient intramolecular deactivation that requires conformation Ia [4, 6]:
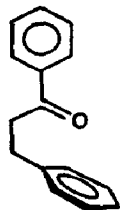


Ia

Molecules of this type have been shown to be excellent probes for molecular mobility and cavity dimensions in a wide range of constrained systems, including zeolites, cyclodextrin complexes and liquid crystals [9 - 13]. It seemed interesting to examine the effect of backbone substitution on the photochemistry of these systems. In particular α-phenoxyacetophenone (II) could be rather informative, since replacement of —CH$_2$— by —O— should make the quenching conformation (IIa)
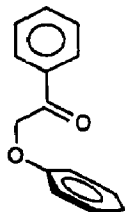


IIa

relatively easy to achieve since this substitution should eliminate hydrogen eclipsing interactions in the —CH$_2$—CH$_2$— moiety which may play a role in determining the behaviour of I.

C—O bonds are also shorter than C—C bonds; this could facilitate the approach of the carbonyl group to the aromatic $\pi$ system. In addition, II is a likely candidate to undergo $\beta$ cleavage to yield phenoxy radicals.

In this report we have examined the photochemistry of II in solution, including laser flash photolysis experiments and product studies. The phosphorescence of II is examined in glasses at 77 K.

## 2. Experimental details

### 2.1. Materials

All solvents were Aldrich of the highest purity commercially available and were used as received.

α-Phenoxyacetophenone II was prepared by reaction of α-chloroacetophenone with phenol using a modification of Möhlav's method and had a melting point (71 - 72 °C) in agreement with that reported in the literature [14]. Its proton nuclear magnetic resonance spectrum showed $\delta$ = 5.08 (CH$_2$, singlet), while its mass spectrum led to $m/z$ (%) values of 212 (16, M$^+$), 106 (9), 105 (100), 77 (51), 65 (74) and 51 (21).

### 2.2. Irradiation and product studies

Irradiations were carried out on deaerated samples contained in Pyrex tubes, using a photochemical reactor fitted with 12-RPR-3000 lamps. Valerophenone in benzene was used as an actinometer, with the quantum yield for acetophenone formation (via the Norrish type II reaction) taken as 0.30 [15]. Quantitative product studies were carried out on a Perkin–Elmer model 8200 capillary gas chromatograph equipped with a 12 m BP-1 column and using an LCI-100 integrator. Product characterizations

were assisted by gas chromatography—mass spectrometry analysis on a Hewlett—Packard model 5995 system. With the exception of $\alpha$-(4-hydroxyphenyl)-acetophenone and/or $\alpha$-(2-hydroxyphenyl)-acetophenone, authentic samples of all other products were available and confirmed unequivocally our product assignments.

## 2.3. Phosphorescence

Spectra were recorded using a Perkin—Elmer LS-5 spectrometer equipped with a PE-3600 data station. Measurements in the zeolite Silicalite were carried out using the same technique as in previous work [9 - 11].

## 2.4. Laser photolysis

Deaerated samples (usually 1 ml) were contained in Suprasil cells made of 3 mm × 7 mm tubing. They were excited with the pulses (337.1 nm, about 8 ns, up to 10 mJ pulse$^{-1}$) from a Molectron UV-24 nitrogen laser. The signals, initially acquired by an R-7912 Tektronix transient digitizer, were transferred to a PDP-11/23 computer that controlled the experiment and provided suitable facilities for processing and storage of the data. Further details have been reported elsewhere [16].

## 3. Results and discussion

The absorption and phosphorescence spectra from II are very similar to those recorded from a wide range of aromatic ketones. In a 1:1 methylcyclohexane:isopentane glass at 77 K the triplet lifetime was 1.5 ms and the well-resolved phosphorescence spectrum showed the 0—0 band at 408 nm, corresponding to a triplet energy of 70.1 kcal mol$^{-1}$, *i.e.* between the values for acetophenone and benzophenone [17].

At room temperature solution II does not yield any detectable phosphorescence. Inclusion in the hydrophobic zeolite Silicalite, where I phosphoresces readily [9 - 11], failed to yield any luminescence. This result was rather surprising, since Silicalite should prevent conformation IIa; however, our product studies (see below) seem to be consistent with this observation.

Laser photolysis of II in various solvents at room temperature does not yield any detectable signals within the time resolution of our system (about 2 ns).

In order to determine the triplet lifetime for II we carried out a series of experiments using 1-methylnaphthalene (MN) as a triplet quencher. In these experiments triplet 1-methylnaphthalene (MN*) was readily formed as expected from the occurrence of triplet energy transfer according to

$$II^* + MN \xrightarrow{k_q} II + MN^* \tag{1}$$

TABLE 1

Quenching of triplet $\alpha$-phenoxyacetophenone by 1-methylnaphthalene at 300 K

| Solvent | $k_q\tau_T$ (M$^{-1}$) | $\eta^a$ (cP) |
|---|---|---|
| Acetonitrile | 1.7 | 0.35 |
| n-Heptane | 2.4 | 0.39 |
| Methanol | 1.1 | 0.55 |
| Benzene | 0.83 | 0.60 |
| Cyclohexane | 2.2 | 0.90 |
| Carbon tetrachloride | 1.1 | 0.97 |
| 2-Propanol | 1.1 | 1.8 |
| tert-Butanol | 3.0 | 3.3 |

$^a$Solvent viscosity.

Triplet 1-methylnaphthalene can be readily characterized through its absorption in the 420 nm region. These transient absorptions $A_{420}$ follow a Stern–Volmer type of dependence with the concentration of 1-methylnaphthalene, i.e.

$$\frac{1}{A_{420}} = \alpha + \frac{\alpha}{k_q\tau_T[MN]} \tag{2}$$

where $\tau_T$ is the triplet lifetime and $\alpha$ is a constant that incorporates instrumental factors as well as the yield of intersystem crossing for the substrate. The technique has been widely used in the characterization of short-lived triplets and those which are generally difficult to detect (see for example ref. 18). The values of $k_q\tau_T$ obtained (300 K) were usually around 1 - 3 M$^{-1}$ (see Table 1). Representative plots are shown in Fig. 1. These results suggest triplet lifetimes around 100 - 200 ps, since $k_q$ for these systems can be expected to approach diffusion control. These values are about one order of magnitude shorter than those determined before for $\beta$-phenylpropiophenone and $\beta$-(p-anisyl)-propiophenone (III) [6]; $\beta$-(p-anisyl)-propiophenone is probably a better analogue of II. We attribute the shorter triplet lifetime of II relative to I and III to conformational factors, specifically the elimination of methylene eclipsing interactions that must play a role in the cases of I and III when they achieve the conformation required for intramolecular deactivation. Similar effects have been observed in free-radical cyclizations, where substitution of —CH$_2$— for —O— can accelerate the reaction by over an order of magnitude [19, 20]. In the case of biradicals we have suggested [21] that a similar mechanism is responsible for the shorter lifetime when there is oxygen in the backbone (such as Paterno–Buchi biradicals) [22, 23] in comparison with their carbon analogues (Norrish type II biradicals) [24]. The effect is probably due to a higher rate of intersystem crossing in the biradicals for those conformations where the termini are in close proximity.

A considerable effort was put into attempts to detect the triplet state of II directly at low temperature (methanol, 190 K). Under these conditions the triplet states of I and III are readily detectable [6], with lifetimes in
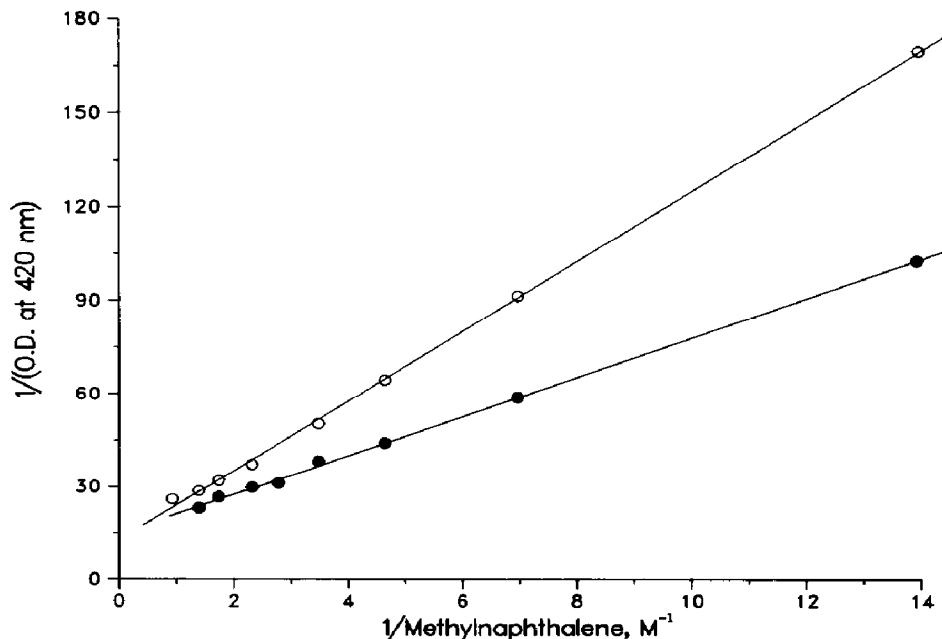
Fig. 1. Representative plots according to eqn. (2) for the quenching of α-phenoxyaceto-phenone triplets by 1-methylnaphthalene in *n*-heptane (○) and in carbon tetrachloride (●) at 300 K.

toluene of 13 ns and 23 ns respectively. In the case of **II** we detected very weak absorption signals in the 380 nm region which systematically followed the shape of the laser pulse. Under the conditions of these experiments a lifetime of 2 ns would have been measurable using deconvolution techniques; thus, we conclude that the triplet lifetime of **II** at 190 K in methanol does not exceed 1 ns.

In spite of this efficient triplet deactivation **II** is not photostable. Steady state irradiation experiments (see Section 2) led to a quantum yield of 0.0031 for acetophenone formation in benzene at about 305 K. Other products and quantum yields were as follows: phenol 0.003; 1,4-diphenyl-1,4-butanedione, $3 \times 10^{-4}$; α-(4-hydroxyphenyl)-acetophenone or its ortho isomer, $1.5 \times 10^{-4}$.

These products can be readily interpreted according to the mechanism given in Scheme 1 below.

It is perhaps surprising that phenoxy radicals should yield phenol as a final product in a system that does not contain any good hydrogen donors. However, the result is not unprecedented: other highly unreactive radicals (such as 2,2,6,6-tetramethylpiperidino [25]) tend to undergo very similar processes when they are formed in low steady state concentrations and their self-reaction is intrinsically an unfavourable process. We note that the product of ring addition (**VII**) has been written at the para position; however, the mass spectrum did not allow an unequivocal distinction between para or ortho coupling. The quantum yield of this product is also too low to justify an attempt to isolate it in any significant amount.
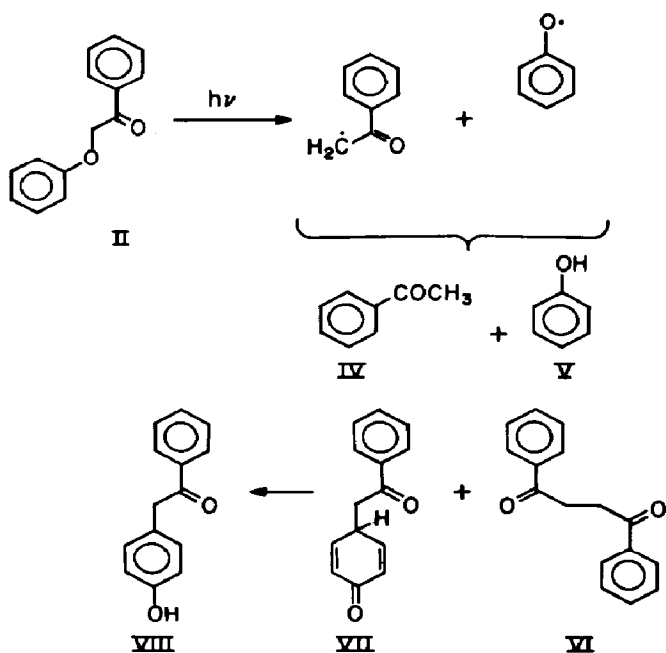
Scheme 1.

When the overall quantum yield of product formation of about 0.004 is combined with triplet lifetimes in the range 100 - 200 ps (and the radical back reaction is neglected), a rate constant for $\beta$ scission of triplet **II** of about $3 \times 10^7$ $s^{-1}$ is obtained. Thus, the expected triplet lifetime of **II** *if intramolecular quenching could be entirely prevented* would be only about 30 ns at room temperature. For comparison, $\alpha$-chloroacetophenone, which decays via Cl· elimination, has a triplet lifetime of about 50 ns at room temperature [26]. These results are entirely consistent with the failure to detect room-temperature phosphorescence when **II** was included in the zeolite Silicalite.

Quite clearly, $\beta$-phenoxy elimination is a very rapid process and its low quantum efficiency is simply a reflection of the ease with which the conformation for the competing intramolecular deactivation can be achieved. The quantum yield of the process is too low to allow the direct detection of phenoxy radicals in the laser flash photolysis experiments.

## 4. Conclusions

The intramolecular deactivation of the triplet state of $\alpha$-phenoxy-acetophenone is about one order of magnitude faster than that of its carbon analogues. The effect is attributed to the reduction of the number of hydrogen eclipsing interactions which play a role in the all-carbon (*i.e.* the $-CH_2-$ $CH_2-$ moiety) analogue. $\beta$ scission to yield phenoxy radicals is a remarkably facile process, occurring with a rate constant of about $3 \times 10^7$ $s^{-1}$ at room

temperature, but its quantum yield is limited to only about 0.004 as a result of its competition with the efficient intramolecular deactivation mentioned above.

## Acknowledgments

## References

1  P. J. Wagner, P. A. Kelso, A. E. Kemppainen, A. Haug and D. R. Graber, *Mol. Photochem.*, *2* (1970) 81.
2  F. R. Stermitz, D. E. Nicodem, V. P. Muralidharan and C. M. O'Donnell, *Mol. Photochem.*, *2* (1970) 87.
3  F. Bergmann and Y. Hirshberg, *J. Am. Chem. Soc.*, *65* (1943) 1429.
4  J. C. Scaiano, M. J. Perkins, J. W. Sheppard, M. S. Platz and R. L. Barcus, *J. Photochem.*, *21* (1983) 137.
5  T. Wismontski-Knittel and T. Kilp, *J. Phys. Chem.*, *88* (1984) 110.
6  J. C. Netto-Ferreira, W. J. Leigh and J. C. Scaiano, *J. Am. Chem. Soc.*, *107* (1985) 2617.
7  J. C. Scaiano, *J. Photochem.*, *2* (1973/1974) 81.
8  D. G. Whitten and W. E. Punch, *Mol. Photochem.*, *2* (1970) 77.
9  H. L. Casal and J. C. Scaiano, *Can. J. Chem.*, *62* (1984) 628.
10  H. L. Casal and J. C. Scaiano, *Can. J. Chem.*, *63* (1985) 1308.
11  J. C. Scaiano, H. L. Casal and J. C. Netto-Ferreira, *ACS Symp. Ser.*, *278* (1985) 211.
12  H. L. Casal, J. C. Netto-Ferreira and J. C. Scaiano, *J. Incl. Phenomena, 3* (1985) 395.
13  W. J. Leigh, personal communication, 1985.
14  R. Möhlav, *Berichte, 15* (1882) 2497.
    G. O. Cyrus, *J. Am. Chem. Soc.*, *71* (1949) 3460.
15  P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, N. H. Schott and R. G. Zepp, *J. Am. Chem. Soc.*, *94* (1972) 7480.
16  J. C. Scaiano, *J. Am. Chem. Soc.*, *102* (1980) 7747.
17  S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973, Section 2.
18  J. P. Bays, M. V. Encinas and J. C. Scaiano, *Macromolecules, 13* (1980) 815.
    G. Beck, G. Dobrowolski, J. Kiwi and W. Schnabel, *Macromolecules, 8* (1975) 9.
19  A. L. J. Beckwith, I. Blair and G. Phillipou, *J. Am. Chem. Soc.*, *96* (1974) 1613.
20  A. L. J. Beckwith and W. B. Gara, *J. Chem. Soc., Perkin Trans.*, *2* (1975) 795.
21  D. H. R. Barton, B. Charpiot, K. U. Ingold, L. J. Johnston, W. B. Motherwell, J. C. Scaiano and S. Stanforth, *J. Am. Chem. Soc.*, *107* (1985) 3607.
22  S. C. Freilich and K. S. Peters, *J. Am. Chem. Soc.*, *103* (1981) 6255.
23  R. A. Caldwell, T. Majima and C. Pac, *J. Am. Chem. Soc.*, *104* (1982) 629.
24  J. C. Scaiano, *Acc. Chem. Res.*, *15* (1982) 252.
25  J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, *95* (1973) 3228.
26  N. J. Bunce, K. V. Ingold, J. P. Landers, J. Lusztyk and J. C. Scaiano, *J. Am. Chem. Soc.*, *107* (1985) 5464.