

PHOTOCHEMISTRY OF α -PHENOXY-*p*-METHOXYACETOPHENONE¹

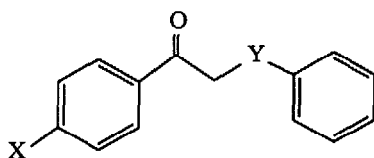
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Summary: The triplet state of the title compound decays by a competition of β -phenyl quenching and β -cleavage leading to $\text{CH}_3\text{OC}_6\text{H}_4\text{COCH}_2\cdot$ and phenoxy radicals. The latter process occurs with a quantum yield of 0.020.

The solution photochemistry of molecules such as β -phenylpropiophenone²⁻⁴ (I) and α -phenoxyacetophenone⁵ (III) is dominated by intramolecular triplet quenching processes involving the interaction of the excited carbonyl with the β -phenyl ring. We have now examined the photochemistry of α -phenoxy-*p*-methoxyacetophenone (IV) in order to explore the effect of the nature of the excited states on intramolecular deactivation processes, as well as on β -cleavage reactions of carbonyl triplets.

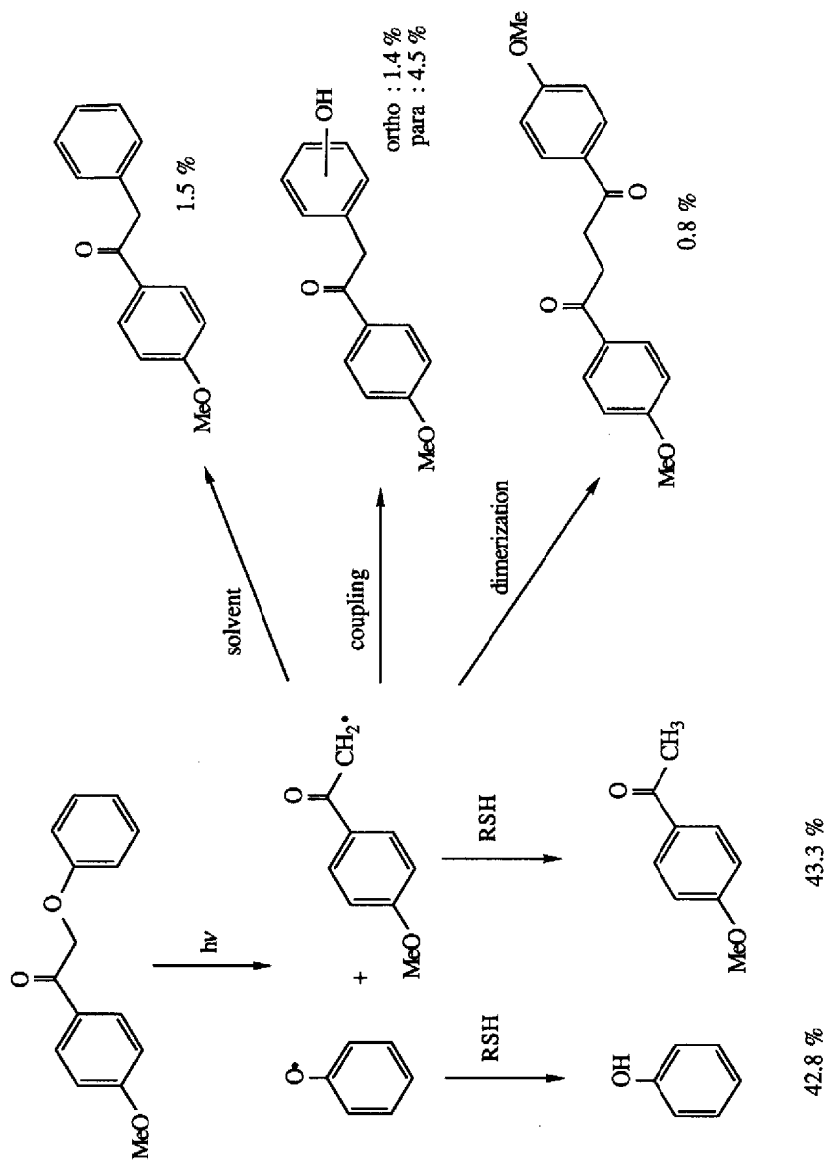


- I: X=H ; Y=CH₂
II: X=MeO ; Y=CH₂
III: X=H ; Y=O
IV: X=MeO ; Y=O

IV was prepared by reaction of α -bromo-*p*-methoxyacetophenone with phenol in alkaline media and had a melting point (63-64 °C) in agreement with that reported in the literature.⁶

Photolysis of IV at 300 nm (employing RPR-3000 lamps) in benzene or cyclohexane yields acetophenone and phenol as major products with quantum yields around 0.005. This very low value reflects the fact that many of the radicals formed undergo back reaction to generate the starting material. The back reaction can be largely prevented by adding a good hydrogen donor to the system. Thiophenol at 0.02 M concentration has been shown to be quite adequate.⁷ Under these conditions we obtained $\Phi=0.020$ in benzene. For comparison we have also repeated earlier work on III in the presence of thiol and obtained $\Phi=0.013$.⁸ The products and their distribution for the photolysis of IV in benzene containing thiophenol are given in Scheme I. In addition to the main products of reaction resulting from β -cleavage followed by scavenging by thiophenol, a number of minor products are also formed. These reflect addition to the solvent, ring (ortho and para) coupling of radicals and dimerization of $\text{CH}_3\text{OC}_6\text{H}_4\text{COCH}_2\cdot$ radicals.

Scheme I



Laser flash photolysis studies employing 337 nm excitation⁹ show triplet-triplet absorption from **IV** virtually identical ($\lambda_{\text{max}}=390$ nm) to those which are common for *p*-methoxybenzoyl chromophores in other molecules^{10,11}. The triplet lifetimes were too short to be easily monitored at room temperature, but triplet decay could be readily examined at temperatures around 200 K. The triplets are readily quenched by conjugated dienes and oxygen, as expected. Arrhenius studies for **IV** were carried out in various solvents and are summarized in Table I. Representative plots are shown in Figure 1. It should be noted that triplet lifetimes at room temperature are extrapolated values.

Table I. Arrhenius data for the decay of triplet **IV** in various solvents

Solvent	T-range(K)	E_a^a	$\log A^b$	τ_{293}^c	τ_{200}^c	$\eta_{200}(\text{cP})$
Methanol	190-236	3.46	11.0	3.8	56	6.2
2-Propanol	191-264	3.33	10.6	7.4	104	30.0
Toluene	179-219	4.25	12.2	0.9	26	1.9
CH_2Cl_2	178-192	2.42	10.2	3.9	27	1.3

^a In units of kcal/mol; ^b With A in units of s^{-1} ; ^c In nanoseconds, the subscript indicates the temperature (K).

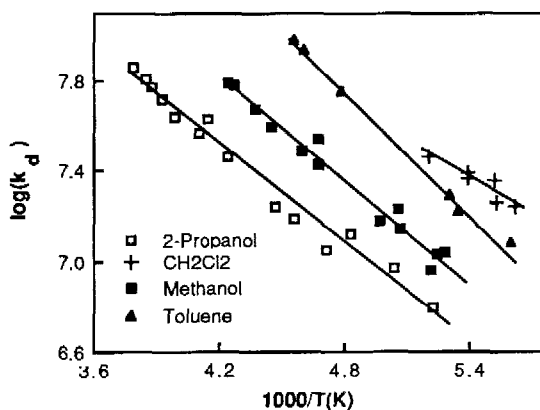


Figure 1. Temperature dependence of the rate constant for triplet decay (τ^{-1}) for **IV** in several solvents.

Given the triplet lifetimes and the quantum yields for photocleavage obtained in the presence of thiophenol, it is straightforward to estimate rate constants for β -cleavage; from this analysis we obtained rate constants of 1×10^8 and $5 \times 10^6 \text{ s}^{-1}$ for the β -cleavage of **III** and **IV**, respectively. The decrease in reactivity by a factor of 20 from **III** to **IV** compares with ratios between 30 and 130 obtained for *p*-methoxy substitution in

ketones that decay via Norrish Types I and II reactions¹² and by β -phenyl quenching.⁴ Just as in these cases, we interpret our results in terms of preferential n,π^* reactivity. That is, **IV** has a low lying π,π^* triplet state, but reactivity must take place predominantly from the thermally populated n,π^* state which lies nearby. Indeed, the fact that β -cleavage quantum yields for **III** and **IV** are so similar (0.013 versus 0.020) suggests that the state responsible for β -cleavage is the same one responsible for β -phenyl quenching. We therefore believe that both types of reactivity are mediated by the n,π^* triplet state.

Acknowledgements: Thanks are due to Mr. S.E. Sugamori for technical assistance.

References

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(Received in USA 20 October 1988)