Effect of Oxygen on the Photochemistry of 4-Methyl-1-phenylpentan-1-one

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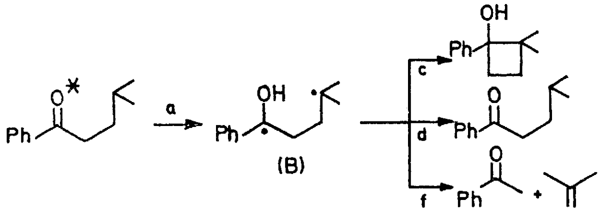
Summary Oxygen increases the yields of type II and photocyclization products in the photochemistry of 4-methyl-1-phenylpentan-1-one; the results are consistent with a biradical trapping mechanism.

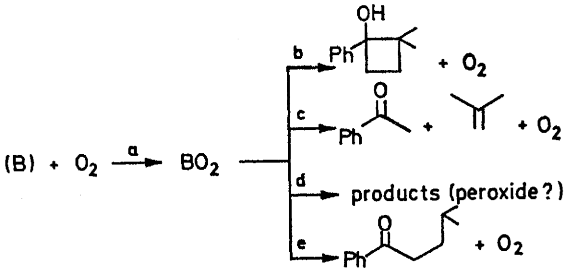
The photochemistry of 4-methyl-1-phenylpentan-1-one has been studied.[1,2] Reaction (1) shows the mechanism in degassed solutions, where * denotes a molecule in its lowest triplet state.



(1)

We have observed that if the solutions (in benzene, 25°) are not degassed, or if the photolyses are carried out under oxygen, the yields of acetophenone, cyclobutanols, and methylpropene are increased. The relative increase in these products shows no induction period and the ratios Φ/Φ^0 (quantum yields in the presence and absence of oxygen) are essentially independent of the irradiation time; it thus seems certain that the effect observed is not the result of secondary photolysis of photo-oxidation products. Neither can the results be explained by interaction between the ketone triplet and oxygen, since this would probably result in a decrease, rather than an increase in quantum yields; further, a simple calculation using the lifetime of the triplet,[2] the solubility of oxygen in benzene, and assuming a rate of interaction of 10^{10} $\text{M}^{-1}\,\text{s}^{-1}$, shows that $< 3\%$ of the triplets can be quenched by oxygen in the pressure range studied (200—600 Torr). The increase in product yield is accompanied by oxygen consumption and by an increase in ketone consumption which cannot be fully accounted by the increase in product yield. If the irradiated samples are treated with potassium iodide (in acetic acid media), iodine is produced, suggesting the presence of a peroxide. For oxygen pressures around 400 Torr Φ/Φ^0 is $1{\cdot}40 \pm 0{\cdot}05$ for acetophenone. The figure for the cyclobutanol is slightly higher than this, but still within experimental error.

We believe that reaction (2) can account for our results, where reaction (2e) has been tentatively included but we have no evidence for or against it. The product of reaction (2d) accounts for the 'excessive' ketone consumption and for the results of the experiments with potassium iodide; presumably this product is the hydroperoxide, $PhCH_2CH_2(Me_2)COOH$.



(2)

Our results are consistent with this mechanism if equation (3) holds. Further, preliminary kinetic studies,‡ suggest

$$\frac{k_{2b}+k_{2c}}{k_{2b}+k_{2c}+k_{2d}+k_{2e}} > \frac{k_{1c}+k_{1f}}{k_{1c}+k_{1d}+k_{1f}} \qquad (3)$$

that in the pressure range studied reactions (**1**) and (**2**) compete for product formation.

Our results support the biradical mechanism, and we hope that the kinetic studies will provide a direct measure of the lifetime of (B). The results also suggest that the use of oxygen as a quencher in systems involving intramolecular abstraction should be avoided and any results obtained in this way used with reserve.

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‡ Plots of $\Phi_{II}/(\Phi_{II}-\Phi_{II}^{0})$ *vs.* $[O_2]^{-1}$ are linear (Φ_{II} = quantum yield of acetophenone formation).

[1] J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 1968, **90**, 6584.
[2] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 1972, **94**, 3852.