Energy Wasting Mechanisms in Benzoate Photochemistry

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Summary Reversible γ-hydrogen abstraction and reversible β-carbon–oxygen cleavage are generally *not* significant factors in the low quantum yields for product formation observed in benzoate photochemistry.

THE photochemistry of aromatic ketones bearing hydrogen atoms in the γ-position is believed to involve γ-hydrogen abstraction (Type II reaction) to form a biradical intermediate.[1] The biradical formation is reversible, accounting for a major fraction of the inefficiency of photodecomposition.[1] Recently, this type of argument has been extended to account for the very inefficient photochemistry of the corresponding aromatic esters.[2] As part of an extended study of ester photochemistry, evidence has accumulated which shows that reversible biradical formation is *not* a significant cause of the inefficiency observed in benzoates, at least through the triplet state.

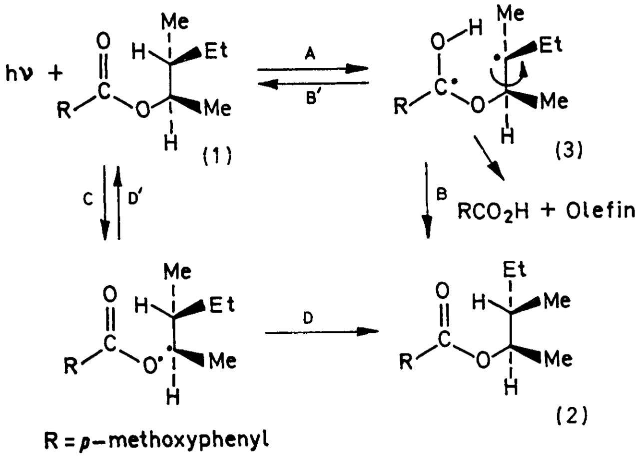
Model compounds *erythro*- (1) and *threo*-1,2-dimethylbutyl *p*-methoxybenzoate (2) were synthesized from the appropriate acid chloride and alcohols and purified (99%) by g.l.c.† Outgassed pentane and acetonitrile solutions (0·14—0·19 M) of each compound were photolysed for 6—9 h in a Rayonet reactor equipped with 15 G8T5 low-pressure mercury lamps. The undecomposed ester was then isolated and analysed by n.m.r. spectroscopy for isomerization to its diastereomer, giving the results shown in the Table.

TABLE

Ester	Solvent	Conversion into acid[a]	Φ_{Acid}	Isomerisation	$\Phi^{\text{b}}_{\text{Isom}}$
(1)	Acetonitrile	5·4%	0·011	1 ± 2%	0·008
(2)	Acetonitrile	6·4%	0·013	2 ± 2%	0·008
(1)	Pentane	2·7%	0·010	0 ± 2%	0·008
(2)	Pentane	3%	0·01	2 ± 2%	0·008

[a] Determined by g.l.c. analysis of the methyl ester prepared with diazomethane; [b] Maximum undetectable quantum yield of isomerization. The actinometer was (0·2 M) 2-ethoxyethyl phenylacetate in hexane.[3]

Photodecompositions of benzoate esters are typically very inefficient with greater than 98% of the absorbed light yielding no products.[2,3] Compounds (1) and (2) are no exceptions, as indicated by the low quantum yields of the major product, *p*-methoxybenzoic acid (Table). It has been suggested that this inefficiency could be due, in part, to reversible formation of biradical (3), as shown above. If significant reversible biradical formation is occurring, ester (1) should isomerize to its diastereomer (2) and *vice versa* as long as bond rotation is considerably faster than biradical disproportionation through pathways B and B′. Considerable evidence exists to show that triplet 1,4-biradicals do fulfil this requirement[4] but photochemically generated singlet 1,4-biradicals may not.‡ Since a reasonable fraction of energy loss and acid formation does occur through the ester triplet,§ the limits placed on photoisomerization of esters (1) and (2) in two solvents of widely differing polarity (Table) show reversible biradical formation accounts for <2% of the total energy loss and <8% of the energy loss through the triplet state in these systems. It should be noted that these limits of error still allow product formation through a triplet biradical, as found in ketone photochemistry; however, biradical collapse *must not* excessively favour pathways B and B′ over product formation.



(Actually pathway D gives the enantiomer, but since the reactants are racemic, it is experimentally undistinguishable.)

It has been suggested that β-carbon–oxygen cleavage (pathway C) is an important product-forming mechanism in some ester photochemistry.[7] Efficient reversible β-cleavage (pathways D and D′) could account for inefficient benzoate ester photochemistry just as α-cleavage has been shown to account for inefficiencies in ketone photochemistry.[8] On account of the unique structures of (1) and (2), the discussion above regarding reversible biradical formation holds equally well for energy losses through reversible β-cleavage. In this case, however, both the singlet and triplet states would be expected to lead to isomerization.[8] The results (Table) show that < 2% of the energy loss can be through reversible β-cleavage.

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† Qualitatively similar results were obtained for the unsubstituted benzoates in pentane.

‡ The situation regarding Type II elimination through carbonyl singlet states is not totally clear.[4–6]

§ Based on data for isobutyl *p*-methoxybenzoate were $\Phi^{\text{Triplet}}_{\text{Acid}} = 0{\cdot}0014$; $\Phi_{\text{ICS}} = 0{\cdot}21$.[2]

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