COMPARISONS OF COMBINATION-DIFFUSION COMPETITIONS FOR t-BUTOXY-BENZOLYLOXY RADICAL PAIRS

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We wish to report the results of our studies on the (re)combination efficiencies of

t-butoxy-benzoyloxy radical pairs generated in hexane solution near room temperature using

direct and acetophenone sensitized photolysis of carbonyl oxygen-18 labelled t-butyl per-

benzoate (1) as the source of the radical pair. The question which we seek to answer is to

what extent does the spin multiplicity or an intervening nitrogen molecule affect the combi-

nation efficiency of the same formal radical pair. The conditions of solvent and temperature

were chosen to match our previous[1] work on 0-benzoyl-0'-t-butyl hyponitrite. Our results

also show significant differences in the overall course of the direct and sensitized reac-

tions. A summary of product studies on the three modes of generation of the pair (2) is

given in Table I.

TABLE I

Products[a] in Hexane Solution

		Acid	CO_2	t-BuOH	$(CH_3)_2CO$	Esters[b]	5
3	Δ[c]	0.21	0.67	0.84	0	0	0
1	hν (Direct)[d]	0.11	0.86	0.87	0.01	0.04	0.05[f]
1	hν (Sen.)[e]	0.26	0.71			0.08	0.01

a) Moles/mole 1 after complete destruction of perester. Benzoic acid by wt., carbon
dioxide by wt. uptake of Ascarite, liquids by glpc. b) Hexyl benzoates by nmr, ir and
glpc comparision with authentic samples. c) Hyponitrite 3 thermolysis, ref. 1. d)
Direct photolysis of 0.1 M solutions of 1 using a 200 watt high pressure Hg lamp and a
quartz reaction vessel. e) Acetophenone sensitized reaction under identical conditions
as c. Zero order kinetics were observed for more than 50% reaction in both cases.
f) 0.08 in hexane at 20% reaction, 0.20 in paraffin oil at 100% reaction. Separate
control experiments showed this product was partially consumed under the conditions
used.

The isolation of t-butyl phenyl ether (5) and hexyl benzoates indicate that the photo-

lytic reactions are not precisely analogous to the hyponitrite (3) decomposition in going

exclusively via the desired radical pair (2). The ester products suggest a minor component

from a chain induced reaction involving a hexyl radical as the chain carrier. The ether

product could be the result of a direct cyclic reaction of the perester excited state. However, the increase in the yield of this product in the more viscous paraffin oil solvent suggests cage combination of phenyl t-butoxy radical pairs (4). Such products are not detected in the hyponitrite reaction and are not expected of a "normal" benzoyloxy radical because of its slow rate of decarboxylation.[2]

The higher ratios of carbon dioxide to benzoic acid (Table II) in the photolyses, compared with the hyponitrite (3) reaction, give further indication of a second carbon dioxide forming pathway which is quantitatively more important than the ether yield would indicate. Assuming the carbon dioxide:acid ratio for the hyponitrite represents the normal behavior of free benzoyloxy radicals, one can estimate[3] the extent of the additional carbon dioxide forming reaction. The results of this analysis are also included in Table II.
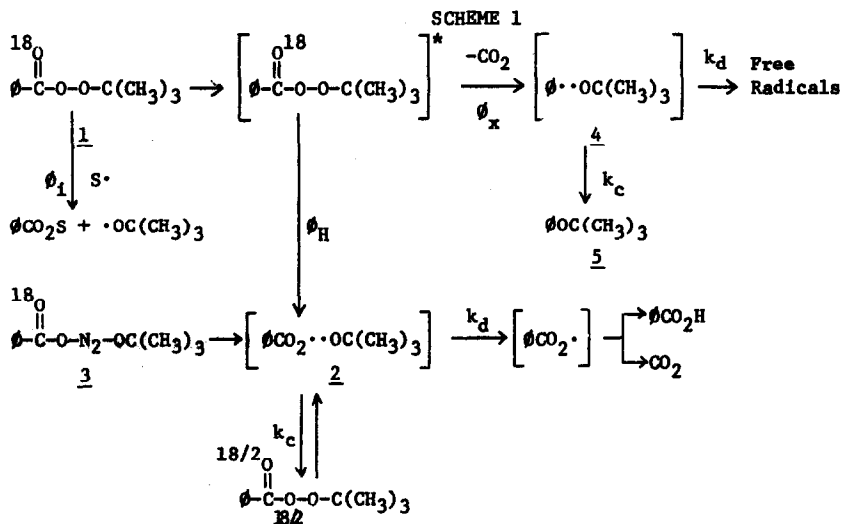
TABLE II

	CO_2/Acid	ϕ_H [a]	ϕ_1 [b]	ϕ_x [c]	$f_{rxn.}$ [d]	$f_{sc.}$ [e]	$f_{comb.}$ [f]
3 Δ	2.3	(1.00)	0	0	1.00	(0.98)[g]	0.089
1 hv (Direct)	7.8	0.36	0.04	0.61	0.46	0.041	0.177
1 hv (Sen.)	2.7	0.86	0.08	0.10	0.40	0.038	0.080

a) Fraction reaction proceeding through 2. b) Fraction reaction proceeding via hexyl radical induced decomposition as indicated by ester product yield. c) Fraction reaction proceeding by direct CO_2 formation. See 3. d) Total fraction reaction when perester was (re)isolated. e) Fraction (re)isolated perester which had randomized oxygen atoms. f_{sc}= [at. % x s^{18}O (starting material)]/[2 x at. % xs^{18}O (p-nitroperbenzoate cleavage product)]. f) Fraction 2 which (re)combines after correction for ϕ_x and ϕ_1, Scheme 1 and equation 1. g) This figure is the fraction of the 13% yield of perester, isolated from 3 in carbon tetrachloride, which had randomised oxygen atoms (ref. 1).

Perester, which was originally labeled with ca. 5% excess oxygen-18 in the carbonyl position, was reisolated from the photolytic reactions after ca. 50% reaction. This material was cleaved with methoxide[1] and converted to the t-butyl p-nitroperbenzoate derivative which was isolated in pure form by thin layer chromatography. The oxygen-18 content of the carbon dioxide from the decomposition of this derivative reflects the fraction of the recovered t-butyl perbenzoate which had scrambled the oxygen atoms in the carboxylate group. These results are also included in Table II.

The analysis of these data requires a normalization to the fraction of the total reaction which proceeds via the desired radical pair (2). Scheme 1 and the usual steady state assumptions give equation 1 which accomplished this normalization analytically.

SCHEME 1

$$\overset{\overset{18}{\underset{\|}{O}}}{\phi\text{-C-O-O-C(CH}_3)_3} \longrightarrow \left[\overset{\overset{18}{\underset{\|}{O}}}{\phi\text{-C-O-O-C(CH}_3)_3}\right]^* \xrightarrow[\phi_x]{-CO_2} \left[\phi\cdot\cdot OC(CH_3)_3\right] \xrightarrow{k_d} \begin{array}{l} \text{Free} \\ \text{Radicals} \end{array}$$

$$\phi_1 \downarrow \underset{S\cdot}{\overset{1}{}}$$

$$\phi CO_2 S + \cdot OC(CH_3)_3 \qquad \qquad \phi_H \qquad \qquad 4 \downarrow k_c$$

$$\phi OC(CH_3)_3$$
$$\underline{5}$$

$$\overset{\overset{18}{\underset{\|}{O}}}{\phi\text{-C-O-N}_2\text{-OC(CH}_3)_3} \longrightarrow \left[\phi CO_2\cdot\cdot OC(CH_3)_3\right] \xrightarrow{k_d} \left[\phi CO_2\cdot\right] \begin{array}{l} \rightarrow \phi CO_2 H \\ \rightarrow CO_2 \end{array}$$
$$\underline{3} \qquad\qquad\qquad\qquad \underline{2}$$

$$18/2 \overset{\overset{O}{\underset{\|}{}}}{} \quad k_c \downarrow\uparrow$$
$$\phi\text{-C-O-O-C(CH}_3)_3$$
$$\underline{18/2}$$

$$\left[\frac{\ln(1-f_{rxn.})}{\ln(1-f_{sc.})} - \frac{(\phi_1+\phi_x)}{\phi_H}\right]\left[\frac{\phi_H}{\phi_H+\phi_x+\phi_1}\right] = \frac{1}{f_{comb.}} - 1 \qquad\qquad (1)$$

Equation 1 relates the measured quantities (Table II) to the ratio of the phenomenologi-
cal rate constant (k_d) for separation of the pair ($\underline{2}$) to that for combination (k_c). The
k_d/k_c ratios are related to the fraction combination as the reciprical plus one. The results
indicate that the pair formed in the sensitized reaction gives only about 50% of the re-
combination which occurs in the direct photolysis. The nitrogen molecule appears to reduce
the combination efficiency to almost the same extent. The magnitudes of these reductions
are very similar to those reported for the sensitized vs the direct photolysis of N-(1-cyano-
cyclohexyl)pentamethyleneketenimine[4] and the thermolysis of azo-bis-cyclohexylnitrile vs.
the ketenimine[5]. They indicate somewhat larger differences than deduced by Kiefer and
Traylor[6] for t-butoxy pairs formed in analogous photolytic and deaminative reactions. Our
results also agree, in a semiquantitative way, with those reported by Kochi and Sheldon.[7]
The fraction recombination which we find implies a quantum yield for photodestruction of
t-butyl perbenzoate which is, within experimental error, unity. This is largely due to the
dominance of the direct decarboxylative path. The mechanism proposed for the formation of
the ether products (Scheme 1) implies that perbenzoate photolysis should show CIDNP effects
similar to those already observed in benzoyl peroxide photolyses.[8] The CIDNP effects which

are observed during the hyponitrite (3) decomposition do not involve products of the phenyl radicals as expected from the absence of the ether.

The most important feature which the present work adds to the previous investigations of peroxide photolysis is the quantitative analysis of the total reaction in terms of the fraction proceding via the benzoyloxy species (2). This analysis is possible here because of the previous results on the pair generated from the hyponitrite which give an independent measure of the abstraction-β-scission ratio for the free benzoyloxy radicals. Without this type of analysis, the directly measured scrambling rates are impossible to interpret. The scrambling fractions directly measured for the two types of photoprocesses are much nearer to each other than the normalized values. This is due to the smaller contribution from the process which bypasses the benzoyloxy radical in the sensitized vs. the direct reaction. Concerted fragmentation of the excited state of the perester[9] or formation of an excited benzoyloxy radical[10] could explain the "abnormal" process. The present results do not allow a distinction between these possibilities.

Acknowledgment:

<div align="center">REFERENCES</div>

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