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Search for chemiluminescence from *tert*-butyl 9-fluorenyl peroxide and 9-fluorenyl hydroperoxide [1]

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Abstract

Thermolysis of solutions of 9-fluorenyl *tert*-butyl peroxide (BOOF; decalin, 137–162 °C, $\log k/\mathrm{s} = 14.28 \pm 0.02 - (144.2 \pm 2\ \mathrm{kJ})/\theta$) or 9-fluorenyl hydroperoxide (FOOH; benzonitrile, 152 °C) did not give detectable chemiluminescence. In contrast, the induced decomposition of 9-fluorenyl hydroperoxide with *tert*-butoxyl radicals at room temperature was highly chemiluminescent. The different behavior was ascribed to the decreased fluorescence of 9-fluorenone at elevated temperatures. Solutions of *tert*-butyl diphenylmethyl peroxide (152 °C) were weakly chemiluminescent in the presence of a fluorescence sensitizer. The photolysis and base-induced decompositions of BOOF were studied. © 1997 Elsevier Science S.A.

Keywords: Chemiluminescence; Peroxide radicals; Hydroperoxide radicals

1. Introduction

9-Fluorenyl *tert*-butyl peroxide (BOOF) was of interest (a) as a potentially chemiluminescent polymerization initiator, and (b) as part of our studies of electronically excited states from free-radical precursors [1–3]. Electronic emission from singlet excited formaldehyde has been reported from the thermolysis of dimethyl peroxide in the gas phase [4]. Since 9-fluorenone has a fluorescence quantum yield about 10^4 higher than most other carbonyl singlets, particularly aliphatic ones, we anticipated that free-radical reactions generating even small yields of excited singlet 9-fluorenone could be studied easily without the conventional addition of fluorescent sensitizers.

2. Materials and methods

2.1. Instrumentation

IR and NMR spectra were obtained with commercial FT instruments. Liquid chromatography was carried out with a 0.46×25 cm C_{18} column (Rainin Instrument Co.) eluting with 35:55:10 MeCN:MeOH:H_2O at 2 ml min^{-1}, with UV detection (HP Model 1050 at 294 (BOOF) or 234 nm ($Ph_2CHOOBu$-t). Decomposition kinetics on BOOF were carried out in serum-capped pyrex tubes previously washed with 5% Me_2SiCl_2 in toluene and dried. The solutions of peroxides (5 ml) were flushed with N_2 for 10 min before immersion in an oil bath maintained at ± 1 °C with a Therm-O-Watch Model L6110. The temperature of the bath was measured precisely with an iron-constantan thermocouple. Aliquots were removed under positive N_2 pressure at intervals for immediate analysis until >90% of the peroxide was consumed. The data are given in Table 1.

The apparatus for measurement of chemiluminescence at elevated temperatures was similar to ones described elsewhere [5]. The solutions for examination, contained in quartz tubes with Teflon caps, were flushed with N_2 for 10 min and then inserted into the heated aluminum block of the apparatus.

Chemiluminescence near ambient temperatures was measured from solutions in capped glass vials in a thermostatted Turner Designs Model 20e instrument. Reagent concentra-

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[2] From the masters thesis of L.Z., Michigan Technological University, 1996.

Abbreviations: BHN, di-*tert*-butyl hyponitrite; BOOF, *tert*-butyl 9-fluorenyl peroxide; CL, d(hν)/dt; decalin, decahydronaphthalene; e, fraction of radicals from BHN escaping solvent cage; FO, 9-fluorenone; FOOH, 9-fluorenyl hydroperoxide; R = 8.31 kJ/mole; θ = 2.303 RT

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Table 1
Decomposition of BOOF in decalin

$[BOOF]_0$mM	T °C	t1/2, min	10^5k/s*	%cage†	*t*, min†
46.5	137	143	8.1 ± 0.4	64 ± 5	27
46.5	152	31.5	36.6 ± 0.2	55 ± 3	22
249	152	28.5	40.7 ± 2.8	78 ± 1	22
46.5	167	8	145 ± 5	56 ± 1	10
41.5	25‡	5.7	–	56	5

* Average of two determinations.

† $[\text{9-Fluorenone}]_t/([BOOF]_0 - [BOOF]_t)$ at earliest sampling time, *t*.

‡ UV photolysis.

tions were varied by addition of weighed solid or a concentrated stock solution to 4 ml of the other components.

Photolysis of solutions of BOOF was carried out in 5 mm O.D. pyrex tubes that were degassed three times (− 196 °C, 0.01 torr) and sealed off with a torch. The tubes were irradiated all at once with unfiltered, focused light from a 500 w Hg-arc lamp in an Oriel Model 6188 housing, at a distance of 55 cm. Individual tubes were removed at various times for analysis.

2.2. Chemicals

Decalin was purified by stirring overnight with sulfuric acid followed by washing with water, drying (Na_2SO_4), and distillation. Benzonitrile was redistilled before use. An acidic fluoropolymer, Nafion-H, was obtained from Aldrich Chemical Co. Other reagents were from conventional sources or were synthesized by procedures in the literature.

2.2.1. tert-Butyl 9-fluorenyl peroxide (BOOF) [6]

9-Diazofluorene (1.03 g, 5.36 mmol) and *tert*-butyl hydroperoxide (extracted from 70% aqueous solution with CH_2Cl_2, dried with sodium sulfate, and concentrated under reduced pressure; 5 ml) were dissolved in CH_2Cl_2 (50 ml), cooled to 0 °C in an ice-salt bath, and 50 μl of $HClO_4$ in CH_2Cl_2 (2.3 M, extracted from freshly-prepared 70% aqueous $HClO_4$-25% fuming H_2SO_4 [7]. CAUTION: this mixture of acids is unstable [7]) was added in one portion. The mixture was stirred until there was no further change in color, washed three times with H_2O, and concentrated (aspirator) to an orange oil (1.37 g). Addition of hexanes precipitated a yellow solid (9-fluorenol by IR and NMR) that was removed by centrifugation. The supernatant was concentrated (aspirator) to a sticky red-brown solid that was crystallized twice from MeOH to give light yellow crystals, 0.18 g (14%), mp 97–99 °C. Further crystallization gave a colorless product, mp 96–97 °C. IR (KBr pellet) 3052, 2969, 1461, 1377, 1362, 1193, 1183, 1018, 765, 740, 723 cm^{-1}. UV (MeCN) λ_{max}, nm ($\log_{10} \epsilon$) 274 (3.980), 228 (4.188), 210 (4.449). ^{1}H-NMR ($CDCl_3$): δ1.31 (s, 9 H), 5.92 (s, 1 H), 7.22–7.40 (mlt, 4 H), 7.10–7.74 (dd, *J* = 8 Hz, 4 H). EIMS (%) 254 (M^+,5), 181(24), 165(100), 73(3), 57(8), 43(7).

The reaction was repeated on a 0.8 mmol scale, and a 0.079% solution of the crude product in i-octane was subjected to chromatographic analysis. Comparison with stock solutions indicated 25 and 60% yields, respectively, of 9-fluorenol and BOOF. Reaction of 9-fluorenol itself with *tert*-butyl hydroperoxide under these conditions for 3 h/25 °C gave 23% BOOF together with 9-fluorenone and about 45% starting alcohol (HPLC).

2.2.2. tert-Butyl diphenylmethyl peroxide

Diphenyldiazomethane (1.00 g, 5.00 mmol), CH_2Cl_2 (50 ml), *tert*-BuOOH (2 ml), and anhydrous $HClO_4$ in CH_2Cl_2 (200 μl) were reacted and worked up as described for BOOF. Concentration of the hexane solution gave a yellow oil that was purified by chromatography (silica gel, 1:1 hexanes: $CHCl_3$). Fractions containing only product were identified by HPLC, combined, and concentrated to give an off-white solid, 0.19 g (15%), mp 30–34 °C. Analysis (HPLC) of the crude yellow oil from a second reaction mixture indicated a 50% yield of peroxide. ^{1}H-NMR ($CDCl_3$) : δ1.24 (s, 9 H), 5.97 (s, 1 H), 7.25–7.35 (mlt, 10 H). Davies and Feld prepared this compound as a liquid by a conventional route [8].

2.2.3. 9-Fluorenyl hydroperoxide (FOOH)

The compound was prepared in 40% crude yield from diazofluorene and 70% hydrogen peroxide by the procedure of Kropf and Winter [9]. Recrystallization from 1:1 toluene:hexane gave an off-white solid, mp 90 °C (rep. [9] 92–4 °C). ^{1}H-NMR ($CDCl_3$): δ5.96 (s, 1 H), 7.29–7.49 (mlt, 4 H), 7.67–7.83 (mlt, 4 H), 7.93 (s, 1 H). 9-Fluorenol was detected as a persistent impurity (5–10%) by its 9-CH at δ5.56 (d, *J* = 10 Hz), and it had the same chromatographic retention time as the hydroperoxide.

3. Results and discussion

3.1. Experiments with BOOF

The yields of BOOF (and *tert*-butyl diphenylmethyl peroxide) from the diazo precursor and *tert*-butyl hydroperoxide in the reaction mixtures were higher than reported by other routes, but isolated yields were low because of tarry by-products. The synthesis was not improved when the anhydrous perchloric acid was replaced with sulfuric acid, an acidic fluoropolymer [10], or with an organometallic catalyst (η_5-C_5H_5) Fe^+ (CO) (PPh_3) (THF) that catalyzes certain reactions of diazo compounds [11].

Preliminary kinetic trials with BOOF gave irregular results, and we inferred that the glass surfaces were catalyzing the decomposition. In a test for basic catalysis, addition of triethylamine (60 μl) to acetonitrile (8 ml) 0.425 M in BOOF instantly gave a yellow solution containing 88% of the theoretical 9-fluorenone (uv, hplc). After silanizing the glass vessels, reproducible first-order decays of BOOF were obtained under all conditions (Table 1 and Fig. 1). The initial point deviated from the exponential fit due to the time required for temperature equilibration. A small contribution

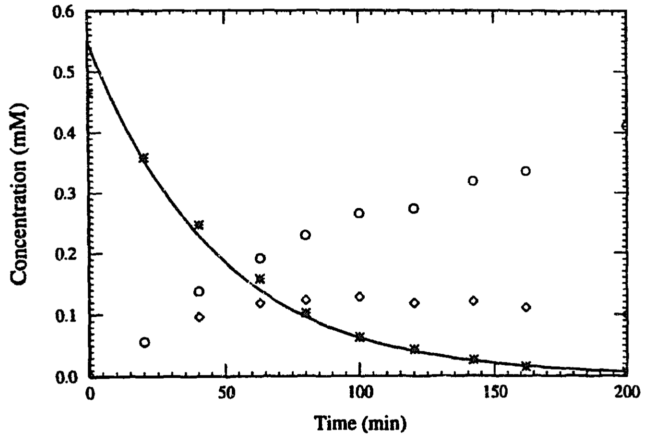

Fig. 1. Thermolysis of BOOF, showing BOOF (*), FOH (◇), FO (○), and fitted exponential curve. The initial conditions are given in Table 1, second entry.

from radical-induced decomposition was indicated at the higher concentration (152 °C) by the shorter half-life. The activation parameters, determined from the low-concentration runs, were $Ea = 144.2 \pm 2$ kJ/mole, and $\log A/s = 14.28 \pm 0.02$. The activation energy is close to those of other simple peroxides [12]. The value of $\log A$ is somewhat lower and indicates a tight transition state [13], or contribution from a small amount of induced decomposition.

Photolysis of BOOF in degassed decalin gave 9-fluorenone and 9-fluorenol as major products (Fig. 2). Rather surprisingly, the photolytic loss of BOOF could be described fairly well by pseudo-first order kinetics to 99.5% consumption. The approximate cage effect (56%), calculated from the composition early in the photolysis, is close to the values obtained by thermolysis. The mass balance (Fig. 2) is not as good as for thermolysis (Fig. 1), although there were no other strongly absorbing products in the HPLC trace (294 nm) that might account for the discrepancy.

The yield of 9-fluorenol reached an approximately constant concentration during thermolysis, which we ascribe to its oxidation to 9-fluorenone by attack of cage-escaped radicals. During photolysis (Fig. 2), the yields of 9-fluorenol fell even lower than during thermolysis, possibly because of its removal by both free-radical and direct [14] photolytic processes.

To our disappointment, no chemiluminescence could be detected from thermolysis of solutions of BOOF at 150 °C in decalin, or in the more polar benzonitrile, in which the fluorescence quantum yield of 9-fluorenone is higher [15]. Qualitative studies with a hand-held UV source showed that the fluorescence from solutions of the ketone in both solvents was largely extinguished at 150 °C.

Very weak chemiluminescence could be observed from solutions of the related *tert*-butyl diphenylmethyl peroxide (22 mM) and 32 mM in 9,10-diphenylanthracene (but not with 9,10-dibromoanthracene or without sensitizer) in benzonitrile at 148 °C. The luminescence decay was fitted to an exponential rate law (10^4 k/s = 2.9, 2.5).

3.2. Experiments with 9-fluorenyl hydroperoxide (FOOH)

If the lack of chemiluminescence from thermolysis of BOOF was due to low fluorescence of the excited ketone, then other sources of excited 9-fluorenone should also be non-luminescent at elevated temperatures. A dioxetane precursor was considered, but we were unsuccessful in attempts to add singlet molecular oxygen or triphenyl phosphite ozonide to bis-9, 9′-fluorenylidene (N. Xu, unpublished work). We then prepared FOOH, which should give peroxyl radicals upon thermolysis. In agreement with our hypothesis, no chemiluminescence could be observed at elevated temperatures from solutions under the same conditions as BOOF.

However, free-radical induced decomposition of FOOH with di-*tert*-butyl hyponitrite (BHN) *at room temperature* gave easily detectable light emission (Figs. 3 and 4). In these experiments the initiator does not decay significantly during the measurement times. The induced decomposition is assumed to result from abstraction of the hydroperoxyl

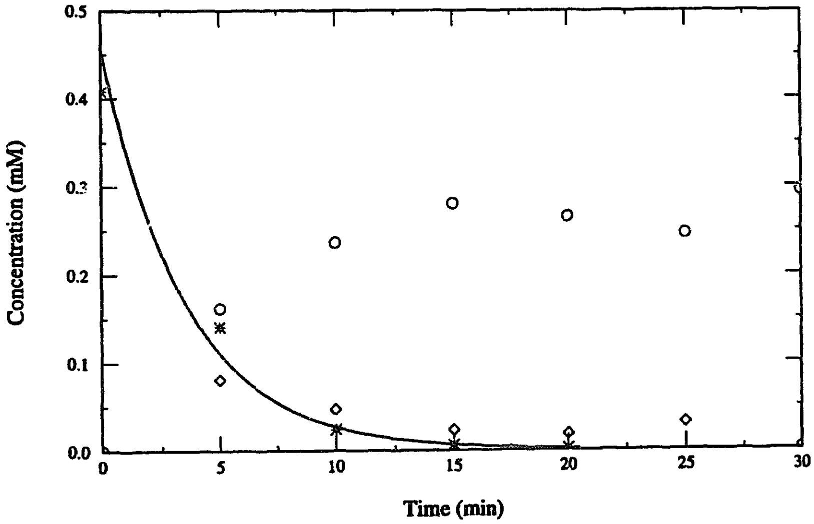

Fig. 2. Photolysis of BOOF (initially 0.415 mM in N_2-flushed decalin). Symbols as in Fig. 1.

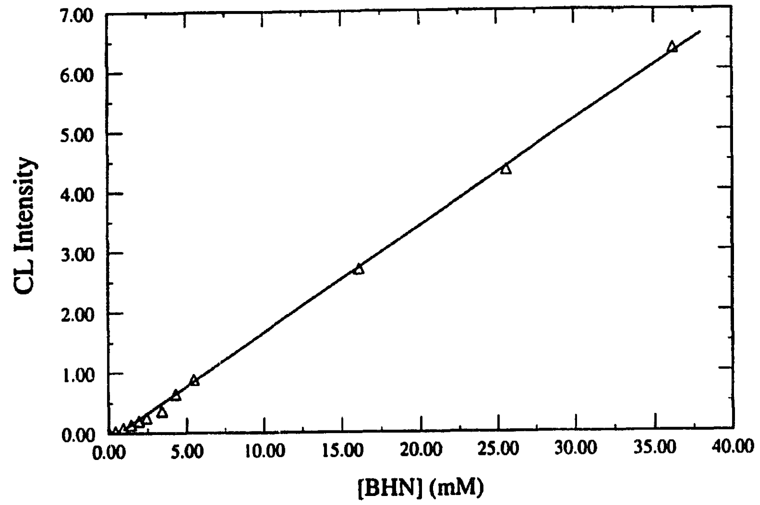

Fig. 3. Relative chemiluminescence vs. BHN in benzene 9.20 mM in FOOH at 26 °C.

H-atom in the following sequence, giving the ultimate products 9-fluorenone (FO) and 9-fluorenol FOH):

$$\text{t-BuON=NOBu-t} \rightarrow \text{2t-BuO}\cdot + N_2 \tag{1}$$

$$\text{t-BuO}\cdot \rightarrow \text{FOOH} \rightarrow \text{FOO}\cdot + \text{t-BuOH} \tag{2}$$

$$2\text{FOO}\cdot \rightarrow \text{FO} + \text{FOH} + O_2 \tag{3}$$

$$2\text{FOO}\cdot \rightarrow\rightarrow h\nu \tag{4}$$

Assuming that the other major fate of the butoxyl radical is β-scission, followed by termination of methylperoxyl radicals, the significant reactions are:

$$\text{t-BuO}\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \tag{5}$$

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot \tag{6}$$

$$2CH_3O_2\cdot \rightarrow CH_3OH + CH_2O + O_2 \tag{7}$$

$$CH_3O_2\cdot + \text{FOO}\cdot \rightarrow \text{FOH} + CH_2O + O_2 \tag{8}$$

$$CH_3O_2\cdot + \text{FOO}\cdot \rightarrow \text{FO} + CH_3OH + O_2 \tag{9}$$

$$CH_3O_2\cdot + \text{FOO}\cdot \rightarrow\rightarrow h\nu \tag{10}$$

In this sequence reactions Eqs. (4) and (10) represent the rate-limiting production of excited states that give detectable light emission. If we assume that the yield of detectable chemiluminescence is about the same regardless how each 9-fluorenylperoxyl radical terminates, i.e. $k_4/(k_4+k_3) \approx k_{10}/(k_8+k_9+k_{10})$, then for initial conditions we can derive:

$$CL \equiv d(h\nu)/dt = \frac{2ek_1k_2[\text{BHN}][\text{FOOH}]}{k_5 + k_2[\text{FOOH}]}$$

and

$$1/CL = \frac{k_5}{2ek_1k_2[\text{BHN}][\text{FOOH}]} + \frac{k_2}{2ek_1k_2[\text{BHN}]}$$

For a plot of 1/CL vs. 1/FOOH, the ratio of slope to intercept is simply k_5/k_2. The data are in agreement with this derivation (Fig. 5; $r^2 = 0.997$), and lead to $k_5/k_2 = (9 \pm 4) \times 10^{-4}$ M. We may calculate this quantity from a value for first-order decay of t-BuO· of $k_5 = 2.3 \times 10^5$ s^{-1} in the literature [16], together with a value of $k_2 = 2.5 \times 10^8$ M^{-1} s^{-1} for the analogous reaction of t-BuO· with t-BuOOH

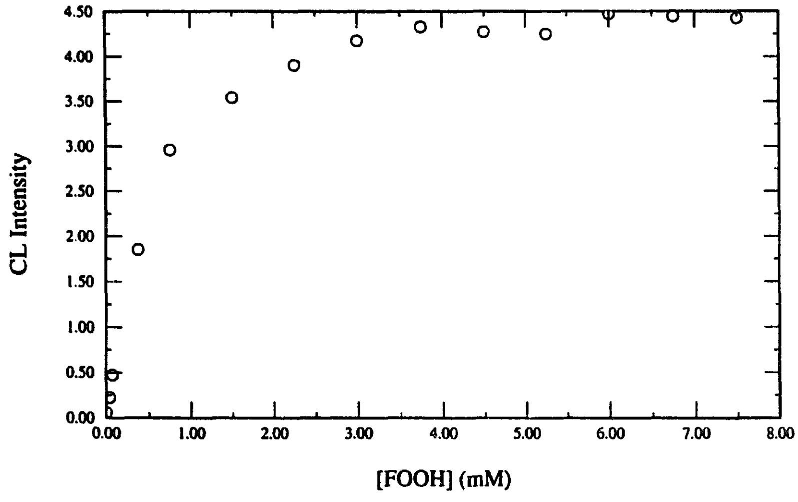

Fig. 4. Relative chemiluminescence vs. FOOH in benzene 19.7 mM in BHN at 26 °C. The concentrations of FOOH were corrected for the presence of FOH impurity.

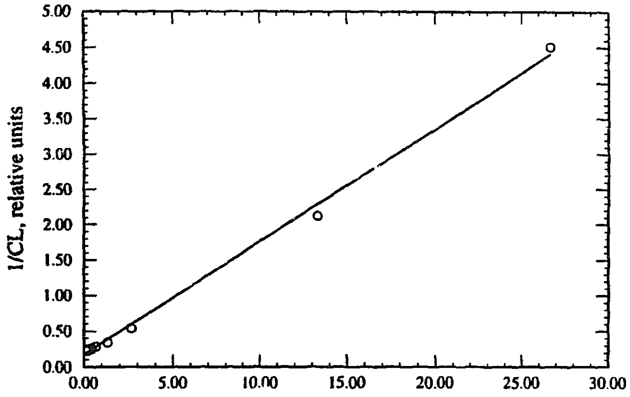

Fig. 5. Double reciprocal plot of data in Fig. 4.

[17], giving a ratio of 9.2×10^{-4} M in excellent agreement. However, we caution that our kinetic scheme contains neither terms for quenching of excited states nor for reaction of $CH_3O_2\cdot$ with FOOH. In addition, there is uncertainty about the value of k_5 and about the validity of our mathematical assumptions.

The solution from which Fig. 4 was derived generated radicals at a rate of about 10^{14} s^{-1}. The lower limit of detectability in our apparatus would correspond to about two orders of magnitude less than this value. The addition of FOOH to organic media at ambient temperatures may be a useful way to measure the low rates of radical production found in autoxidizing systems. In the presence of sufficient FOOH, all reactive radicals should be converted to FOO· and will subsequently give the same excited-state product with a uniform yield of excitation. In practice, of course, FOOH itself may contribute to initiation in such systems especially in the presence of amines or transition metals.

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