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Chemiluminescence in the Reaction of a Sulfurane with Alkyl Hydroperoxides

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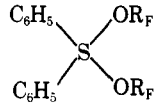
Abstract: The reaction of Martin's sulfurane **1** with *tert*-butyl hydroperoxide, in the presence of 9,10-dibromoanthracene, emits light in two stages. The early stage, beginning on warming to about −40 °C, coincides with the formation of olefin, and is intensified by degassing and quenched by oxygen or by organic sulfides. The later stage, seen on warming from −20 to −10 °C, occurs during the formation of acetone from the hydroperoxide; this luminescence is eliminated by degassing and quenched by 2,6-di-*tert*-butyl-*p*-cresol and organic sulfides. Similar phenomena are observed with cumyl hydroperoxide. Relevant observations are reported on the NMR shifts produced in alcohol proton signals by diphenyl sulfoxide and dimethyl sulfoxide and on the CIDNP signals occurring during the reaction. Some conclusions are drawn concerning the mechanism of the luminescence.

Introduction

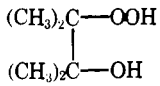
Martin's sulfurane **1** was observed[1] to afford smooth de-



$R_F = -C(CF_3)_2C_6H_5$

1

hydration of 1,2-diols to epoxides and of 1,3-diols to oxetanes. Despite the fact that the sulfurane also reacts with hydrogen peroxide and alkyl hydroperoxides to yield sulfur oxidation products,[2] we hoped that intramolecular dehydration might afford a new route to dioxetanes from the readily available β-hydroxy hydroperoxides such as **2**. In trying the reaction between **1** and **2** in chloroform we found none of the hoped-for



2

HOOH

3

$(C_6H_5)_3COOH$

4

$C_6H_5C(CH_3)_2OOH$

5

$(CH_3)_3COOH$

6

dehydration to dioxetane, the products being acetone, diphenyl sulfoxide, and R_FOH. (Tetramethyldioxetane, added in a control experiment, underwent no reaction with sulfurane **1**, showing that it could not even have been an intermediate in the acetone formation.) It was noted, however, that the reaction between **1** and **2** in the presence of certain anthracenes was chemiluminescent, and we therefore made some further observations on this previously unreported property of the oxidation of sulfuranes. It was found that there are two distinct luminescent stages in the sulfurane-*tert*-butyl hydroperoxide reaction, associated with the formation of different products and responding oppositely to oxygen. The NMR observation of the stages in the reaction involved distinguishing some important interactions between products and observing a number of dynamic nuclear polarization effects. In this paper we undertake to present these observations in perspective and to indicate what progress has been made and what remains to be done in interpreting the mechanism.

Results

Chemiluminescence was observed in the reaction of **1** with hydrogen peroxide (**3**), triphenylmethyl hydroperoxide (**4**), cumyl hydroperoxide (**5**), and *tert*-butyl hydroperoxide (**6**). The luminescence either requires, or is enormously enhanced

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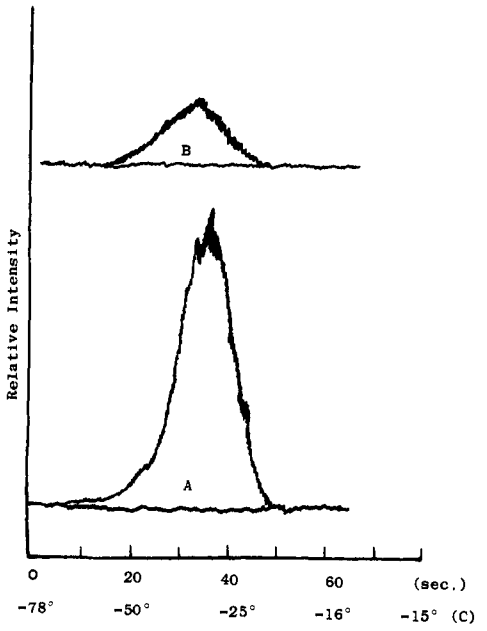


Figure 1. The comparison of the total emission of fluorescers (A:DBA; B:DPA) in the reaction of 0.442 M sulfurane and 0.442 M *tert*-butyl hydroperoxide in CH_2Cl_2 under thoroughly degassed conditions. Both DBA and DPA are 6×10^{-3} M.

by, fluorescers such as 9,10-dibromoanthracene (DBA), 9,10-diphenylanthracene (DPA), and rebrene, the intensity from DBA being from 5 to 30 times that from equivalent amounts of either of the other two fluorescers. The emission from DBA had the same spectrum as the DBA fluorescence excited by the 313- or 366-nm line from a mercury lamp, or by other means, such as the reaction of hydrogen peroxide with aryl oxalates[3] or the thermal decomposition of tetramethyldioxetane.[4] The superiority of DBA as an energy acceptor is typical of the involvement of a triplet excited state.[5]

The course of the reaction was studied at first by mixing the reactants at −75 °C, then allowing the mixture to warm up in the spectrometer at the rate of about 40 °C/min and recording the total emission intensity. In the cases of hydroperoxides **3**–**5**, emission occurred immediately on mixing the reactants at −75 °C and lasted less than 2 s. However, with *tert*-butyl hydroperoxide (**6**), without degassing, the luminescence began only after warming to about −40 °C, reached maximum intensity 50 s later at an estimated temperature of −11 °C, and disappeared 5 s after reaching maximum intensity. Evidently the preluminescent intermediates are of very different stabilities in the *tert*-butyl compared with the other hydroperoxide reactions.

Two Stages of Luminescence. The chemiluminescence is dramatically affected by degassing before warming. The total emission drops by 70–80% but, as shown in Figure 3, the decrease is caused by a total disappearance of the later luminescence having its peak in these experiments at about −15 °C, while the emission from −40 to −25 °C is greatly enhanced. Thus the two successive luminescences can be sharply differentiated and, as shown below, correlated with two different processes in the sulfurane-hydroperoxide reaction.

The two stages of chemiluminescence differ importantly in several respects: (1) The second stage requires oxygen; the first stage is quenched by oxygen. (2) As a corollary of this, the profile of the first emission with rising temperature shows a fairly symmetrical rise and fall, while the second stage falls abruptly from its maximum, being sharply terminated by sudden exhaustion of oxygen.[11] (3) The second stage of luminescence, but not the first, is inhibited by 2,6-di-*tert*-butyl-*p*-cresol, which also has appropriate effects on the product composition (see below). (4) The relative emission

Table I. Ratio of Intermediates **12** and **19** and of Products in Reaction of *tert*-Butyl Hydroperoxide **6** with Sulfurane **1** at −50 °C in Deuteriochloroform

6/1	initial concn, M: 1	initial concn, M: 6	19/12 at −50 °C[a]	product ratio acetone/isobutylene: 0 °C[d]	product ratio acetone/isobutylene: 25 °C
0.24	0.35	0.083	~1.6	~0.55	~0.9
0.47	0.35	0.166	~2.1	~0.84	~0.9
0.95	0.35	0.333	~2.6	~1.0	1.14
1.9	0.35	0.0666	*b*	*c*	*c*

[a] From integrated areas: (peak *b*)/(peak *a*). [b] No peak *a*. [c] No isobutylene. [d] (Column 5)/(column 4) = 0.375 ± 0.025.

intensities from dibromoanthracene (DBA) and diphenylanthracene (DPA), with all other factors the same, are different in the early and the late stages of the luminescence: ratios 5 and 30, respectively.

The relative effects of DBA and DPA as fluorescers are shown in Figure 1 for a thoroughly degassed solution, which therefore exhibits only the first stage of the luminescence. Figure 2 shows the emission with DBA from the same reaction run without degassing; the low-temperature luminescence seen in Figure 1 is now very small (oxygen inhibited), while a relatively large emission is seen in the higher temperature late stage. The early part of the emission of Figure 2 can be eliminated by holding the solution first at −40 °C, then cooling to −55 °C and warming on the same schedule as before. The second case is shown as the dotted line in Figure 2.

Figure 3 shows a direct comparison of emission from otherwise identical undegassed and repeatedly degassed solutions.

Timing of Product Formation. From the organic hydroperoxides, the chief products from the sulfurane, as reported by Martin and Martin,[2] were the fluorinated alcohol R_FOH (essentially quantitative) and diphenyl sulfoxide, with lesser amounts of sulfide and sulfone. These tertiary hydroperoxides gave rise to ketone and di(tertiary peroxide), while the products from cumyl and *tert*-butyl hydroperoxides also contained α-methylstyrene and isobutylene, respectively.

A series of NMR scans of the reaction of **1** with *tert*-butyl hydroperoxide (**6**), each 0.6 M, in deuteriochloroform solvent, initially at −78 °C and with the probe temperature rising about 20 °C per scan, showed that (a) there was rapid disappearance of the hydroperoxide to yield one or more intermediates, which then produced isobutylene, acetone, *tert*-butyl methyl peroxide, and di-*tert*-butyl peroxide more slowly; (b) some sulfurane remained unconsumed, indicating that more than one hydroperoxide molecule reacted with one sulfurane; (c) the isobutylene was formed at an earlier time and lower temperature than the acetone, indicating that these two products came from *tert*-butyl groups in different intermediates. Variation of the ratio of the reactants indicated that the higher the relative concentration of hydroperoxide, the greater the proportion of acetone in the product: for initial ratios of **6**/**1** of 0.25, 0.5, and 1.0 the product at 0 °C showed the NMR signals of acetone and isobutylene in the ratio respectively of 0.56, 0.84, and 1.0. With precautions to assure complete mixing of the reactants at −78 °C, there was no detectable isobutylene in the product when the ratio of **6**/**1** was 2 or higher. The period during which isobutylene was formed coincided with that of the early, oxygen-quenchable luminescence (see Table I and Figure 4), while acetone was formed during the later period in which the more intense, oxygen-enhanced luminescence was seen.

NMR Signals from Intermediates. The correlation of the products with the sulfurane/hydroperoxide reactant ratio (**1**/**6**) is paralleled by the appearance of the NMR scans taken immediately at −50 °C after mixing the reactants. The initial peak due to *tert*-butyl hydroperoxide at 1.23 ppm is immedi-

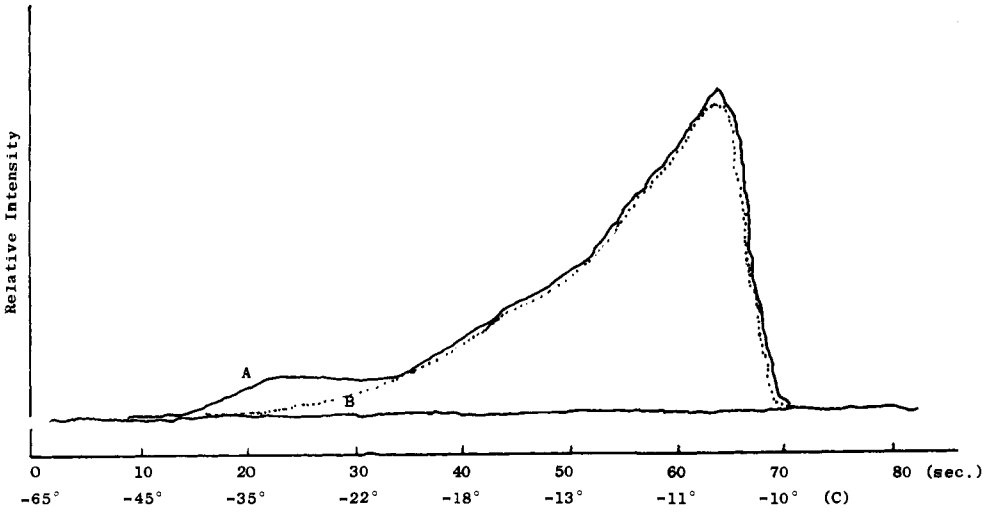


Figure 2. The total emission of DBA (5×10^{-3} M) during the reaction of sulfurane **1** and *tert*-butyl hydroperoxide **6** (not degassed) at the same concentration (~0.5 M) in $CDCl_3$. (A) The reactants were mixed at −65 °C and warmed up to −10 °C. (B) The reactants were mixed at −40 °C, cooled to −65 °C, and then warmed to −10 °C.

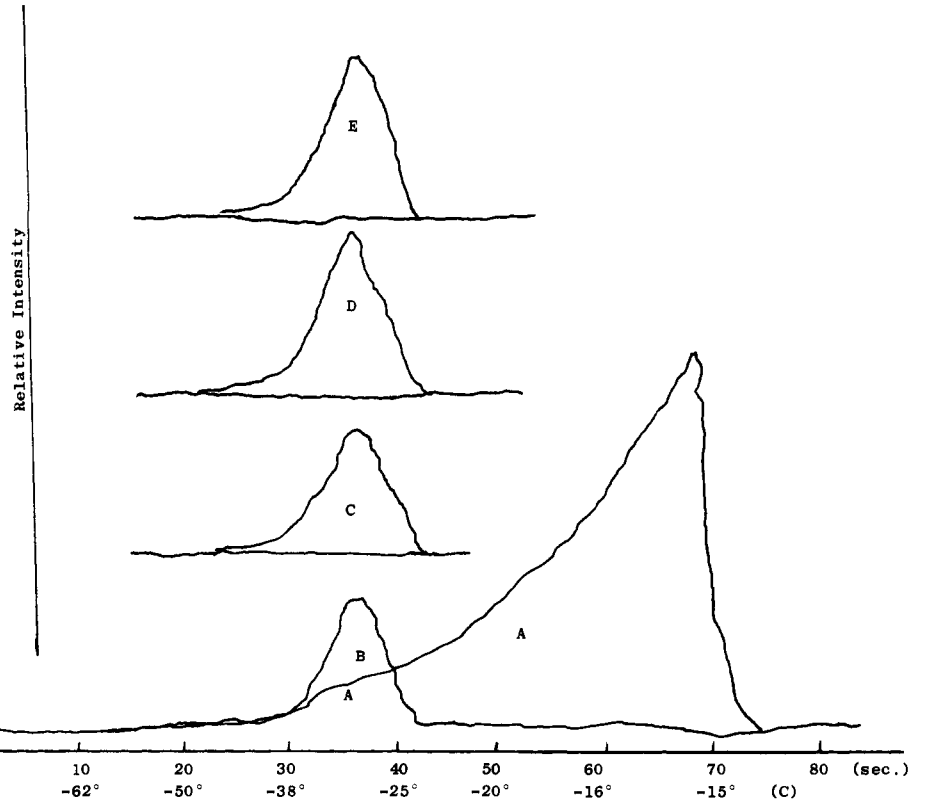


Figure 3. The total emission of DBA (5×10^{-3} M) during the reaction of sulfurane **1** and *tert*-butyl hydroperoxide at the same concentration (0.5 M) in CH_2Cl_2: (A) nondegassed reaction mixture, (B) (one cycle), (C) (three cycles), (D) (five cycles), (E) (eight cycles) of degassing: pump (−196 °C) and thaw (−78 °C) reaction mixture. All emissions were recorded from −78 °C warming up to −15 °C.

ately replaced by two signals, *a* at 1.43 and *b* at 1.28, whose relative intensities vary with the relative initial concentrations of hydroperoxide **6** and sulfurane **1**, and parallel the relative yields of isobutylene and acetone (Table I). It is clear from these relationships that the NMR peaks at 1.43 and 1.28 ppm represent the displacement products of the original sulfurane in which one and two *tert*-butylperoxy groups have replaced hexafluorocumyloxy groups, R_FO (**12** and **19**, Scheme II). Although peak *a* is no longer seen in these runs with a ratio of **6**/**1** greater than 2, peak *b* is still prominent in even the runs with a deficiency of hydroperoxide and much unreacted sulfurane. None of the sulfurane **1** survives if the ratio of **6** to **1** is greater than 2. This can be seen from the disappearance of the NMR peak at 7.8 ppm, which is due to the ortho aromatic protons of **1**.

Sulfur-Containing Products. The NMR spectrum of sulfurane **1** is dominated by a complex aromatic multiplet and not readily used to follow the conversion of **1** into diphenyl sulfide, sulfoxide, and sulfone. For this reason we prepared a sample of sulfurane **7**, the chemical shift of whose *o*-methoxy group was expected to respond to the state of oxidation of the sulfur in the product compounds **8**–**10**. Indeed, the methoxy chemical shifts in deuteriochloroform (ppm from Me_4Si) were, for **7**, 3.04; **8**, 3.82; **9**, 3.75; **10**, 3.70. This made it possible to survey by NMR the rate of formation of the sulfur reaction products from **7** and *tert*-butyl hydroperoxide. The sulfoxide **9**, at 3.75

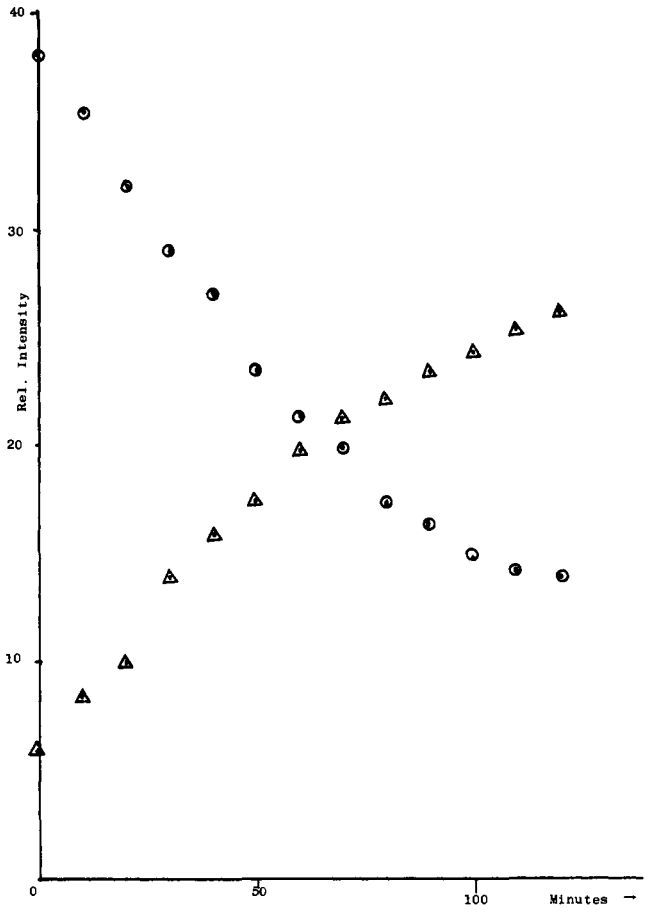
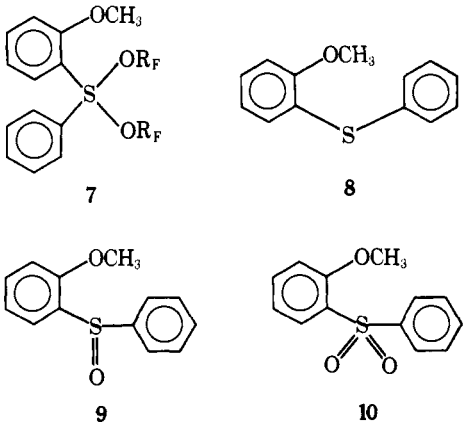


Figure 4. Change with time at −40 °C of NMR peak *a* at 1.43 ppm, corresponding to intermediate **12** (circles), and of the peak at 1.62 ppm (isobutylene) (triangles).



7 8 9 10

ppm, is the chief product from this sulfurane in reaction with *tert*-butyl hydroperoxide. A peak at 3.82 ppm, the chemical shift of the sulfide **8**, builds up slowly, reaching a maximum in the sixth scan, at which time the acetone signal has almost reached full strength. The 3.82-ppm peak then declines; by the 12th scan it represents a low shoulder on the 3.75-ppm peak, while the latter may be slightly increased in intensity. Thus, the direct NMR observation in the case of **7** checks the chromatographic analyses in the case of **1** in showing the sulfoxide to be the main sulfur-containing product. It was not possible to distinguish more than a minute ripple corresponding to the sulfone **10** at 3.70 ppm.

CIDNP. The most striking feature of the intermediate NMR scans in the case of *tert*-butyl hydroperoxide is the appearance of some five major and six minor CIDNP emission signals, in addition to small absorptions at 1.54 and 2.66 ppm and a larger

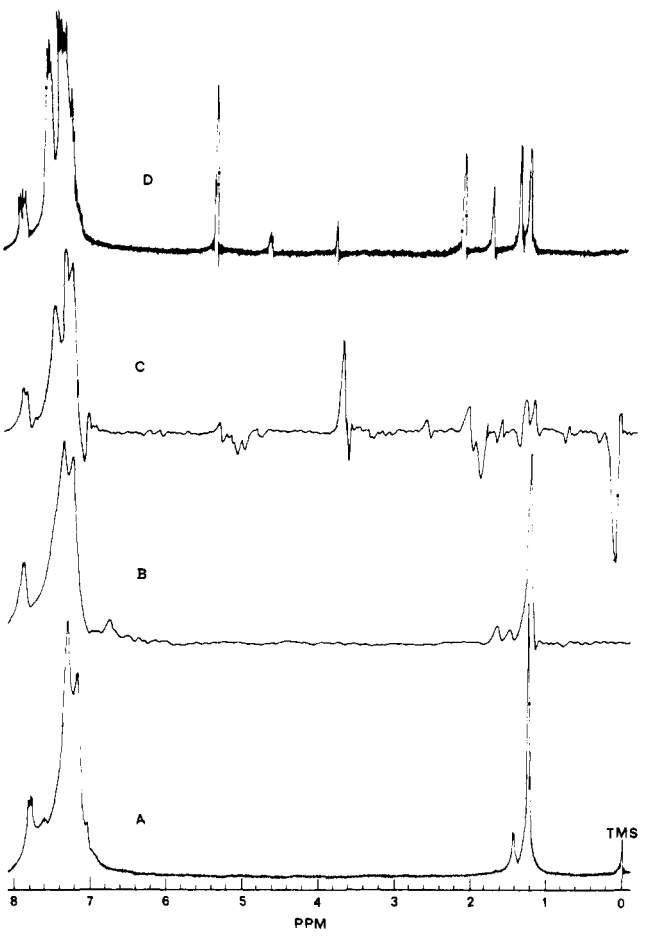


Figure 5. Representative NMR spectra of the reaction of sulfurane **1** (0.35 M) and *tert*-butyl hydroperoxide **6** (0.17 M) in $CDCl_3$. (A) The reaction mixture at −50 °C (slow scan at 250 s/8 ppm). (B, C) Two representative spectra at temperatures between −50 °C and room temperature (~25 °C) (fast scans at 10 s/8 ppm). (D) The product mixture at room temperature (slow scan at 250 s/8 ppm).

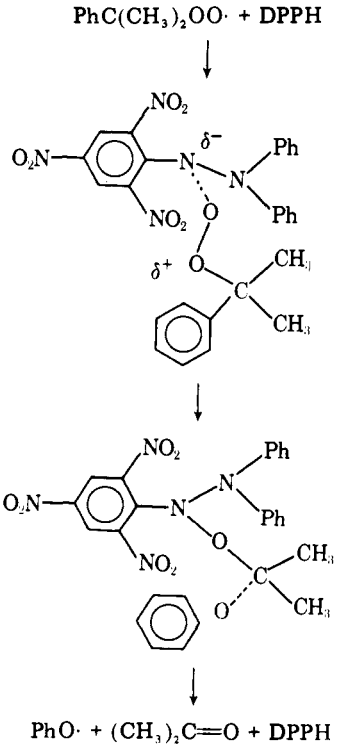
absorption at 3.70 ppm, which appear and disappear at different times during the course of the reaction and may be either CIDNP of trace products or normal NMR absorption of substantial intermediates. The major emission signals, seen within the first 70 s of reaction, are at 0.14, 0.80, 1.47, 1.76, 2.0, and 5.00 ppm. The absorption at 1.54 ppm was seen between 20 and 60 s, and those at 2.66 and 3.70 ppm were seen between 100 and 160 s. Representative scans are shown in Figure 5. Because of the conditions of rising temperature, these scans provide accurate information as to the order of events in one sample, but they are not strictly comparable as to time and temperature between different samples. In the case of cumyl hydroperoxide, only a single emission signal, at 0.16 ppm, was observed.

It was also observed that the detailed make-up of the CIDNP signals varied greatly with the solvent: in acetone-d_6 with external Me_4Si no emission signal upfield of 3 ppm was observed. These facts are all consistent with the great sensitivity of CIDNP to trace amounts of material, and with the possibility that most of these signals represent insignificant diversions of methyl or other radicals during the reaction. The importance of these observations is that *some of the products in the sulfurane reaction, but not others, are formed by a free-radical mechanism:* this mechanism becomes prominent during the formation of acetone from *tert*-butyl hydroperoxide and *after* the formation of isobutylene is largely complete.

Rate Studies on Intermediates. If the intermediates **12** and **19** are formed irreversibly and if they decompose respectively to isobutylene and *tert*-butoxy radicals, the latter leading to

acetone and dialkyl peroxides, then one might hope to follow the decomposition of these products by observing the declining intensity of the corresponding peak in the NMR at constant temperature. A number of such time studies were made at constant temperatures between −45 and −25 °C (for **12**, peak *a*) and between −25 and −5 °C (for **19**, peak *b*). As illustrated by Figure 4, the appearance of isobutylene keeps pace with the disappearance of the intermediate **12**, and acetone similarly appears as **19** disappears. It was possible to get first-order rate constants for the disappearance of the first intermediate, and to calculate an activation energy of about 16 kcal. However, peak *b* at 1.28 ppm was not free from interference from the signals of other *tert*-butyl compounds present in the reaction; *tert*-butyl hydroperoxide, *tert*-butyl alcohol, and di-*tert*-butyl trioxide[7] all absorb within the range 1.19-1.25 ppm, and are not cleanly differentiable from peak *b* at 1.28. Therefore, reproducible rate constants and meaningful activation energies could not be obtained for the decline of **19**.

Effects of Additives. The evidence of free-radical processes suggested a possible role of inhibitors such as diphenylpicrylhydrazyl (DPPH) in the reaction. The effect of 0.3 M DPPH added to the reaction of **1** with the hydroperoxides at 0.6 M each was to alter the hydroperoxide-derived products without any great change in the sulfur-containing products (Table II). In all three cases the tertiary alkyl peroxides were reduced to zero; the acetone from *tert*-butyl hydroperoxide (**6**) went down from 23 to 12% and the acetophenone from **5** declined from 58 to 5%, consistent with the *tert*-alkoxy radicals having been precursors to the ketones. In the two cases, however, where the ketone could be attributed to migration of a *phenyl* group within the tertiary alkoxy radical, an opposite effect occurred: benzophenone from trityl hydroperoxide (**4**) was increased from 40 to 64%, and acetone from cumyl hydroperoxide (**5**) went up from 2 to 12% in the presence of DPPH. This observation is consistent with a duality of mechanism in ketone formation such that with the benzylic hydroperoxides some polar rearrangement is possible, related to that in the formation of phenol from cumyl hydroperoxide. Whereas any stable free radical can simply scavenge an alkylperoxy radical by combining with it, the electron-acceptor character of DPPH may result in such a polarized radical pair that rearrangement occurs:



Although the α-methylstyrene from cumyl hydroperoxide appears to be formed by a nonradical mechanism, before the CIDNP occurs, DPPH increased the α-methylstyrene from 6 to 68%. No such effect was seen in the case of *tert*-butyl hydroperoxide; the yield of isobutylene was unchanged by DPPH addition.

There are two possible interpretations of the effect of DPPH in increasing the yield of α-methylstyrene from the cumyl hydroperoxide-sulfurane reaction. (1) Both olefin and ketone in this case are formed at the same low temperature; if these processes are in competition and the ketone formation has any chain character, its inhibition would allow the olefin formation to gain in importance, as would not be possible in the *tert*-butyl hydroperoxide case. (2) The ketone formation may not have chain character, but in the normal, uninhibited reaction free radicals accompanying the ketone formation may attack the α-methylstyrene after it is formed. Although α-methylstyrene does not readily form a homopolymer, its reactivity toward the methyl radical is greater than that of styrene,[10] which makes it a prime target for the free radicals formed in the present reaction.

Results similar to those in the presence of radical inhibitors were had when the sulfurane-alkyl hydroperoxide reaction was carried out in the presence of 1.2 M added dialkyl sulfides. Again di-*tert*-butyl peroxide was absent in the product from *tert*-butyl hydroperoxide when either phenyl methyl or dimethyl sulfide was added to the reaction. Acetone in the product declined from 25 to 5 and 7%, respectively, and isobutylene increased from 23 to 31 and 46%, respectively, with phenyl methyl and dimethyl sulfides. In the cumyl hydroperoxide case the acetophenone/α-methylstyrene ratio went from 58/6 without sulfide to 3/35 with phenyl methyl sulfide added. The sulfides had no detectable effect on the distribution of sulfur products from the sulfurane in the cases of *tert*-butyl or cumyl hydroperoxides; in the reaction with hydrogen peroxide, however, the two sulfides shifted the diphenyl sulfoxide/diphenyl sulfone ratio from 43/49 to 69/22 and 81/15, respectively.

Effect of Additives on the Luminescence. Figure 6 shows the effect of adding the free-radical inhibitor 2,6-di-*tert*-butyl-*p*-cresol (DBC) in the reaction between sulfurane **1** and *tert*-butyl hydroperoxide. Increasing amounts of the phenol progressively inhibit the later luminescence without affecting the earlier luminescence at lower temperature. A conclusion consistent with precedent[11] is that *excited* carbonyl compounds are produced, not by the simple cleavage of an alkyl group from a tertiary alkoxy radical ($\Delta H \sim 13$ kcal) but in the interaction of two nontertiary alkylperoxy radicals which can occur only after the cleaved alkyl group has reacted with oxygen, and can be exothermic by as much as 126 kcal. This would explain why the late reaction, generating ketone, is luminescent only in undegassed solutions (Figure 3).

In contrast to di-*tert*-butyl-*p*-cresol, methyl phenyl sulfide acts similarly on both the early and late luminescence (Figure 7). Combined with the observation of the effect of oxygen on the two stages of emission, this evidence suggests that sulfides are able to react to some extent with free radical chain carriers as well as intercepting peroxy sulfides[6,8] which thus become plausible precursors to the excited sulfone in Scheme I.

Mechanism of the Reaction. Olefin Formation. Although excited ketones are often implicated in chemiluminescent reactions, the early chemiluminescence in the case of *tert*-butyl hydroperoxide and sulfurane **1** begins before ketone generation, and some other excited molecule must be responsible for the early luminescent emission. As noted by Martin and coworkers,[6] and confirmed in the present study, the reactions of sulfurane **1** are associated with initial very rapid displacements of the R_FO groups by nucleophilic reactants. The immediate consumption of hydroperoxide and appearance of R_FOH in

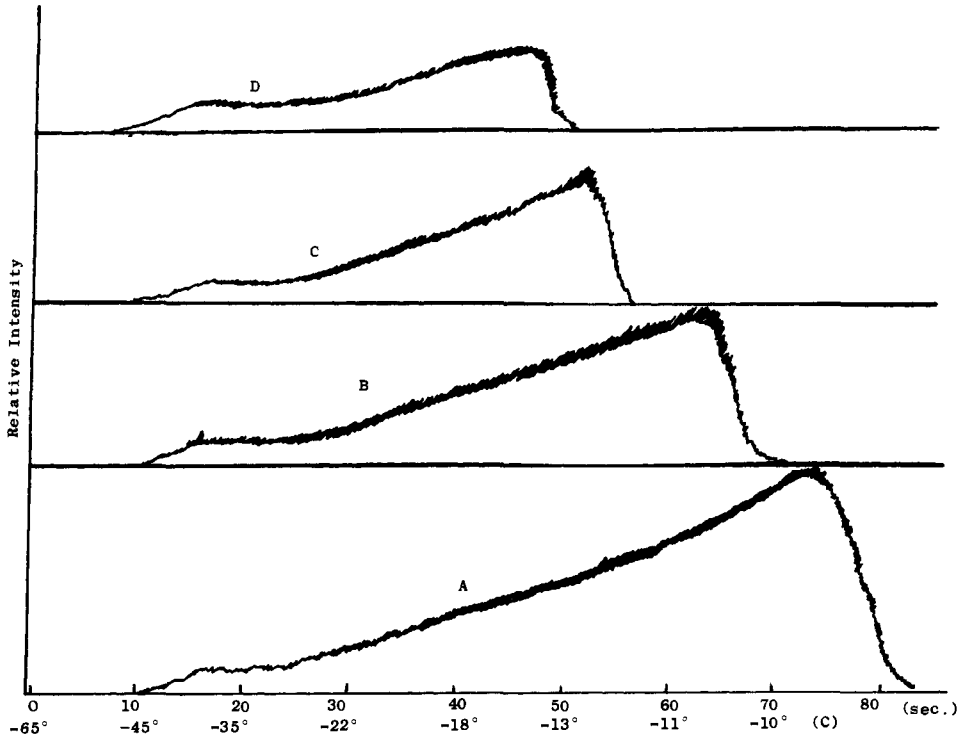


Figure 6. Effect of the inhibitor di-*tert*-butyl-*p*-cresol on luminescence in the reaction of sulfurane **1** and *tert*-butyl hydroperoxide **6** at a uniform concentration (0.003 M) of DBA. (**1**) = (**6**) = 0.28 M. Inhibitor concentrations: (A), 0; (B), 0.0066; (C), 0.0132; (D), 0.0198 M.

Table II. Effect of DPPH[b] on Product Distribution[a]

hydroperoxide	product and yield, %							
					PhSPh			R_FOH
0.3 M DPPH	24	12		~0	2	94	2	185
(without DPPH	25	23		~7	5	88	7	193)
					PhSPh			R_FOH
0.3 M DPPH	68	5	12	~0	2	93	2	187
(without DPPH	6	58	2	~10	5	89	3	192)
					PhSPh			R_FOH
0.3 M DPPH	64			~0[c]	8	87	2	184
(without DPPH	40			14	8	85	3	188)

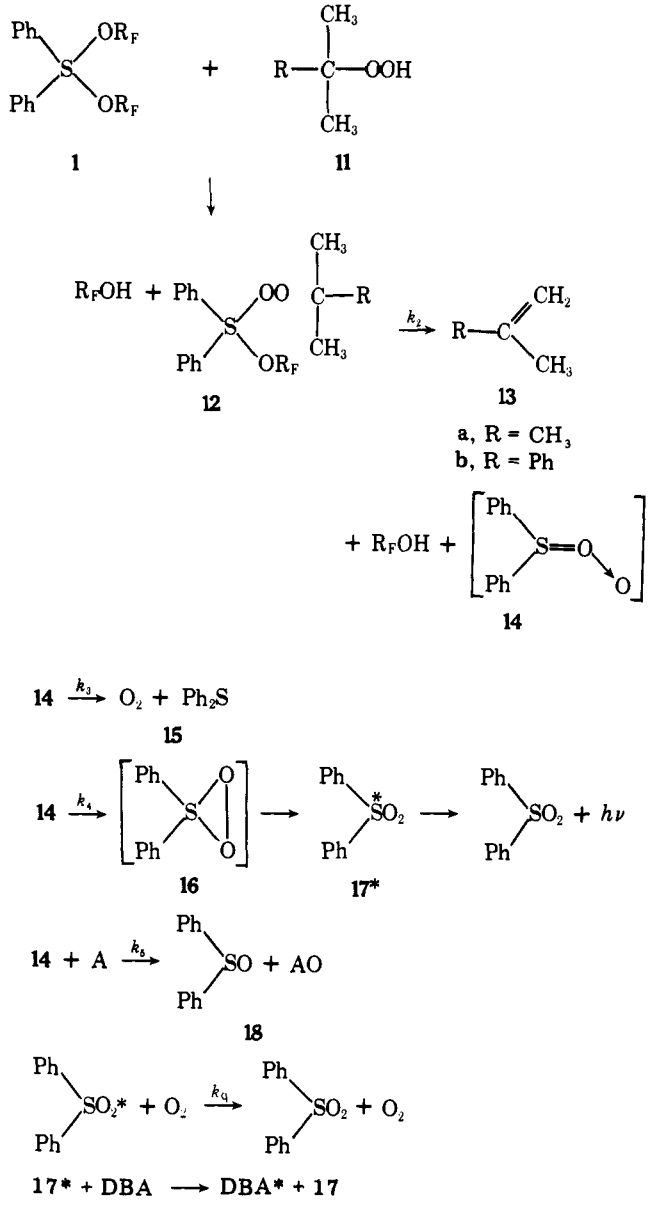
[a] Reactions were carried out in $CDCl_3$, initially at −75 °C, in an NMR tube between 0.6 M sulfurane **1** and 0.6 M hydroperoxide. [b] 2,2-Diphenyl-1-picrylhydrazyl, 0.3 M. [c] Absence of peroxide shown by TLC.

the present reaction are in accord with the intermediacy of a monoperoxysulfurane in the first reaction which leads to olefin without ketone and without any evidence of free-radical processes. Scheme I indicates a rapid process controlled by k_1 accounting for the quick disappearance of hydroperoxide and appearance of R_FOH. The resulting monoperoxysulfurane **12** is well constituted to undergo an intramolecular elimination by way of k_2 to the olefin **13** and the energy-rich sulfur compound **14**, along with a second molecule of R_FOH. The persulfoxide **14** is a type of compound shown by Foote and Peters[8] to be intermediate in the reaction of singlet oxygen with organic sulfides. They have demonstrated the reality of the cleavage of aliphatic persulfoxides by k_3 to sulfide and oxygen and their ability to act as oxygen donors (by k_5) to aliphatic or aromatic sulfides (A) and, in the absence of such processes, to isomerize to sulfones by k_4. There is therefore precedent for the formation of all the observed products if **14** is formed as indicated in Scheme I, as well as a prediction that the addition of phenyl methyl or dimethyl sulfide will divert products and, depending on the relative values of the rate constants, diminish the luminescence.

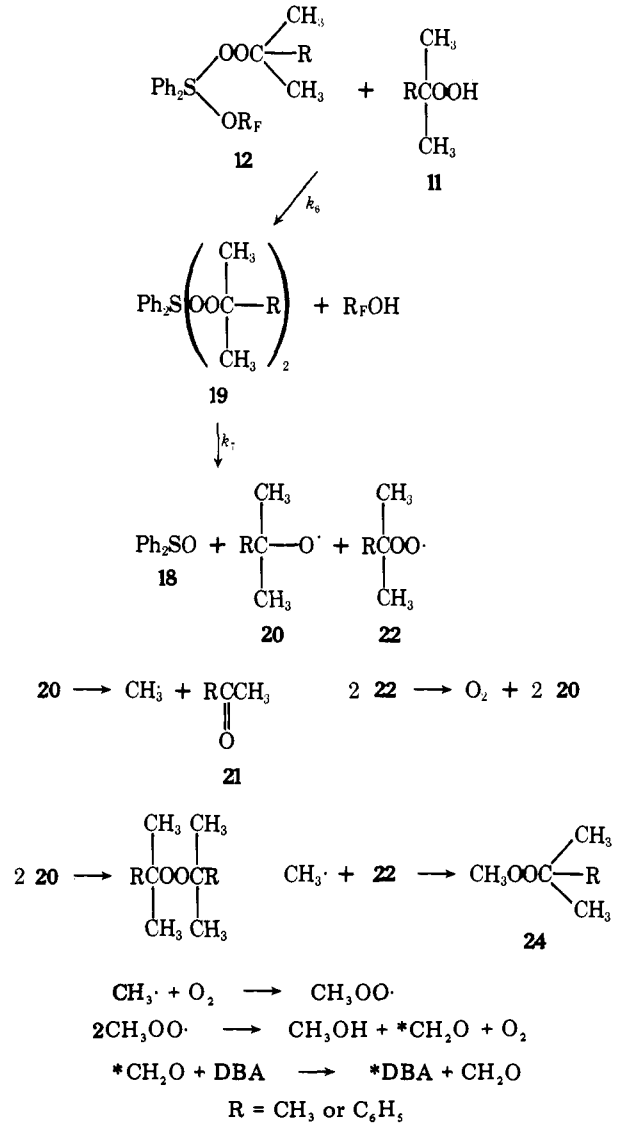
In Scheme I it is suggested that some luminescence may arise from excited sulfone generated by way of k_4. Other ways for the luminescence to arise might include a bimolecular reaction of **14** to yield molecular oxygen and two molecules of sulfoxide **18**, one of these products being formed in an excited state. However, we have not found a way to produce luminescent DBA via photoexcited diphenyl sulfoxide or diphenyl sulfone.

Free-Radical and Ketone Formation. An obvious competitor

Scheme I



Scheme II



with the direct formation of **13** from **12** is the reaction of **12** with a second molecule of the hydroperoxide **11** as shown in Scheme II. The new diperoxysulfurane **19**, instead of polar intramolecular elimination, is favorably constituted for homolytic fission, and indeed for concerted fission into a molecule of sulfoxide or sulfone and two tertiary alkoxy radicals (k_7). The formation of sulfoxide rather than sulfone is indicated by the product analysis, although it is not impossible that a minor product, such as sulfone, might still be a major contributor to the luminescence. The alkoxy radicals, **20**, can cleave to ketone and methyl radical, which can in turn produce other radicals by hydrogen capture or by reaction with oxygen. Scheme II thus also provides a framework for all the observations of the latter part of the reaction—ketone formation, peroxide buildup, CIDNP, and oxygen-dependent luminescence.

It may be noted that any cage recombination of radicals **20** and **22** in Scheme II would lead to di-*tert*-butyl or dicumyl trioxide,[7] whose thermal decomposition occurs in the same temperature range as the decomposition of **19**. The formation of these trioxides would be compatible with the dehydrating capability of sulfurane **1** toward alcohols,[1] but because of its reversibility it would make no difference in the chemical outcome indicated in Scheme II.

Role of the Fluorescer. A simple hypothesis for the early light emission would be that sulfoxide, sulfone, and/or ketone is produced in an excited state, undergoes intersystem crossing to a triplet, and transfers its energy to the fluorescer whose emission is detected. According to this hypothesis we should expect to be able in the absence of fluorescers to detect some direct emission from the excited reaction product; this would be especially desirable since the direct emission spectrum would reveal the identity of the emitter. Such experiments, however, failed to reveal any detectable emission in the absence of fluorescer; unassisted chemiluminescence could have been detected in our apparatus if its quantum efficiency were greater than 10^{-7}. In a series of experiments the reactants were mixed at −78 °C, then brought to −35 or −20 °C and the emission intensity was observed in the presence of varying concentrations of 9,10-dibromoanthracene. This emission extrapolates to zero at zero concentration of fluorescer. These experiments show that the quantum yield for direct emission from the excited state in question is very low (less than 10^{-7}), while being much higher for direct energy transfer to DBA. Tests showed that the *rate of reaction* of **1** with *tert*-butyl hydroperoxide at −35 or −20 °C (i.e., the rate of decomposition of **12** or **19**) is not dependent upon the concentration of the added fluorescer. Thus the participation by the fluorescer occurs after the rate-determining step of the sulfurane-peroxide reaction. In early luminescence **14**, **16**, or an excited form of **17** would qualify as energy donor, allowing the emission, but not the

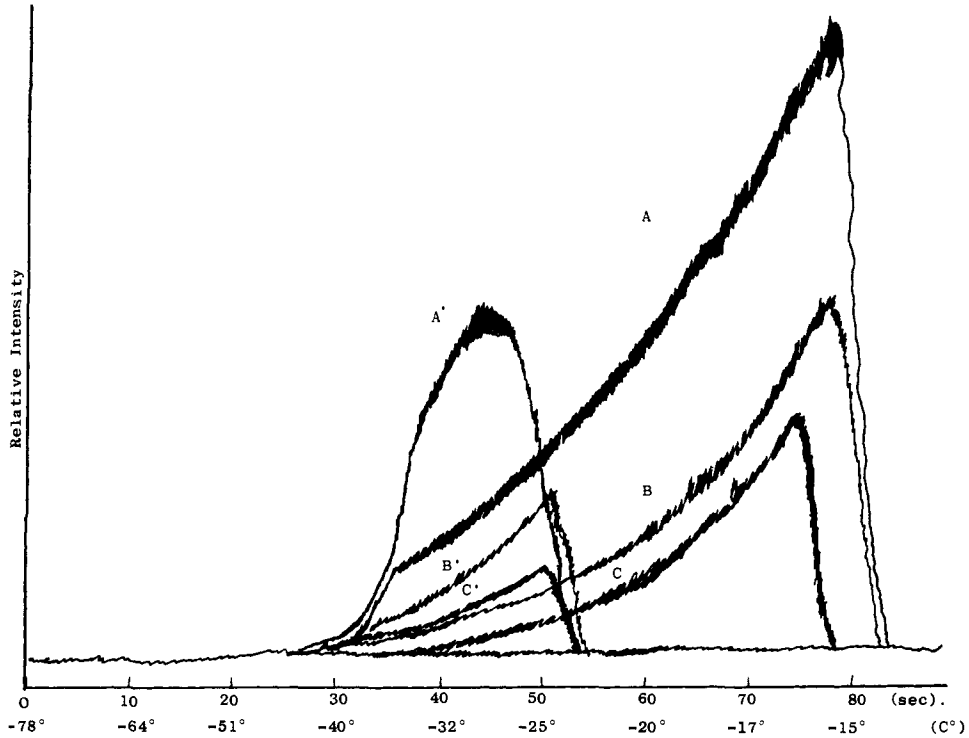


Figure 7. The total emission of DBA (4.4×10^{-3} M) during the reaction of sulfurane **1** and *tert*-butyl hydroperoxide **6** (both 0.278 M). A, B, and C are nondegassed samples, while A′, B′, and C′ are degassed samples: (A, A′) no methyl phenyl sulfide; (B, B′) 0.0435 M methyl phenyl sulfide; (C, C′) 0.0623 M methyl phenyl sulfide.

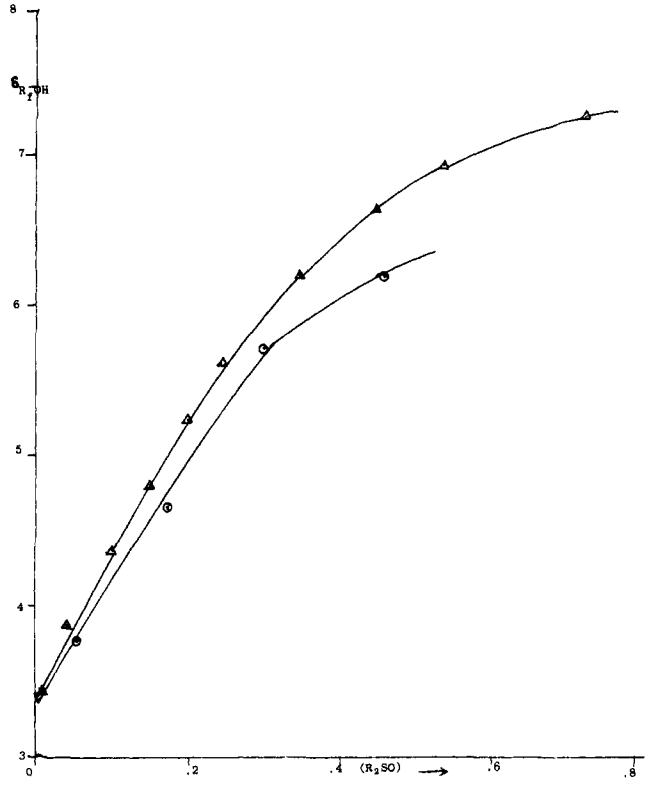


Figure 8. Effect of dimethyl sulfoxide (triangles) and of diphenyl sulfoxide (circles) on the chemical shift δ_H of the hydroxy proton of hexafluorocumyl alcohol. (R_FOH) = 0.5 M in $CDCl_3$.

consumption of sulfurane or of hydroperoxide, to depend on the concentration of fluorescer.

Shifts of NMR Absorptions during Sulfurane–Hydroperoxide Reactions. Some of the successive NMR scans showed not only growing or declining peak intensities due to reaction components, but sometimes substantial changes in position of a peak during the course of the reaction. In some cases a signal was seen to shift by as much as −0.64 ppm from mixing of the components at −78 °C to completion of the reaction at room temperature. The signal in question is that due to the hydroxy proton on the fluorinated alcohol, $C_6H_5(CF_3)_2COH(R_FOH)$. These shifts, in a reaction generating diphenyl sulfoxide, recall the observations of Chapman and King[9] on the large chemical shifts produced in O–H signals by dimethyl sulfoxide. We accordingly investigated the effects of varying concentrations of diphenyl sulfoxide on the hydroxyl chemical shifts of some of the OH compounds important in this study. As seen in Figure 8, the hydroxyl signal of a 0.5 M solution of R_FOH is shifted steadily downfield from 3.81 ppm with 0.05 M diphenyl sulfoxide to 6.22 ppm in the presence of 0.46 M sulfoxide. The shifts produced by dimethyl sulfoxide are very similar (Figure 8). At low concentrations of sulfoxide (up to 0.2 M) the shifts are approximately proportional to the sulfoxide added, but it is evident from the upper parts of the curve that the complexation of the alcohol by the sulfoxide reaches an equilibrium. The value of the equilibrium constant assigned depends upon the assumed chemical shift of the alcohol–sulfoxide complex and an unambiguous assignment of both quantities could not be obtained from the data.

This difficulty is, at least in part, due to the fact that association of R_FOH is itself attended by a downfield chemical shift: the change in δ from 3.29 ppm at 0.1 M to 3.63 ppm at 3.2 M is compatible with a dimerization equilibrium constant of 0.62 and a δ of 3.97 ppm for the dimer.

It was also observed that the hydroxy proton chemical shift of a mixture of 0.54 M R_FOH and 0.19 M diphenyl sulfoxide moved from 4.63 ppm at 25 °C to 6.03 ppm at −52 °C. This temperature dependence of the effect of sulfoxide as a shift reagent explains why often in a series of NMR scans of the reaction of sulfurane with hydroperoxides the shifting peak, instead of moving from right to left with time (due to increasing sulfoxide concentration), moved from left to right because of the dominating effect of rising temperature when the concentrations had become fairly constant. An example is seen in Figure 5.

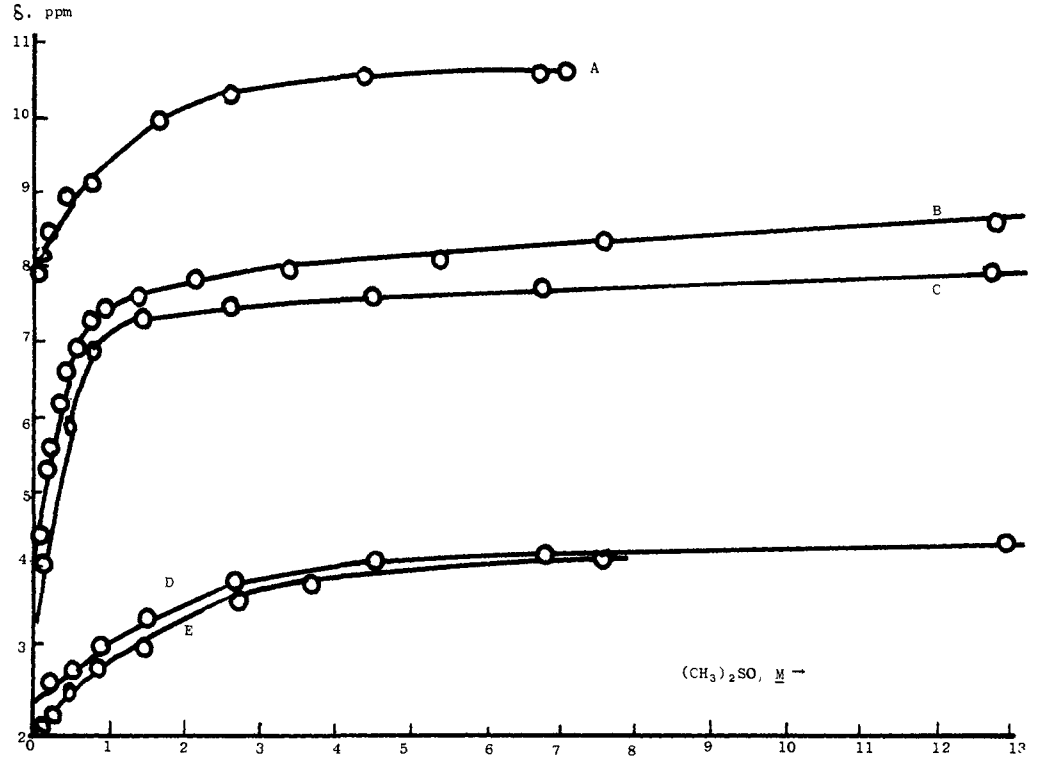


Figure 9. Chemical shift of hydroxylic hydrogen in the presence of dimethyl sulfoxide in deuteriochloroform: (A) *tert*-butyl hydroperoxide, 0.9 M; (B) $C_6H_5C(CF_3)OH$ (R_FOH), 0.5 M; (C) 1,1,1,3,3,3-hexafluoro-2-propanol, 0.9 M; (D) isopropyl alcohol, 1.1 M; (E) *tert*-butyl alcohol, 0.9 M.

The special position of sulfoxides as shift reagents is illustrated by the relative shifts in the signal of the R_FOH proton produced in 0.5 M solutions by the addition of equivalent diphenyl sulfoxide (2.77 ppm), diphenyl sulfone (0.90 ppm), and diphenyl sulfide (no shift).

The ability of a sulfoxide to shift the NMR peak of an alcoholic proton appears to be related to the acidity of the alcohol. Figure 9 shows the response to dimethyl sulfoxide by isopropyl and *tert*-butyl alcohols, two fluorinated alcohols, and *tert*-butyl hydroperoxide.

Experimental Section

Sulfurane **1** was prepared as described by Martin and co-workers;[12,13] carbon tetrachloride[14] was used instead of ether in the chlorination of the mixture of diphenyl sulfide and suspended, finely ground potassium 2-phenyl-1,1,1,3,3,3-hexafluoro-2-propoxide. All handling of the sulfuranes was done in a drybox under dry nitrogen. The white, granular crystals of **1**, obtained from pentane solution at −75 °C, were identical spectroscopically with those reported by Martin et al. Sulfurane for the chemiluminescence experiments was further recrystallized from dry pentane at −75 °C.

Phenyl *o*-anisyl sulfide (**8**) was prepared by the reaction of sodium thiophenoxide with diazotized *o*-anisidine. The sulfide was distilled at 126 °C (0.02 mm) and characterized in product mixtures by its ^1H NMR absorption at 3.82 ppm.

Sulfurane **7** was prepared in the same manner as **1**, but with **8** instead of diphenyl sulfide as starting material (OCH_3, δ 3.04 ppm).

tert-Butyl hydroperoxide (**6**), Aldrich technical grade, was fractionally distilled under vacuum several times. The fraction used, bp 27–28 °C (1.1 mm), appeared by NMR to be at least 99% pure.

Methyl *tert*-butyl peroxide[15] was prepared from the reaction of equimolar quantities of dimethyl sulfate and potassium *tert*-butyl peroxide. ^1H NMR of the product showed singlets at 3.70 (3 H) and 1.20 ppm (9 H).

^1H NMR spectra were taken on a JEOL MH-100 spectrometer. Low temperatures for the NMR measurements were controlled and monitored by a JNM-VT-3C temperature controller, which was calibrated by the chemical shift of methanol and an iron-constantan thermocouple. Luminescence spectra were taken either on an American Instrument Co. fluorimeter or on the more sensitive EMI 9558QB photomultiplier equipped with a Keithley Instruments picoammeter. For these studies the E-257 variable-temperature accessory of a Varian ESR spectrometer was employed to control the temperature; the range of this accessory is from −185 to +300 °C with an accuracy of ±2 °C in the sample. The temperature was read directly by inserting an iron-constantan thermocouple into the reaction mixture.

NMR Survey of the Course of the Reaction. The NMR spectra of the initial solution were run at −50 °C at normal scan speed. For a typical temperature-rise survey, the sulfurane (0.20 g) and hydroperoxide solutions in $CDCl_3$ were cooled separately in a dry ice–acetone bath to −65 °C and mixed in the desired proportion at this temperature in an NMR tube. The tube was placed quickly (within 1–2 s) into the NMR probe at −10 °C, and a series of 25-s scans were run during the temperature rise. The rate of temperature rise in the NMR tube could be determined from the methanol chemical shift in an identical tube.

The kinetic measurements of the decline of intermediate **12** were run by observing the change in peak heights *a* and *b* with time at four constant temperatures.

In a typical luminescence measurement sulfurane **1** (0.20 g, 0.30 mmol) and DBA (0.005 g) were dissolved in 1.0 mL of anhydrous chloroform and introduced into the photocell by injection through the silicon rubber septum. After 10 min in a dry ice–acetone bath, the cell was quickly placed in the housing of the fluorimeter, and 100 μL of a chloroform solution of *t*-BuOOH (0.045 g, 0.3 mmol) was injected through the septum. The wavelength to be detected was set at 445 nm, λ_{max} of DBA.

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Conformational Effects in the Fluorescence and Photochemistry of [2.*n*](9,10)Anthracenophanes (n = 4, 5)

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Abstract: A molecular force field model has been used to predict the number of possible conformations of [2.4](9,10)anthracenophane (I) and [2.5](9,10)anthracenophane (II). The model predicts four conformers for I and six for II. Calculated heats of formation and observed X-ray structure data provide the most likely conformational arrangements of I and II in their ground states. These have the largest mean interchromophore separations. Absorption of light can lead to excited state intramolecular relaxation in which this separation is reduced. For I there are two recognizable relaxation paths. In the first, there is a relative translation of the two chromophores, in opposite directions, parallel to the long axis of the molecule. This leads to a reduction of fluorescence yield (to 0.68) and a reduction of decay time (to 63 ns) as well as a small red shift of the fluorescence band. In the second, there is a change of conformation of the butane bridge which brings the two chromophores closer together. It is accompanied by an activation barrier of 8.3 kcal mol^{-1} and the new conformation has a fluorescence band with a large red shift. Photochemistry proceeds via this conformation with the formation of the photoisomer. The likely structure of this molecule has an arrangement of the butane bridge which has been found in the crystal structure of the photoisomer of 1,4-di(9-anthryl)butane. For II, the properties of the fluorescence can be rationalized on the basis of only two conformations, each with the same conformation of the pentane bridge. No photochemistry could be observed and no red-shifted fluorescence band, analogous to that of I, was found. Two rotational barriers would be involved to reach the conformation of the pentane bridge in the most likely molecular structure of the photoisomer and the rate is too low to be measurable.

Introduction

The [2.*n*](9,10)anthracenophanes provide a particularly useful series of linked anthracene chromophores. The ethane bridge, common to the series, acts as a hinge permitting the chromophores to open away from the most constrained conformation as the length of the second bridge is increased from n = 2. For the latter molecule there exist two crystalline polytypes. In the β form, crystal-structure analysis[1] shows that the arrangement of the two chromophores involves a small relative translation of one chromophore over the other in a direction parallel to the long axis of the molecule. Similar analyses of [2.4](9,10)anthracenophane (I) and [2.5]-(9,10)anthracenophane (II) have been carried out in this laboratory.[2]

I crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 10.551 (1) Å, b = 26.512 (3) Å, c = 8.952 (1) Å, and β = 114.735 (8)°. The structure has been refined to a conventional R factor of 0.041 for 2178 observable data. The model obtained exhibits large thermal parameters and some discrepancies in the molecular geometry, characteristic of a disordered structure. It results from the superposition of two molecular conformations which differ (mainly) in the ethane bridge configurations. The two possible skew conformations have been identified by their distinct hydrogen atom locations. The average position of every other atom has been determined.

II crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 10.607 (3) Å, b = 26.881 (8) Å, c = 9.499 (2) Å, and β = 115.87 (2)°. The structure has been refined to a conventional R factor of 0.052 for 1979 observable data. There is a similar conformational disorder as for I. However, insufficient resolution prevented the accurate location of each hydrogen atom in the disordered ethane bridge.

The existence of more than one stable molecular conformation in the ground states of [2.2](9,10)anthracenophane and [2.3](9,10)anthracenophane has been shown in another paper[3] and earlier work,[4] so it seemed essential to have an independent model for the assessment of the probable conformations for I and II and their molecular geometries. We have found molecular mechanics calculations to be particularly useful in this regard and we have employed them with considerable success to predict the various conformations of the anthracenophanes and their respective photoisomers.

A general feature of the molecular force field calculations for [2.*n*](9,10)anthracenophanes (n = 2–5) is the predicted existence of pairs of conformers. Compared with a hypothetical structure in which the two anthracene fragments would have an eclipsed conformation, one member displays a small relative rotation of the anthracene framework about the interchromophore axis while the other shows a small relative translation parallel to the long molecular axis. The number of pairs is determined by the number of possible conformations of the n carbon atom bridge (as constrained by the 1,2-di(9-anthryl)-ethane framework).

The force-field calculations have made possible a rationalization of the spectroscopic and photochemical properties of the [2.*n*](9,10)anthracenophanes. The present paper deals with

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