## Stabilization of Singlet Oxygen in Solution. Catalysis of the Thia-allylic Rearrangement by Various Oxygen Species

*Summary:* All sources of $^3O_2$ and both photochemical and endoperoxide sources of $^1O_2$ show strong catalysis of the thia-allylic rearrangement of phenylallyl sulfides at temperatures in the range of 140–200 °C where, normally, $^1O_2$ is rapidly quenched.

*Sir:* A long-lived singlet oxygen species has been identified in $CS_2$ solution by Foote, Peterson, and Lee.[1] This could be correlated with the fact that sulfides form adducts[2] with $^1O_2$, thioanisole forming phenylmethyl persulfoxide. In the course of studies of catalysis in the thermal rearrangement of phenylallyl sulfides[3] singlet oxygen has now been found to form reversibly an adduct which remarkably prevents its conversion to the more stable $^3O_2$ even at elevated temperatures in the range 140–200 °C.

The sources of $^1O_2$ showing this behavior are the usual dye-sensitized preparations[4] as well as certain endoperoxides such as rubrene peroxide, **1**. This latter substance is known[5] to evolve molecular oxygen rapidly and quantitatively at ~140 °C. When **1** is mixed with aliphatic sulfides and the thoroughly degassed solution is heated in a sealed tube to this temperature, the red color of rubrene (**2**) rapidly emerges, and the reaction forming aliphatic sulfoxide appears to be completed in a short time. This is one of several indications that the initial product of decomposition of **1** is $^1O_2$, which eagerly complexes with sulfides prior to sulfoxide formation.[2] Ordinary $^3O_2$ does not produce sulfoxides under these conditions.

When **1** was added to the deuterated phenylallyl sulfide, **3**, and the solution heated, the isomerization to **3a** was greatly accelerated (Table I). The rate of thia-allylic rearrangement[3] of $\alpha$-methylallyl (**4**) to crotylphenyl sulfide (**4a**) was also strongly enhanced by the presence of **1** (Table II); the catalyzed reaction, $k_c$, required nearly 7 *kcal* less activation than the unimolecular isomerization, $k_1$. Apparently, the catalytic species remained at constant concentration and the effective concentration of $^1O_2$ was not diminished by the reaction. The kinetics were cleanly pseudounimolecular for the entire course of reaction pursuit (~80% completion), and no products indicative of oxidation by $^1O_2$ could be found despite the presence of an olefin in the allyl substrate. Moreover, neither the sulfoxide nor the sulfone, possible oxidation products of the sulfide moiety, showed any catalytic activity of the nature displayed by the $^1O_2$.

Atmospheric oxygen saturating a solution of **3** appeared to have even greater catalytic activity than $^1O_2$. Measured amounts of $^3O_2$ could be introduced via the (in situ) thermal decomposition of a mixture of *tert*-butyl hydroperoxide (TOOH) and di-*tert*-butyl peroxide (TOOT) which is known[6] to give rise to molecular oxygen according to the equation $2(TOOH) \rightarrow 2(TOH) + O_2$, when heated in the chlorobenzene solution. Though the $k_c$ for the $^3O_2$-catalyzed isomerization at 160 °C appears to be ~$10^3$ times as great as that for $^1O_2$ (see Table I), this comparison is meaningless since it was not possible to estimate what proportion of the singlet oxygen formed from rubrene peroxide decomposition was initially quenched and what fraction remained to function as an effective catalyst.

Further proof, however, that catalysis by **1** involves an entirely different species ($^1O_2$) than took part in the molecular oxygen process could be obtained through studying the effect of added rubrene. By itself **2** has no influence on the rate of isomerization, but, in the presence of $^3O_2$, a small quantity of rubrene (~$2 \times 10^{-3}$ mol/l.) in a 0.03 M solution of **4** retards the isomerization rate nearly 55-fold. On the other hand the results of rate studies in which varying amounts of **2** are added to the isomerization reaction of **4** in the presence of **1** afford a very different picture. Only a 25% rate retardation is experienced upon addition of the same amount of rubrene; i.e., rubrene competes with the phenylallyl sulfide substrate for $^3O_2$ in reversible complex formation some 200 times as effectively as it does for $^1O_2$. The rapid absorption of oxygen by rubrene solutions which has been observed here prior to conversion to peroxide **2** under the influence of light suggests

$$2 + {}^3O_2 \rightleftharpoons \underset{\text{rubrene–oxygen triplet complex}}{[\cdot\mathbf{2}\text{-}O_2\cdot]} \overset{h\nu}{\rightleftharpoons} \underset{\text{singlet endoperoxide}}{\mathbf{1}} \xrightarrow{\Delta} 2 + {}^1O_2$$

the possibility that a relatively stable Rubrene-oxygen triplet intermediate can form under these circumstances. This would also explain the effectiveness of rubrene inhibition of $^3O_2$ catalysis.

The unusual stabilization of $^1O_2$ by phenylallyl sulfides is also confirmed in studies of the oxidation of thioanisole to its sulfoxide by endoperoxide sources of $^1O_2$. For example, ru-

**Table I. Catalysis of the Rearrangement $C_6H_5SCH_2CH{=}CD_2$ (3) $\rightleftharpoons$ $C_6H_5SCD_2CH{=}CH_2$ (3a) at 160 °C in *o*-Dichlorobenzene at 0.954 mol/l.[a]**

| $k_{obsd}$ ($10^4$) $sec^{-1}$ | Rubrene peroxide ($10^2$), mol/l. | TOOH[b] in TOOT ($10^4$), mol/l. | $k_{obsd}$[b] ($10^4$), $sec^{-1}$ |
|---|---|---|---|
| 0.162 | 0 | 0 | 0.162 |
| 0.585 | 1.65 | 0.151 | 0.430 |
| 0.690 | 2.19 | 1.27 | 2.94 |
| 0.980 | 3.37 | 1.94 | 4.33 |
| 1.225 | 4.18 | 3.02 | 6.75 |

[a] Rubrene peroxide, $k_c = 2.5 \times 10^{-3}$ $M^{-1}$ $sec^{-1}$; TOOH/TOOT, $k_c$[b] = 2.2 $M^{-1}$ $sec^{-1}$; $k_{obsd} = k_1 + k_c[c]^{1.0}$, where [c] is the catalyst concentration. [b] Estimated concentration of TOOH in the TOOT; this estimate could be in error by as much as a factor of two, but the percent error in the [TOOH] is identical in all the entries. Thus, both the $k_{obsd}$ and the $k_c$ here are considered only *apparent* values.

**Table II. Kinetics of the Rearrangement (0.03 mol/l.) $\alpha$-Methylallyl (4) $\rightleftharpoons$ Crotylphenyl (4a) Sulfide in the Presence of Rubrene Peroxide (0.025 mol/l.) in *o*-Dichlorobenzene Solution[a]**

| Temp, °C | $k_{obsd}$ ($10^6$), $sec^{-1}$ | $k_1$ ($10^6$), $sec^{-1}$ | $[k_{obsd} - k_1]$ ($10^6$), $sec^{-1}$ | $k_c$ ($10^4$), $M^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|
| 170.0 | 24.9 | 1.50 | 23.4 | 9.36 |
| 160.0 | 13.7 | 0.70 | 13.0 | 5.20 |
| 150.0 | 6.99 | 0.29 | 6.7 | 2.68 |
| 140.0 | 3.37 | 0.12 | 3.25 | 1.30 |

[a] $k_1 = (2.78 \times 10^9) \exp(-30{,}800/RT)$; $k_c = (6.34 \times 10^8) \exp(-23{,}900/RT)$.

**Table III. Kinetics of Decomposition of Rubrene Peroxide (1) at 1.5 mol/l. in Benzene Solution[a]**

| Reagents added | Concn ($10^4$), mol/l. | $10^6k$ (temp, °C), $sec^{-1}$ | Reagents added | Concn ($10^4$), mol/l. | $10^6k$ (temp, °C), $sec^{-1}$ |
|---|---|---|---|---|---|
| None | 1.5 | 4.5 (100), 33 (120), 176 (140) | Thioanisole in decalin | 3.0 | 6.1 (100) |
| Thioanisole | 3.0 | 5.5 (100), 36 (120) | Thioanisole | 30 | 31 (120), 171 (140) |
| Thioanisole<br>Phenylallyl sulfide | 3.0<br>3.0 | 5.9 (100), 36 (120) | Phenylallyl sulfide | 12 | 32.5 (120), 160 (140) |
| Thioanisole<br>Phenylallyl sulfide | 3.0<br>3.0 | 5.9 (100), 36 (120) | | | |

[a] Computed: log $A$ = 10.1; correlation coefficient = 0.999; $E_a$ = 26.2 ± 0.12 kcal/mol.

brene peroxide (0.85 g, 1.5 mmol) and thioanisole (0.16 g, 1.26 mmol) were combined in benzene (3.1 ml) and the thoroughly degassed, pressure tubes with such solutions were heated at 140° for 72 h. Other tubes, the same in every respect but containing in addition phenylallyl sulfide (0.15 g, 1.0 mmol), were subjected to identical reaction conditions. The yield (9 ± 1%) of phenylmethyl sulfoxide realized in the absence of **3** was nearly doubled (17%) in the presence of the allylic sulfide; yet no phenylallyl sulfoxide could be detected by NMR, GLC, or other chromatographic means. Comparable results were obtained using diphenylanthracene peroxide (0.545 g, 1.4 mmol) with thioanisole (0.15 g, 1.24 mmol) in benzene (2.5 ml) solution heated for 17 h at ~95 °C. The yield of thioanisole sulfoxide again was more than doubled when the oxidation took place in the presence of phenyllyl sulfide (0.15 g, 1.0 mmol). Replacement of **3** by β-phenyl-*p*-nitrophenylallyl sulfide produced further increases in the yield of sulfoxide and sulfone.

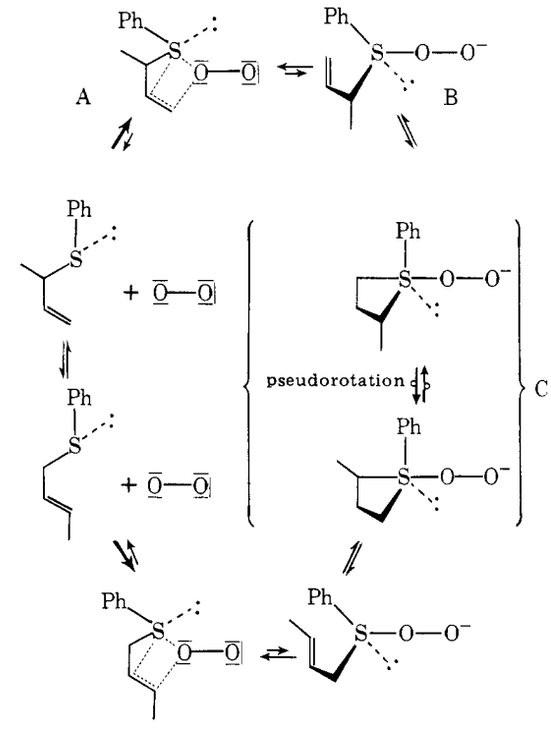
Photogeneration of $^1O_2$ during 8 h of uv irradiation of an eosin-phase transfer agent–benzene solution of thioanisole continuously saturated with oxygen gave ~2.1% sulfoxide, but in the presence of an equimolar amount of phenylallyl sulfide the yield was more than doubled (4.5% thioanisole sulfoxide, 0.5% sulfone with no phenylallyl sulfoxide to be found).

The kinetics of decomposition of **1**, pursued spectrophotometrically in solution in sealed cuvettes, were studied over a 40 °C temperature range. The data (Table III) show that **1** forms **2** and $^1O_2$ unimolecularly and that the rate is almost totally unaffected by the presence of thioanisole, phenylallyl sulfide, or a combination of these reagents. This indicates that there is no induced decomposition of the transannular peroxide involved in the catalysis of thia-allylic rearrangement by $^1O_2$. Moreover, since there is no evidence that $^3O_2$ is present or has been formed during the course of kinetic study with **1**, it can be said the $^1O_2$ is not quenched at the elevated temperatures because it is very rapidly and reversibly sequestered in the form of a phenylallyl sulfide complex of persulfoxide nature. In other words, the $^1O_2$ is surrendered in bimolecular complex formation with phenylallyl sulfides without ever experiencing any freedom as such in the high temperature medium. In this type of complex it is held more tightly than with ordinary sulfides or $CS_2$.[1,2] In the presence of a large excess of **3** or **4** it appears to be bound and prevented from quenching even at temperatures in excess of 140 °C where there is little tendency for complexing between $^1O_2$ and rubrene.

The simplest explanation of the role of electrophilic catalysts such as $^3O_2$, $^1O_2$, and others[7] in bringing about acceleration of thia-allylic rearrangement must encompass some common features in the catalytic action of all of these reagents. Fortunately it does not seem necessary to devise a uniquely different catalytic mechanism for each recognized catalyst.[8] This is deducible from the previously established fact[3] that the thia-allylic rearrangement involves octet expansion with formation of a trigonal bipyramid (TBP) intermediate which undergoes permutational isomerism[9-11] in the rate-determining step. Thus, the role of catalysts seems most likely to involve lowering of the pseudorotation barrier. It has been anticipated[12] that the higher the hypervalency of the central atom the lower the barrier to permutational isomerism among 3rd row elements. In the case of sulfur this has already been verified experimentally, wherein it has been found in these laboratories[13] that the rearrangement occurs with allylic sulfoxides and sulfones with considerably greater ease than in the case of divalent sulfur, but with very similar reactivity patterns (solvent effects, substituent effects, and isotope effects). Consequently, the most reasonable deduction is that electrophilic catalysts, which can coordinate one of the unshared pairs of the allylic sulfur and thereby effect some increase in its valency, speed up the process of permutational isomerism and thus the thia-allylic rearrangement rate.

Since there are no products formed from direct covalent bonding of $^1O_2$ to either the S or C centers of the substrate, it must be assumed that its preservation against quenching must be the result of a reversible donor–acceptor complex which is considerably more stable than that formed with (say) thioanisole. Scheme I is presented as a rationalization of the

Scheme I. Thia-allylic Catalysis by Singlet Oxygen[a]




[a] A, donor–acceptor complex stabilizing $^1O_2$; B, rearrangement of complex with octet expansion and TBP formation; C, TBP with weak axial bond in the persulfide.

facts discussed above. A similar scheme can also be applied for $^3O_2$ catalysis.

### References and Notes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(6) The decomposition of *tert*-butyl hydroperoxide in its presence has been discussed by (a) E. R. Bell, J. H. Raley, F. F. Rust, and W. E. Vaughn, *Discussions Faraday Soc.*, **10**, 242 (1951); (b) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968).
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(8) A referee has suggested several ingenious mechanisms which do account for many of our observations. However, unique and unrelated mechanims are required respectively for $^1O_2$ and $^3O_2$, which, moreover, involve strong covalent bonding to either S or C at intermediate stages. Such postulates presage some formation of S–O and or C–O bonded products which are not found in this reaction where the rate dependence on the first power of the initial concentration of catalyst has been an invariable rule.
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(13) Unpublished results of D. Benko of these laboratories to be presented in a future article.



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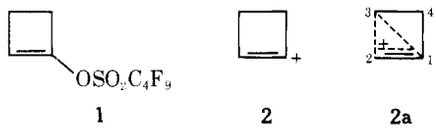
## Vinyl Cations. 25.[1] Solvolysis of Cyclobuten-1-yl Nonaflate. Evidence for a Cyclic Vinyl Cation Intermediate


*Summary:* Cyclobuten-1-yl nonaflate (**1**) solvolyzes in absolute trifluoroethanol via a cyclic vinyl cation intermediate giving rearranged products. Other probable solvolysis mechanisms were experimentally excluded.


*Sir:* Compared to other ring vinyl derivatives cyclobuten-1-yl nonaflate (**1**) solvolyzes with an exceptionally high reaction rate.[2] This was explained by postulating a cationic intermediate (**2a**) in which the positive charge is stabilized by nonclassical interaction.[3] Earlier MO calculations[4] supported the view that the $\sigma$-bond orbitals of $C_2$–$C_3$ came into overlap with the vacant p orbital of the cation at $C_1$ (**2a**). Recent ab initio




calculations are in agreement.[5] (At the completely optimized RHF/STO 3G level, **2a** is 2 kcal/mol less stable than the cyclopropylidene cation, **9**.) To obtain an unambiguous insight into the mechanism of the solvolysis of **1**, we have now carried out several experiments which clearly point out a cyclic vinylic cation intermediate.

Beside the vinyl cation mechanism, other compatible pathways in the solvolysis reactions of cyclobuten-1-yl nonaflate (**1**) are the oxygen–sulfur cleavage and electrophilic/nucleophilic addition–elimination reactions.[2] They have, however, been ruled out by kinetic studies which showed that the solvolysis rate of **1** was independent of the pH in the range of 3.2–9.2.[3] An experiment to exclude the oxygen–sulfur cleavage by conducting the solvolysis of **1** in EtOH–$H_2{}^{18}O$ failed owing to the incorporation of $^{18}O$ into the cyclobutanone oxygen in a blank experiment. The solvolyses of **1** are always carried out at lower temperatures (~75 °C), while an oxygen–sulfur cleavage, including a nucleophilic attack of the solvent at sulfur as in the case of phenyl triflates, occurs only at higher temperatures.[6]

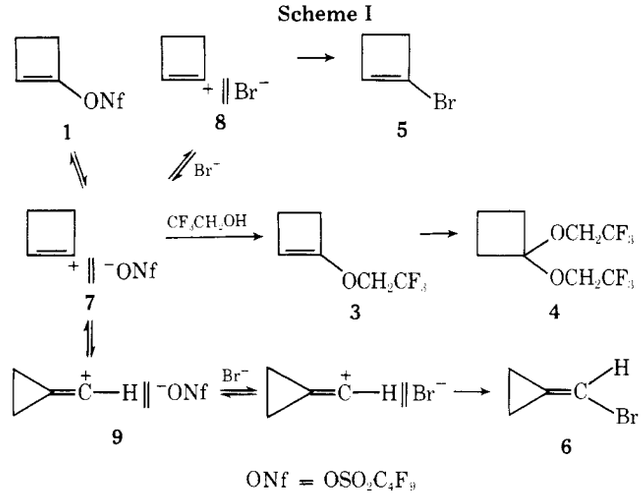
In order to capture the intermediate cyclobuten-1-yl cation, we have now carried out the solvolysis of **1** in absolute trifluoroethanol (TFE) buffered with triethylamine at 75 °C for 10 days. Cyclobuten-1-yl trifluoroethyl ether (**3**) and the ketal (**4**) which were formed[7] in the ratio of 10:1 were isolated by preparative gas chromatography and identified. **3**: NMR $\delta$ 4.61 (s, 1 H), 4.18 (q, 2 H), 2.64 (m, 2 H), 2.13 (m, 2 H) ppm; MS *m/e* (rel intensity) 153 (5.5), 152 (61.4, $M^+$), 151 (6.4), 53 (74.3, cyclobuten-1-ium ion), 39 (base peak, cyclopropenium ion). **4**: NMR $\delta$ 3.78 (q, 4 H), 1.6–2.5 (m, 6 H). The formation of the enol ether **3** can be explained only by postulating an intermediate cyclobuten-1-yl cation **2**. The ketal **4** is formed by the addition of TFE to **3**.

An addition–elimination mechanism for the solvolysis of cyclobutenyl nonaflate (**1**) in TFE was excluded unequivocally by carrying out the solvolysis of **1** in absolute $CF_3CH_2OD$ under the conditions mentioned above. The enol ether **3** obtained was examined by GC–MS and found not to contain any deuterium. **3** was separated by preparative gas chromatography and its NMR analysis also showed the complete absence of any deuterium incorporation. The fact that no deuterium was incorporated in **3** rules out an addition–elimination mechanism in the solvolysis of **1**.

A conclusive experiment to prove the intermediate formation of the four-membered cyclic vinyl cation was made as follows. The solvolysis of **1** was carried out in absolute TFE buffered with triethylamine and containing a tenfold excess of tetraethylammonium bromide at 75 °C for 10 days. The product analysis showed that cyclobuten-1-yl bromide (**5**) and cyclopropylidenemethyl bromide (**6**) were formed (53.3% in total) in a ratio of 85:15, along with 34% **3** and 0.9% **4**. The compounds **5** and **6** were identified by GC–MS and NMR spectra, respectively, which were compared with those of authentic samples.[8]

The formation of the bromide **5** and the rearranged cyclopropylidenemethyl bromide (**6**), along with **3** and **4**, are explained as shown in Scheme I, involving ion pairs. In the solvolysis reaction the solvation of the leaving group leads to the solvent separated ion pair **7**. From **7** both the product **3** or the intermediate ion pair **8** are formed which react either with the

Scheme I




ONf = $OSO_2C_4F_9$