Singlet Oxygen Generation from [Bis(trifluoroacetoxy)iodo]benzene and Hydrogen Peroxide

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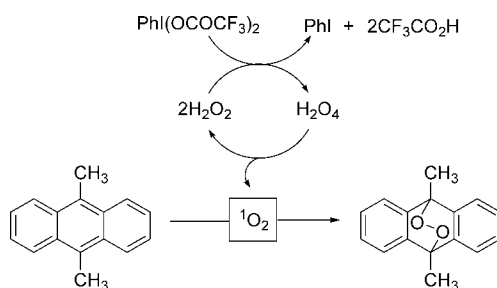
Decomposition of hydrogen peroxide with a hypervalent iodine compound was examined. The results indicate that treatment of a hypervalent iodine compound with hydrogen peroxide produces singlet molecular oxygen ($^1O_2$). Convergent evidence for the production of singlet molecular oxygen ($^1O_2$) by decomposition of hydrogen peroxide with a hypervalent iodine compound comes from chemical trapping experiments and the specific chemiluminescence detection of $^1O_2$ at 1270 nm. Substantial evidence demonstrates that hydroperoxyl radical produced from hydrogen peroxide with hypervalent iodine reacts via a tetraoxidane intermediate, decomposing to give singlet molecular oxygen.

Introduction

One of the most important aspects of oxygen chemistry differentiating it from carbon chemistry is that oxygen does not form chain analogues since the capacity of oxygen to form hydrogen polyoxides is limited. Hydrogen peroxide, the first member of the hydrogen polyoxides, has a weak O–O single bond and decomposes at room temperature to release water and molecular oxygen.[1] Higher members of the hydrogen polyoxides, trioxidane[2] (H_2O_3) and tetraoxidane[2a,3] (H_2O_4), are difficult to prepare and isolate. Indeed, they are prone to decomposition

at low temperature since the presence of strong lone pair–lone pair repulsions in compounds decreases bond dissociation energy. Trioxidane (H_2O_3) has been characterized by NMR including ^1H and O^{17} as well as IR spectroscopy.[4] Recently, the structure of trioxidane (H_2O_3) has been determined by microwave spectroscopy.[5] A preparative synthesis of trioxidane (H_2O_3) from MTO-catalyzed transformation of silyl and acetal hydrotrioxides has been reported by Cerkovnik and Plesničar.[6] The first report of the existence of H_2O_4 was spectroscopically confirmed by Giguere in 1971 through an analysis of the glassy

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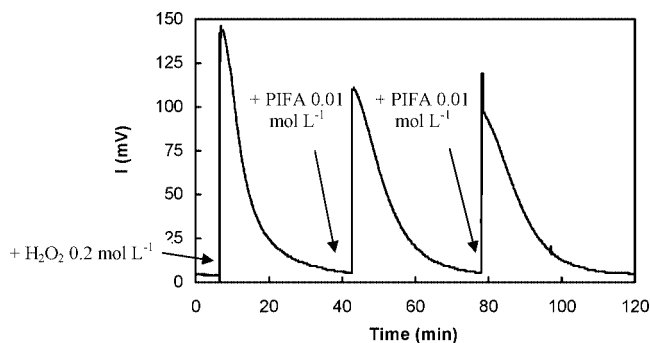(6) Bergant, A.; Cerkovnik, J.; Plesničar, B.; Tutle, T. *J. Am. Chem. Soc.* **2008**, *130*, 14086–14087.

FIGURE 1. IR luminescence signal of $^1O_2$ generated by a solution containing 0.01 M PIFA, 0.1 M NaHCO$_3$ and 0.2 M H$_2$O$_2$ in toluene at T = 20 °C.
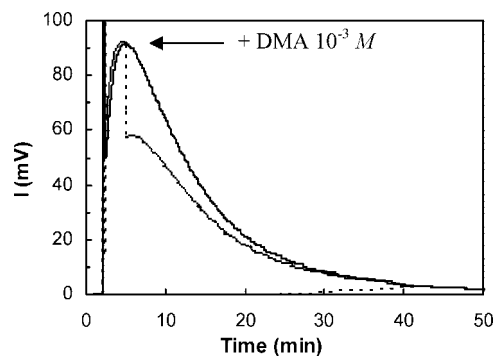

FIGURE 2. Comparison of the IR luminescence signals of $^1O_2$ generated with and without addition of 10^{-3} M DMA. Conditions: 0.01 M PIFA, 0.1 M NaHCO$_3$, and 0.2 M H$_2$O$_2$ in toluene at T = 20 °C.

solid formed when a water vapor stream was dissociated by passing it through a microwave or electric discharge and then rapidly frozen onto a microcrystalline cadmium telluride plate for IR analysis.[3] Then, in 1982, Diem reported the photolytic preparation of H$_2$O$_4$ and its matrix isolation IR spectrum.[7] In a recent report, Sawyer described in situ generation of H$_2$O$_4$ at an electrode surface via radical coupling of two hydroperoxyl groups HOO[•] and showed that H$_2$O$_4$ decomposes into singlet oxygen and hydrogen peroxide.[8] Bond dissociation energies of H$_2$O$_2$, H$_2$O$_3$, and H$_2$O$_4$ were calculated as 49.9, 33.9, and 17.8 kcal/mol, respectively.[9] Heats of formation of H$_2$O$_3$ and H$_2$O$_4$ were calculated as −21.50 and −10.61 kcal/mol, respectively.[3d] In accordance with the theoretical findings, H$_2$O$_3$ decomposes at near −50 °C, and H$_2$O$_4$ decomposes at −100 °C.[2−6] In a recent communication, we reported that treatment of hydrogen peroxide with [bis(trifluoroacetoxy)iodo]benzene (PIFA) (**1**) results in the formation of expected singlet oxygen products in the presence of singlet oxygen acceptors.[10]

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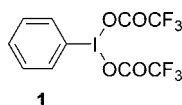
These results were submitted as evidence that the molecular oxygen formed during the decomposition of hydrogen peroxide with PIFA was in the excited singlet state, and singlet oxygen formation via H$_2$O$_4$ intermediate is postulated. Thus, this reaction appeared to be particularly interesting as a possible chemical method for the generation of singlet oxygen to allow the preparation of organic peroxides. In this paper, we report the 1270 nm chemiluminescence characteristic of singlet oxygen from the decomposition of hydrogen peroxide with PIFA. Quantitative measurements of singlet oxygen yield and a discussion of possible reaction mechanism for the production of singlet oxygen from hydrogen peroxide/PIFA are presented.

Results and Discussion

Singlet oxygen generation from the decomposition of hydrogen peroxide with PIFA was studied by chemiluminescence (CL) spectroscopy. Although chemical trapping (CT) of $^1O_2$ has been most widely used to quantify the amount of $^1O_2$ produced,[11] detection and measurement of the monomol light emission of

$^1O_2$ in the near-infrared (NIR) spectral region (λ = 1270 nm) constitute unambiguous proof of $^1O_2$ formation since the detection of a signal at 1270 nm is specific for this excited species.[12] Furthermore, it allows the direct determination of the amount of $^1O_2$ involved in the process. The observed photo-emission corresponds to the deactivation of one molecule of $^1O_2$ to the triplet ground state (eq 1). CL spectroscopy has already been proven to be very useful for the study of reaction kinetics and yields of $^1O_2$ formation in homogeneous media.[13]

$$^1O_2(^1\Delta_g) \rightarrow {}^3O_2(^3\Sigma_g-) + h\nu \ (\lambda = 1270 \ nm) \quad (1)$$
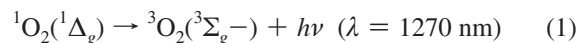
Evidence for Singlet Oxygen Generation from the PIFA/H$_2$O$_2$ System. The generation of singlet molecular oxygen, $^1O_2$ ($^1\Delta_g$), from the PIFA/H$_2$O$_2$ system was first studied in toluene by resorting to the detection of the IR luminescence at 1270 nm. Figure 1 represents the chemiluminescence signal obtained in toluene through the decomposition of H$_2$O$_2$ 0.2 mol L^{-1} with PIFA 0.01 mol L^{-1} in the presence of NaHCO$_3$ 0.1 mol L^{-1} at 20 °C.

We can see that as soon as H$_2$O$_2$ is added to the PIFA solution, a relatively high signal with a maximum intensity of about 150 mV is detected. Most of the PIFA is decomposed within 40 min, and successive additions of PIFA provide a similar chemiluminescence signal. The yield of $^1O_2$ generated from the PIFA/H$_2$O$_2$ system was measured by addition of a known amount of 9,10-dimethylanthracene (DMA), which reacts rapidly with $^1O_2$ by a pure chemical process (k_r = 2.5 × 10^7 M^{-1} s^{-1} in benzene[14]) (Figure 2).

Addition of DMA leads, as expected, to a decrease in the chemiluminescence signal, indicating that a part of the $^1O_2$ produced is chemically quenched by the trap. As the total area under the curve is directly related to the cumulated amount of $^1O_2$ generated, the missing area corresponds to an amount of $^1O_2$ equal to the initial concentration of DMA. Thus, the yield of $^1O_2$ generated from the H$_2$O$_2$/PIFA system was assessed to be 55%.

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TABLE 1. Chemiluminescence Detection of $^1O_2$ Generated from PIFA (0.01 M) and Hydrogen Peroxide (0.2 mol L^{-1}) in the Presence of $NaHCO_3$ (0.1 mol L^{-1}) at 20 °C in Various Organic Solvents^a

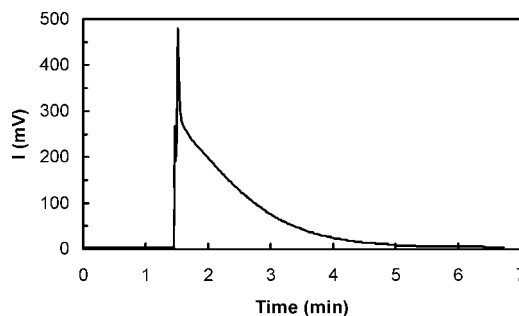| solvent	τ_Δ (μs)[15]	I_{max} (mV)	Δ_t (min)	area (mV min)
CH_3OH	10	255	0.1	6
MTBE	30	370	4	233
toluene	30	145	40	1250
THF	22	450	2	200
CH_2Cl_2	97	280	5	370
$CHCl_3$	230	252	40	1890
CCl_4	1300	319	60	4632

^{a} I_{max} = maximal intensity of the luminescence signal, Δ_t = time corresponding to 5% of I_{max}, area = area under the curve of the luminescence signal, τ_Δ = lifetime of $^1O_2$ in the pure solvent.

TABLE 2. Influence of Base, Temperature, and Hydrogen Peroxide Concentration on Chemiluminescence Detection of $^1O_2$ Generated from PIFA (0.01 M) and Hydrogen Peroxide under Variable Conditions

| reaction media	T [°C]	$[H_2O_2]$ (mol L^{-1})	I_{max} (mV)	Δ_t (min)	area (mV min)
$CHCl_3$ + pyridine (0.1 M)	20	0.2	180	a few seconds	not significant
$CHCl_3$	20	0.2	300	25	880
$CHCl_3$ + $NaHCO_3$ (0.1 M)	20	0.2	252	40	1890
THF	2	0.2	132	8	195
THF	20	0.2	450	2	200
toluene	20	0.01	40	50	450
toluene	20	0.02	80	60	1170
toluene	20	0.05	80	60	1270
toluene	20	0.1	80	60	1400
toluene	20	0.3	100	50	1100

Influence of the Solvent. The generation of singlet oxygen from the PIFA/H_2O_2 system was also studied in seven other typical solvents of different polarity. The solvents were compared in terms of maximal signal intensity (I_{max}) and time required to decompose a given amount of H_2O_2 (Δ_t). The results are listed in Table 1. Among the studied solvents, methanol does not allow significant production of $^1O_2$ from the H_2O_2/PIFA system. The initial chemiluminescence signal is relatively high (255 mV) but disappears within a few seconds. On the other hand, if we compare toluene, MTBE (methyl-*tert*-butylether), and THF, in which the lifetimes of $^1O_2$ are quite similar, the highest $^1O_2$ production is obtained in toluene even if the other two produce the excited species faster as attested from the I_{max} values. By comparing the area under each curve, it can be deduced that the yield of $^1O_2$ generated is about 5 times higher in toluene than in THF or in MTBE. Finally, it appears that quite efficient generation of $^1O_2$ also occurs in chlorinated solvents. It is noteworthy that in some solvents, especially CCl_4, there is a latent period that can be from 10 to 45 min before the production of $^1O_2$.

Influence of Base, Temperature, and Hydrogen Peroxide Concentration. Other CL experiments have been performed by varying either the base (no base, pyridine instead of $NaHCO_3$) and by changing the temperature. The results are listed in Table 2. In the presence of pyridine, no singlet oxygen seems to be formed. In the absence of $NaHCO_3$, relatively good production of $^1O_2$ is observed, but this is doubled in the presence of $NaHCO_3$ 0.1 mol L^{-1}.

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FIGURE 3. IR luminescence signal of $^1O_2$ generated by a solution containing 0.01 M PIFA, 0.1 M $NaHCO_3$, and 0.1 M *rac*-1-phenylethyl hydroperoxide (**7**) in toluene at $T = 20$ °C.

The temperature has no effect on the yield of $^1O_2$, but decreasing the temperature below 18 °C causes a slowing down of the reaction by a factor 4. Concerning the H_2O_2 concentration, the results indicate that 2 molar equiv compared to PIFA is required to obtain maximum $^1O_2$ production. In the presence of a stoichiometric amount of H_2O_2, the signal is two times lower in terms of both the rate of $^1O_2$ generation and yield. Above 2 molar equiv, no improvement is observed, suggesting that the excess of hydrogen peroxide has no influence on the reaction. This result indicates that the reaction of $^1O_2$ production from the H_2O_2/PIFA system is first-order compared to H_2O_2.

Mechanistic Aspects. Ligand exchange reactions of hypervalent iodine compounds with nucleophiles are widely used for the synthesis of other hypervalent iodine compounds in which the oxidation state of iodine does not change.[16] Milas and Plesnicar[17a] reported the reaction of [bis(acetoxy)iodo]benzene with *tert*-butyl hydroperoxide and proposed the in situ generation of labile peroxyiodane [bis(*tert*-butylperoxy)iodo]benzene (**2**), which decomposes even at −80 °C to *tert*-butyl peroxy radical, molecular oxygen, and iodobenzene (**3**).
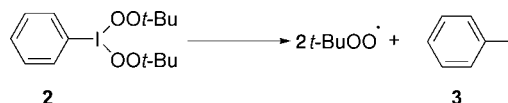

This ready decomposition of [bis(*tert*-butylperoxy)iodo]benzene (**2**) is rationalized in terms of the small dissociation energy of the apical hypervalent peroxy-iodine(III) bond and is facilitated by conjugative overlap of the breaking hypervalent bond with π-orbitals of the benzene ring.[17b,c] In our preliminary communication[18] we reported the nucleophilic addition of hydrogen peroxide to PIFA in THF at 10 °C, yielding molecular

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SCHEME 1.   Proposed Decomposition Mechanism of H₂O₂ with PIFA
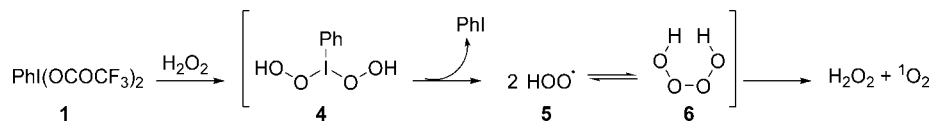
SCHEME 2.   Decomposition of (S)-7 with PIFA
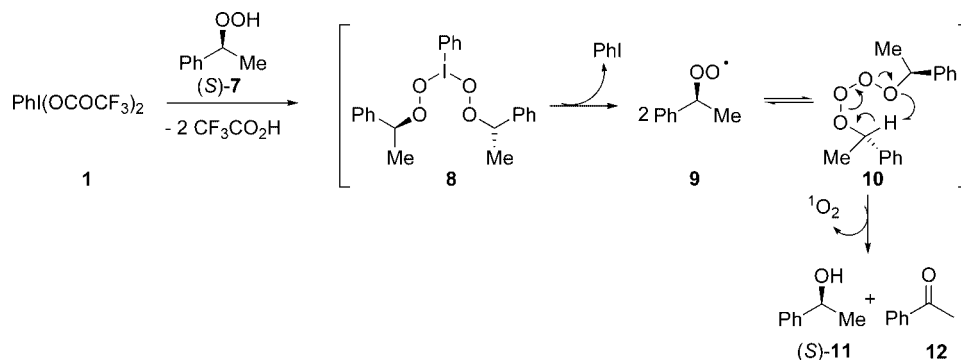
oxygen and iodobenzene (**3**). Ligand exchange of PIFA with hydrogen peroxide yields labile intermediate bis(hydroperoxy)-(phenyl)-λ^3-iodane (**4**), which dissociates peroxyl radicals **5** and iodobenzene (**3**). The homolytic dissociation of the tetraoxidane (**6**) intermediate formed via radical−radical coupling of two hydroperoxyl radicals results in the formation of singlet oxygen (Scheme 1).

Preliminary evidence for the production of singlet oxygen was obtained by isolating ascaridole in 85% yield after the decomposition of hydrogen peroxide with PIFA in THF at 10 °C in the presence of α-terpinene. The product had spectroscopic data identical to those of the product from sensitized photo-oxygenation known to involve singlet oxygen. We established that omission of PIFA or hydrogen peroxide does not lead to the formation of ascaridole, indicating that both hydrogen peroxide and PIFA are essential for peroxidation. To elucidate the mechanistic details of whether or not singlet oxygen results from the homolytic dissociation of hydrogen tetraoxide inter-mediate, the decomposition of the experiment has been con-ducted with optically pure (1S)-1-phenylethyl hydroperoxide (**7**)[19] instead of hydrogen peroxide. After the reaction at −30 °C, (1S)-1-phenylethanol (**11**) (ee> 99) and 1-phenylethanone (**12**) formed in a ratio of 1:3 determined by ¹H NMR. It is well-known that high ketone/alcohol ratios from self-reaction of several secondary alkylperoxyls were observed at low tempera-tures.[20a,b] In agreement with the published results the ratio of alcohol **11** and ketone **12** was approximately equal when the decomposition of (S)-**7** with PIFA was conducted at room temperature. Since only the oxygen−oxygen bond breaks in this reaction and no reaction occurs at the stereogenic carbon atom, the (S) configuration is preserved. The results from this experiment confirm that nucleophilic addition of (S)-**7** to PIFA yields phenyl{bis[(1-phenylethyl)peroxy]}-λ^3-iodane (**8**) as a primary intermediate that loses (1-phenylethyl)dioxidanyl (**9**).[20c,d] The production of singlet oxygen proceeds via a cyclic, *concerted* reaction of the intermediate bis(1-phenylethyl)tet-raoxidane (**10**) formed by coupling of two alkyl hydroperoxyl radicals (Scheme 2). The evidence for the production of singlet oxygen from the decomposition of (S)-**7** is the formation of ascaridole when α-terpinene is present in the reaction. The

generation of ¹O₂ from *rac*-1-phenylethyl hydroperoxide (**7**) (0.1 mol L⁻¹) in the presence of PIFA (0.01 mol L⁻¹) has been studied by the CL technique in toluene.

Figure 3 shows the resulting chemiluminescence signal as a function of time. In toluene, ¹O₂ generation can be significantly detected with a curve exhibiting a maximum at 300 mV (I_{max}) and a total area of 320 mV min, suggesting that, in comparison with hydrogen peroxide, the reaction is about 2 times faster but also about 4 times less efficient, providing a yield of ¹O₂ formation of about 13%. It is noteworthy that no significant CL signal was observed when *rac*-(1-hydroperoxyethyl)benzene (**9**) was replaced by *tert*-butyl hydroperoxide or cumene hydroperoxide. For the latter, the yield of ¹O₂ would be about 1%. No trace of ascaridole was detected in the decomposition of *tert*-butyl hydroperoxide or cumyl hydroperoxide with PIFA under conditions similar to those employed with hydrogen peroxide and (1S)-1-phenylethyl hydroperoxide (**7**) when α-ter-pinene was used as a trapping agent.

It is well-known that alkylperoxyl radicals yield a tetraoxide intermediate that decomposes to give radical or nonradical products.[20b,24] Russell suggested that primary and secondary alkylperoxyl radicals undergo decomposition via a tetraoxide intermediate.[21] The reaction may generate either singlet oxygen or an electronically excited ketone. The formation of singlet oxygen was confirmed by Howard and Ingold,[22] who were able to trap singlet oxygen in about 1% yield. Yields of ¹O₂ from peroxyl radicals generated from radical-initiated autoxidation of ethylbenzene and cumene were found to be 11.5% and 0.8%, respectively.[23] The present results taken together with the fact that singlet oxygen is evolved in the self-reaction of (1-phenylethyl)dioxidanyl (**9**) showed that the Russell mechanism plays a role in the decomposition process. Decomposition of **7** with PIFA was also carried out in CD₂Cl₂ at low temperature (−80 to 10 °C) and at different concentrations in a NMR instrument in order to monitor the formation of **10**. In all cases

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we observed only signals belonging to **11** and **12**. Our results indicate that although di-*tert*-butyltetraoxidane[24] is stable at −70 °C, peroxyiodane **10** decomposes too rapidly to be detected.

In conclusion, the present study clearly reveals that the mechanism of singlet oxygen production from the PIFA/H_2O_2 system is best explained by the decomposition of the transient formed tetraoxidane (**6**). The present system also demonstrates a novel singlet oxygen generator for oxygenation of alkenes using a hypervalent iodine/hydrogen peroxide system, although with moderate singlet oxygen production.

Experimental Section

Detection of Singlet Oxygen Chemiluminescence. Infrared emission of $^1O_2$ was measured with a liquid-nitrogen-cooled germanium photodiode detector, sensitive in the spectral region from 800 to 1800 nm with a detector of 0.25 cm² and a sapphire window. The detector was connected to a lock-in amplifier and was powered by a supply.

Typical Chemiluminescence Experiment. A solution (10 mL of solvent) containing 45 mg PIFA (0.01 mol L^{-1}) and 85 mg $NaHCO_3$ (0.1 mol L^{-1}) was maintained at 20 °C under stirring and put in circulation, by a peristaltic pump, through a quartz cell placed in front of the germanium detector. When the background noise of the IR signal was stabilized, 120 μL of H_2O_2 50 wt % (0.2 mol L^{-1}), was introduced. The intensity of the luminescence signal, I_p, was recorded as a function of time.

Determination of Singlet Oxygen Yield from Chemiluminescence Measurement. The chemiluminescence spectrum was first recorded according to the procedure given above. When the reaction ended, a new batch of PIFA 0.01 mol L^{-1} was added to the reaction medium. When the signal reached its maximum after stabilization, 10^{-3} mol L^{-1} of dimethylanthracene (DMA) was added to trap chemically the $^1O_2$ produced. Comparison of the areas under the two curves allows the determination of the $^1O_2$ yield.

Procedure for Oxidation of α-Terpinene with PIFA−H_2O_2 System. To a solution of α-terpinene (0.27 g, 2 mmol) and 35% hydrogen peroxide (12 mmol) in 10 mL of THF at 10 °C was added $NaHCO_3$ (1.68 g, 20 mmol). Then, a freshly prepared solution of PIFA (2.15 g, 5.0 mmol relative to α-terpinene) in 15 mL of THF was added over 2−3 h. The suspension was filtered, and solvent removed under reduced pressure (5 °C/50 mbar). The residue was extracted with CH_2Cl_2 (2 × 20 mL) and washed with saturated $NaHCO_3$ (10 mL) and water (20 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed at reduced pressure (5 °C/50 mbar). The products were purified on a silica gel column (40 g) by eluting with hexane/diethyl ether (95:5). First fractions gave iodobenzene. Further elution afforded ascaridole (0.28 g, 85%) as a colorless oil.