GAS PHASE GENERATION OF SINGLET OXYGEN AT ATMOSPHERIC PRESSURE

Walter C. Eisenberg,* Alan Snelson, Ronald Butler, and James Veltman
IIT Research Institute, Chemistry and Chemical Engineering Division, Chicago, Illinois 60616

Robert W. Murray
Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121

Abstract. Evidence is presented for the gas phase generation of singlet oxygen using hetero-
geneous photosensitization and atmospheric pressure.

There have been a number of reports of the gas phase generation of singlet oxygen.[1(a-z)]
With one exception, all of this work was carried out at reduced pressure. Bourdon and
Schnuriger[2(a,b)] did report that rubrene and diphenylanthracene present in thin films, and
separated from sensitizer by oxygen permeable stearate layers, could be oxidized at atmospher-
ic pressure. No product identifications were made in this work, however. The gas phase gen-
eration of singlet oxygen using photosensitization has been reported by a number of groups.[1(j-z)]
These reports suggest that the atmospheric pressure generation of $^1O_2$ *via* photosensitization
might be achieved. Of particular significance to the work described here is the recent re-
port[1(g)] that anthracene, which has been dispersed into atmospheric particulate matter and then
subjected to ambient solar irradiation, gives products associated with singlet oxygen oxidation.

We report here evidence for the gas phase generation of singlet oxygen using heterogenous
photosensitization, intense illumination, and *atmospheric pressure*. Singlet oxygen ($^1\Delta g$) was
consistently produced in detectable quantities when air or oxygen was flowed through an ir-
radiated tube coated with Rose Bengal. Evidence for $^1O_2$ formation was obtained from chemical
trapping, product distribution, and physical quenching experiments. While additional work on
reaction parameters is required before optimal conditions are established, it appears that the
rapid air flow rates (ca 50 ℓ/min), the intense illumination (four 1000W General Electric Model
DPT projection lamps) and reactor design are critical.

Photochemical sensitization appeared to be the most desirable approach to generating sin-
glet oxygen in the gas phase providing an easily available source of this activated species devoid
of impurities. In 1933 Kautsky[1(h-k)] described an ingenious series of experiments which demon-
strated that a reactive metastable form of oxygen was involved in dye-sensitized photooxidation
reactions. The observed reaction occurred only at low pressure, i.e., below 0.004 mm, and was
found to be dependent on the separation between the sensitizer and acceptor. All of the experi-
mental evidence pointed to a diffusible, highly reactive species, subsequently shown[3] to be
singlet molecular oxygen as the oxidant.

Petterson, *et al,*[1(l)] had earlier attempted to generate $^1O_2$ at low pressures by passing
oxygen over an irradiated sensitizer. Singlet oxygen was trapped chemically downstream using

rubrene. These experiments required long irradiation times and the detection of $^1O_2$ showed poor reproducibility. Foote and Ando[1(m)] have carried out similar experiments which yielded only "miniscule" amounts of product, often indistinguishable from that of autooxidation. Foote and coworkers[1(n)] have also recently reported the gas phase generation and trapping of $^1O_2$ using P-Rose Bengal[4] as the sensitizer and a polymer bound olefin (6-methyl-5-heptenoate) as the acceptor. However, when air was used at atmospheric pressure this system gave no singlet oxygen product. Recently, Rawls and Estes[1(o)] have described exploratory experiments designed to detect $^1O_2$ as a component in polluted atmospheres. In this work, NO_2 sensitization was used and (+)-limonene was used as acceptor. The authors were able to detect products characteristic of $^1O_2$ oxidation.

The work described here was undertaken to determine the conditions under which $^1O_2$ ($^1\Delta g$) might be generated in the atmosphere, and to test the possibility that reactions involving $^1O_2$ may be important in atmospheric pollution. Oxygen or air was passed down a Rose Bengal coated generator tube at a rate of ca. 50 ℓ/min. The generator tube was cooled with a water jacket and was irradiated with four 1000w General Electric Model DPT projection lamps. This entire assembly was enclosed in a metal light shield and further cooled with a cage blower. At the exit of the generation zone an inlet for the introduction of acceptors and quenchers was attached, followed by light baffle, reaction zone and product traps.

The production of detectable quantities of $^1O_2$ using this system was demonstrated in several ways. As shown in Table 1, tetramethylethylene, 1, is consistently converted to its known[3] singlet oxygen product, 2,3-dimethyl-3-hydroperoxy-1-butene, 2.[5] In separate experiments, we have shown that no detectable singlet oxygen is formed in the generator in the absence of sensitizer or when the reaction zone only is coated with sensitizer. Also, no sensitizer was found in the product traps. These experiments indicate that the reacting singlet oxygen is produced in the generation zone.[6]
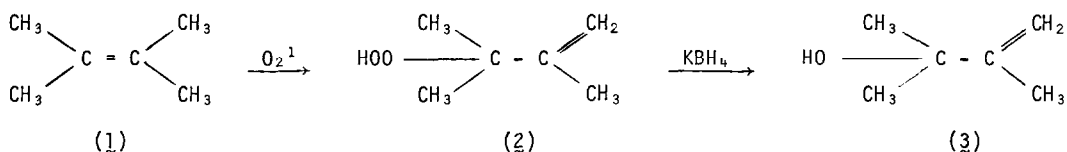
Further evidence demonstrating that singlet oxygen is produced in the reactor was obtained by carrying out a similar oxidation of 2 in the presence of the known[1(p)] singlet oxygen quencher, triethylamine. As shown in Table 1 (expt. 6) these conditions lead to a 90% reduction[5] in the net production of 2.[7] This is to be compared to the 93% reduction predicted on the basis of the previously reported quenching rate for triethylamine.[1(a)]

When 1,2-dimethylcyclohexene, 4, was used as acceptor the products, 2-hydroperoxy-2-methyl-methylenecyclohexane, 5, and 1-methyl-6-hydroperoxy-6-methyl-cyclohexene, 6, were formed in a ratio of 87:13,[8] which is to be compared with the ratio of 89:11 produced under the conditions where singlet oxygen is known to be the oxidant.[9]

Table 1. ATMOSPHERIC GAS PHASE PHOTOOXIDATION OF TETRAMETHYLETHYLENE (TME) SENSITIZED BY ROSE BENGAL[1]

Experiment	TME Alcohol Product Rate (moles/min) Blank Lights Off	Experiment Lights On	Rx Time (min)	Air Flow (ℓ/min)	TME/N_2 Flow (mℓ/min)	Net Production Rate (moles/min)
1	4.0×10^{-8}	1.2×10^{-7}	15	45	500	8.1×10^{-8}
2	3.2×10^{-8}	1.1×10^{-7}	15	45	500	7.8×10^{-8}
3	1.5×10^{-8}	9.8×10^{-8}	15	45	500	8.3×10^{-8}
4[4]	4.1×10^{-8}	4.7×10^{-8}	15	45	500	6.0×10^{-9}
5	6.1×10^{-8}	1.1×10^{-7}	15	50	250	4.9×10^{-8}
6[2]	5.4×10^{-8}	6.0×10^{-8}	15	50	250	5.8×10^{-9}
7[3]	2.0×10^{-8}	3.4×10^{-8}	15	50	250	1.4×10^{-8}

1. Oxidation conditions: 25°C, 760 mm Hg.   2. Triethylamine quencher added.   3. No sensitizer in the generation tube.   4. Reaction vessel only coated with Rose Bengal.

The experiments to date, demonstrate that singlet oxygen was consistently formed in our generation system and suggests that it is sufficiently long lived to react with proximate chemical and biological acceptors under atmospheric conditions. The concentration of O_2 ($^1\Delta g$) in the reaction zone was calculated to be 1.2×10^{-8} moles/liter or 0.4 ppm.[10] Although the concentration of singlet oxygen formed in the gas stream was low, this generation system is useful since it approximates the environmental situation in which long exposure times are typical. In addition, estimates of the intensity of the light source in the generation system indicate it is only ten times the normal solar flux.[1(q)] It is not clear whether the results obtained are optimal, we are now varying a number of system parameters to improve the generation of singlet oxygen. Further work using sensitizers known to be in polluted atmospheres is also planned, as well as experiments to determine kinetic data for reaction of singlet oxygen with suitable substrates.

ACKNOWLEDGEMENT

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5. The hydroperoxide was reduced to the corresponding alcohol, 3, (KBH$_4$ reduction in experiments 1-4, $(C_6H_5)_3$P in 5-7), for the purposes of glc sample. The hydroperoxide was identified by comparing IR and NMR data with those of an authentic sample. The alcohol, 3, has the same mass spectrum and glc retention times (2 columns) as an authentic sample. Coinjection of 3 and authentic alcohol led to glc peak enhancement. Yields were determined by glc based on calibration with authentic alcohol.

6. As indicated in Table 1 background hydroperoxide is present in blank runs. Even when zero levels of hydroperoxide were achieved by twice chromatographying 1 on silica gel levels of 2 reported in Table 1 could be detected in the blank runs. It should be noted that there is a consistent and nearly constant net level of hydroperoxide produced in the reaction chamber. Pitts[1](q) has described this problem of background hydroperoxide in 1

7. It was shown that no other products are formed in this reaction and that triethylamine does not react with 2 under the reaction conditions.

8. The hydroperoxide products were converted to the respective alcohols by reduction with potassium borohydride. The alcohol products were identified by comparison with authentic samples prepared by photosensitized oxidation of 4 in solution.

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10. This is a minimum concentration of $^1O_2$ because it neglects the collisional deactivation of $^1O_2$ by $^3O_2$.