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Photochemical Generation of Singlet Oxygen on Non-transition-metal Oxide Surfaces

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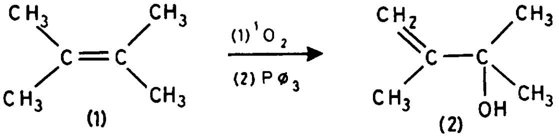
Irradiation of the non-transition-metal oxide powders silica gel, aluminium oxide and magnesium oxide in the presence of oxygen results in the formation of singlet oxygen ($^1O_2$). Two specific chemical traps were used to detect $^1O_2$: 1,2-dimethylcyclohexene and geminally deuterated [$^2H_6$]-2,3-dimethylbut-2-ene. Both compounds gave product distributions characteristic of singlet-oxygen reactions when irradiated on the metal oxide surfaces. These results support previous suggestions that singlet oxygen is formed through an energy-transfer process involving oxygen and excitons on the metal oxide surface. Under the same reaction conditions TiO_2 showed no production of $^1O_2$.

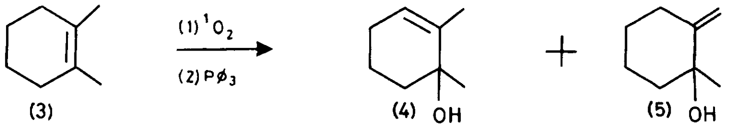
Production of oxidants on metal oxide surfaces has been an area of active research in recent years, and reactive species such as O_3^- and O_2^- have been identified on irradiated surfaces.[1] The photochemical production of singlet oxygen ($^1O_2$) has also been suggested to occur on non-transition-metal oxide surfaces such as MgO,[2] although experimental support is lacking. During a study on the photochemical generation of singlet oxygen on soil surfaces[3] we observed that irradiation of 2,3-dimethylbut-2-ene (1) adsorbed on chromatographic silica gel and alumina resulted in production of the characteristic singlet-oxygen product, 2,3-dimethylbut-1-en-3-ol (2) (scheme 1). Further experiments were then performed to demonstrate conclusively the photochemical production of $^1O_2$ on these surfaces.



Scheme 1.

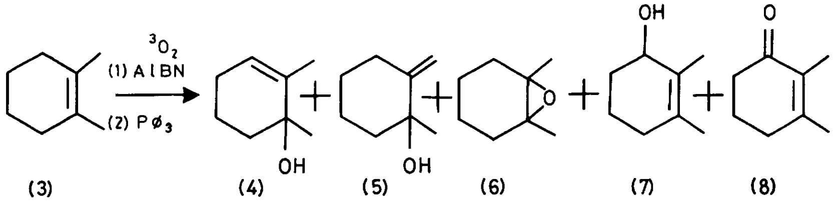
Singlet-oxygen involvement in ground-state catalysis has not been considered likely because it has energy levels of 22.4 kcal mol^{-1} ($^1\Delta_g$) and 37.37 kcal mol^{-1} ($^1\Sigma_g^+$) above ground-state oxygen. However, light of wavelength < 1.29 μm has sufficient energy to result in photocatalytic $^1O_2$ production on metal oxide surfaces, provided the energy is being absorbed by the system and is efficiently transferred to oxygen.

Singlet oxygen can be detected by a variety of methods,[4] including chemicals that specifically trap $^1O_2$. The chemical trap chosen must have sufficient reactivity and a high specificity for $^1O_2$. In this work singlet oxygen was detected using two chemical traps specific for singlet oxygen. 1,2-Dimethylcyclohexene (3) reacts with singlet oxygen by the 'ene' mechanism to form two isomeric allylic alcohols (scheme 2) which are readily distinguished from products formed through radical oxidation.



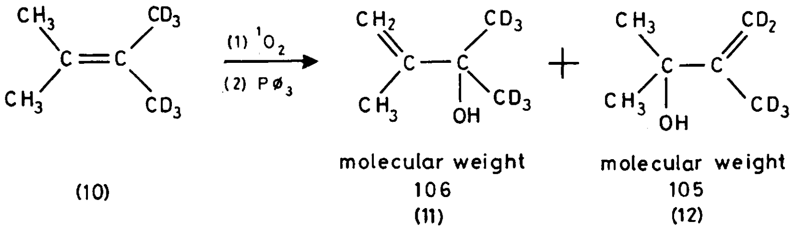
Scheme 2.

Alternatively, during the radical oxidation of (3), the product formed in highest yield is (7), with varying amounts of (4)–(6) and (8) also formed[5] (scheme 3). The ratio of (4) to (5) is inverted compared with authentic singlet-oxygen reactions.



Scheme 3.

A second chemical $^1O_2$ trap consisted of geminally deuterated [$^2H_6$]-2,3-dimethylbut-2-ene (10). This compound also reacts through an 'ene' mechanism to form (11) and (12) (scheme 4), but has $^1O_2$ specificity owing to a kinetic isotopic effect of 1.45 in the abstraction of hydrogen over deuterium.[6]



Scheme 4.

EXPERIMENTAL

Rose bengal, methylene blue, 1,2-dimethylcyclohexene and 2,3-dimethylbut-1-en-3-ol were obtained from ICN-KNK Pharmaceuticals, Inc. 2,3-Dimethylbut-2-ene, triphenylphosphine (PØ$_3$), silica gel grade 923, alumina 99.999%, TiO_2 (IV) 99.999%, *m*-chloroperbenzoic acid and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Aldrich Chemical Co. Deuterated acetone was obtained from Stohler Isotope Chemicals. The epoxide of 1,2-dimethylcyclohexene was synthesized from 1,2-dimethylcyclohexene with *m*-chloroperbenzoic acid. Chromatographic silica was obtained from Muttenz/Schweiz, and MgO and chromatographic alumina were obtained from Merck. Geminally deuterated [$^2H_6$]-2,3-dimethylbut-2-ene was synthesized by a Grignard reaction between deuterated acetone and 2-bromopropane, followed by dehydration with iodine.[7]

In a typical assay, metal oxide powder (1.7 g) was placed in a 50 cm Kimax volumetric flask; the flask was evacuated three times and filled with O_2 or N_2 and sealed with a Teflon-lined septum. The metal oxide powders were not activated by heating or outgassing at high temperatures. The singlet-oxygen-trapping chemical (5.0 mm^3) was then injected into the flask. Since the chemicals rapidly evaporated following injection into the flasks, no further attempt at mixing the chemical and the metal oxide powder was attempted. Irradiation of the flasks was accomplished by an apparatus containing four CW40 Westinghouse fluorescent lamps[8] at 30 °C. Following irradiation, 6 cm^3 of 0.05 mol dm^{-3} $P\O_3$ in methanol was added to reduce the hydroperoxides to alcohols. The flasks were then covered to prevent further exposure to light. The reduction was allowed to proceed for 1 h at 5 °C prior to analysis. The cooled solutions were centrifuged and the supernatant analysed. The analyses were completed within one day, since the epoxide concentrations were observed to decrease over a longer period of time. Gas-chromatographic analysis of compounds (3)–(9) was made on a SPB-5 30 m capillary column (Supelco) using either a flame ionization detector or g.c.–m.s. (Finnigan 4023 gas-chromatograph–mass-spectrometer with Incos data system). Compounds (1), (2), (10), (11) and (12) and their photoproducts were quantitatively estimated either by flame-ionization gas chromatography using a 1.2 m × 2 mm Poropak S column at 180 °C or by g.c.–m.s. with a 2.6 m Carbopak B column at 180 °C. To determine the kinetic isotope effect, molecular ions at 105 and 106 were integrated over the gas-chromatographic peak by g.c.–m.s. and the ratio of integrations calculated. The ^{13}C isotope contribution of 105 and 106 was subtracted.

The radical oxidation of (3) was performed by heating 0.114 mol of (3) and 1.0 mg of AIBN for 3.5 h at 75 °C while bubbling O_2 through the solution.[9] The solution was reduced with triphenylphosphine to prevent further reactions and rearrangements of the hydroperoxides. Aliquots of the solution were then dissolved in methanol and analysed as described above.

Photoproduct identification was accomplished as follows. Compound (2) was identified by co-chromatography and mass spectra with a known standard. Identification of (4), (5), (11) and (12) was by co-chromatography with standards prepared from rose bengal photo-oxidations[3] of the olefins and by mass-spectral data. Compound (6) was identified by co-chromatography and comparison of mass spectra with a standard prepared by *m*-chloroperbenzoic acid oxidation. Compound (9) was identified by its mass spectra and by co-chromatography with a compound made from an acid-catalysed rearrangement of the hydroperoxides of (4) and (5).[10] The epoxides of (1) and (10) were identified by mass spectra.

RESULTS AND DISCUSSION

Reactions of undeuterated 2,3-dimethylbut-2-ene (1) on the surface of chromatographic alumina and silica suggested that singlet oxygen was photocatalytically produced on these metal oxide surfaces. Following illumination in the presence of oxygen, loss of (1) (fig. 1 and 2) resulted primarily in the formation of 2,3-dimethylbut-1-en-3-ol (2), the characteristic product formed on reaction with singlet oxygen. As can be seen in fig. 1 and 2, (1) was lost by a first-order process with (2) being the primary photoproduct. None of the photoproducts was observed in dark controls, or in irradiated flasks without the metal oxides. Irradiation of (1) under a nitrogen atmosphere in the presence of silica gel resulted in a marked change in product distribution. Whereas the irradiation of (1) in an oxygen-purged system gave up to 59% conversion to (2) after 70 h irradiation, a 74 h irradiation under a nitrogen atmosphere resulted in only 12% conversion into (2) and 36% conversion into the epoxide, tetramethyloxirane. Since the silica and alumina were not rigorously outgassed with nitrogen at elevated temperatures, singlet-oxygen reactions cannot be totally excluded. The O_2 adsorbed onto the metal oxide powders in the presence of visible light is suggested to be responsible for the singlet-oxygen-like reaction. Lattice oxygens on the surface of the oxide are implicated in the epoxidation, as this reaction predominates under N_2 atmosphere.

Results of the photocatalytic oxidation of 1,2-dimethylcyclohexene (3) over metal oxides under an oxygen atmosphere (table 1) provided additional evidence that singlet oxygen was being produced on the oxide surfaces. The photoproduct distribution generated on the oxides was compared with that of a known $^1O_2$ sensitizer, rose bengal.[11] The photo-oxidation of (3) with rose bengal affords two specific singlet oxygen products, the endo- and exo-cyclic alcohols (4) and (5), in a characteristic ratio

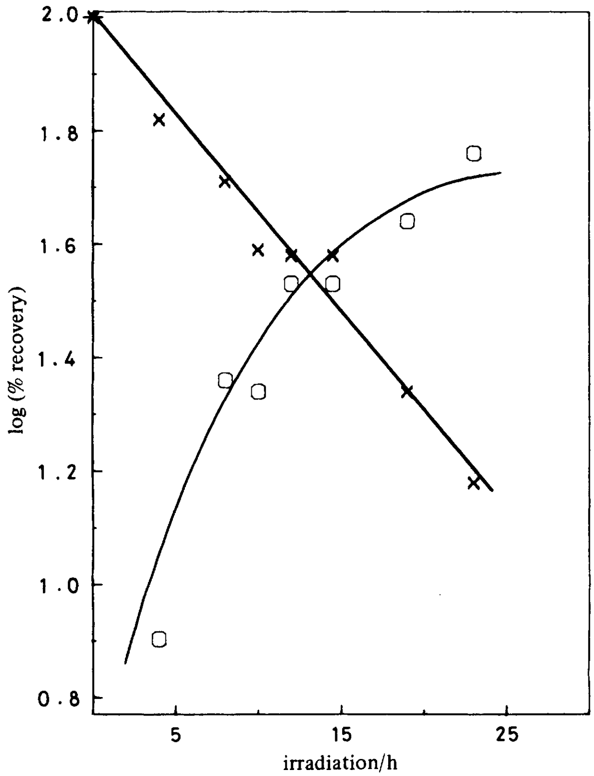
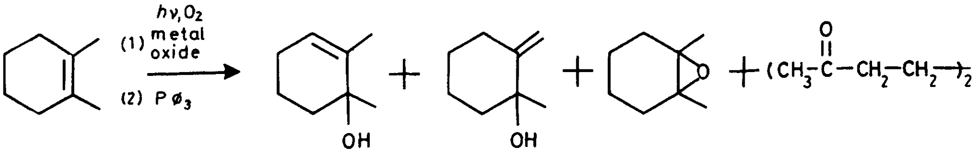


Fig. 1. CW40 irradiation of (1) on chromatographic silica. ×, First-order loss of (1) under an oxygen atmosphere ($r^2 = 0.94$); ○, percentage production of (2).

with (5) predominating (table 1). The same general results were obtained with SiO_2, Al_2O_3 and MgO. The exocyclic product predominated in each case, although the ratios were reduced for Al_2O_3 and MgO. Additional photoproducts observed included the epoxide (6) and the diketone octane-2,7-dione (9) (scheme 5). Production of the epoxide suggests the involvement of lattice oxygens, as observed during photo-oxidation of (1) in a nitrogen atmosphere. Impurities in the metal oxide powders were not the cause of the observed reactions since no differences were observed between a high-purity alumina and chromatographic-grade alumina (table 1). Also, no differences were observed in the reactivity of (1) irradiated on high-purity (low metals) silica gel when compared with chromatographic-grade silica gel.



(3) (4) (5) (6) (9)

Scheme 5.

Conversely, radical autoxidation of (3) with AIBN gives (7) as the predominant product. The radical oxidation favours abstraction of a secondary hydrogen, and the

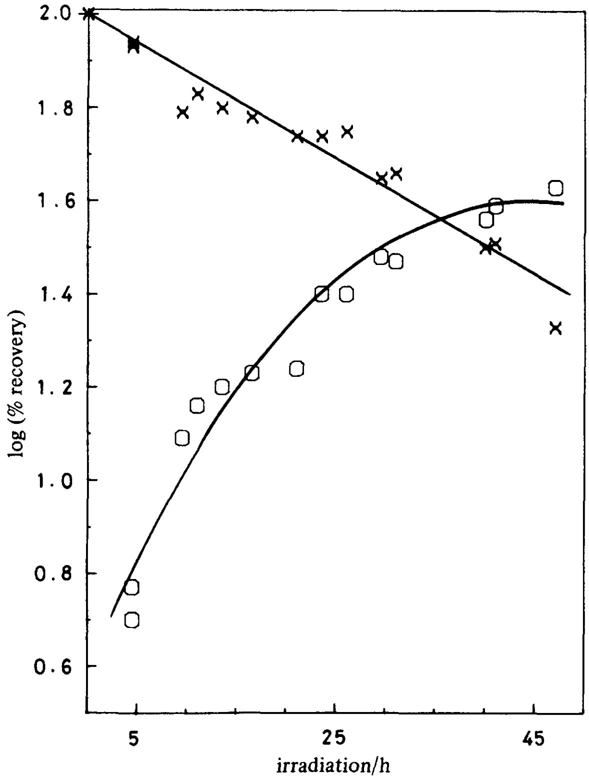


Fig. 2. CW40 irradiation of (1) on chromatographic alumina. ×, First-order loss of (1) under oxygen atmosphere ($r^2 = 0.97$); ○, percentage production of (2).

Table 1. Product distribution for the photosensitized oxidation of 1,2-dimethylcyclohexene[a]

	% recovery of starting material	% recovery of photoproducts						
sensitizer	3	4	5	6	7	8	9	other
SiO$_2$[b,c]	34	nd[i]	59	12	nd	nd	13	16
Al$_2$O$_3$[b,d]	63	31	42	6	nd	nd	9	12
Al$_2$O$_3$[b,e]	49	32	47	9	nd	nd	5	7
MgO[b]	32	23	62	6	nd	nd	2	7
TiO$_2$[f]	31	nd	nd	54	nd	nd	17	29
rose bengal[g]	29	10	90	nd	nd	nd	nd	nd
radical oxidation[h]	—	29	8	23	32	8	nd	nd

[a] Percentage recovery of starting material is shown in column 1; percentage formation of photoproducts is shown in columns 2–8. [b] Irradiation for 18 h under O_2. [c] SiO_2 grade 923. [d] Al_2O_3 grade 99.999%. [e] Al_2O_3 t.l.c. grade. [f] Irradiation carried out with 0.875 g for 1 h under O_2. [g] Irradiation carried out with 10 mg coating the inside of a 50 cm^3 flask for 1 h under O_2. [h] Radical oxidation with AIBN. [i] Not detected.

Table 2. Deuterium isotope effects in the photosensitized oxidation of geminally deuterated tetramethylethylene

sensitizer	K_H/K_D
Al_2O_3[a, b]	1.61
MgO[a]	1.62
SiO_2[a, c]	1.83
TiO_2[d]	nd[e]
rose bengal[f]	1.45
methylene blue[g]	1.45
bare flask	nd

[a] Irradiations carried out for 12 h under O_2. [b] Al_2O_3 t.l.c. grade. [c] SiO_2 grade 923. [d] Irradiation of 0.875 g for 1 h under O_2. [e] Not detected. [f] Irradiation carried out in 3 cm^3 of distilled H_2O with 10 mg rose bengal under O_2 for 0.5 h. [g] Irradiation carried out in 3 cm^3 distilled H_2O with 10 mg methylene blue for 2.5 h.

resulting allyl radical rapidly undergoes O_2 addition, forming products (4) and (7). Further oxidation of (7) leads to (8). The unique radical products (7) and (8) were not observed in the metal oxide photo-oxidations, indicating that radical oxidation is not involved in the photo-oxidation mechanism leading to formation of the singlet-oxygen products. SiO_2, Al_2O_3 and MgO all produced substantial amounts of the predominant $^1O_2$ product (5), consistent with a singlet-oxygen mechanism.

Singlet oxygen reacts with geminally deuterated [$^2H_6$]-2,3-dimethylbut-2-ene (10) to produce a characteristic ratio of (11)/(12) of 1.45.[6] The same kinetic isotope ratio was also found in this work (table 2) using the photosensitizing dyes rose bengal and methylene blue in oxygenated methanol solutions. A kinetic isotope effect near 1.45 provides supportive evidence for singlet-oxygen reactions since kinetic isotope effects for radical-initiated reactions using hydroxy, peroxy, alkyl or alkoxy radicals are generally larger and range from 3 to 30.[12, 13] For example, the kinetic isotope effect of the reaction between OH radical and n-C_4H_{10} (n-C_4D_{10}) is 3.84.[12]

The photo-oxidation of (10) on the metal oxide surfaces gave kinetic isotope ratios of 1.61 to 1.83. All the metal oxides sensitized the formation of the characteristic singlet-oxygen products except TiO_2, which resulted in the most rapid loss of the olefin but only produced the epoxide, acetone and deuterated acetone. The deviations between the metal oxide photo-oxidations and the sensitizing dyes, although significant, are small and probably the result of the different chemical environments in each system. The triplet sensitizing reactions were carried out in methanol, and the chemical environment would therefore be dominated by molecular interactions between the solvent and olefin. The metal oxide photo-oxidations were performed in a gas–solid system in which the olefin was absorbed to the oxide surface. Changes in molecular properties upon adsorption to solids have been documented, particularly u.v. absorbance shifts.[14] A perturbation of the electronic characteristics of the olefin could be expected to result in an alteration of the kinetic isotope ratio.

The photochemical production of singlet oxygen on transition-metal oxide surfaces, including TiO_2 and ZnO, has been reported previously.[15, 16] Subsequent experimental evidence from other laboratories has, however, refuted the claim of $^1O_2$ being produced on irradiated TiO_2.[17, 18] The results of photo-oxidations on TiO_2 surfaces, presented in tables 1 and 2, agree with these results and indicate that $^1O_2$ is not being produced on irradiated TiO_2 surfaces. The photo-oxidations of (3) and (10) on TiO_2 produced none of the singlet-oxygen products observed with either rose bengal or the non-transition-metal oxides. Compounds (7) and (8), which would indicate the presence of hydrogen-abstraction mechanisms, were also absent. This is contrary to the photo-oxidation experiments of simple olefins in acetonitrile + TiO_2 solutions,[19] which produced radical-like oxidations. The primary reaction products observed from (3) were (6) and (9), probably formed by cleavage of the double bond. The photo-oxidations in the present work were carried out in a gas–solid reaction system rather than in solution. The results suggest that the oxidation potentials of the olefins are shifted in the gas–solid system so that the observed reactions involve oxidation of the double bond.

TiO_2 is known to have the photocatalytic property of semiconductors, whereby hole–electron pairs (excitons) are generated by the absorption of photons with an energy at least equal to the bandgap of the semiconductor (3.05 eV).[20] The broadband fluorescent lamps used in this emitted wavelengths to 380 nm,[8] which is energetically sufficient for this transition to occur:

$$TiO_2 + h\nu \rightarrow \text{h–e}(Ti^{3+}O^-). \qquad (1)$$

The photogenerated holes can oxidize the olefins to a radical cation which, after O_2 or O_2^- addition, leads to epoxidation or cleavage.[19] The hole centre, O^-, could be involved in this cleavage reaction.[21]

In contrast, the light was not sufficiently energetic to promote the same exciton formation in the bulk ions of the non-transition-metal oxides (silica, 8.1 eV; MgO, 8.7 eV).[22] However, the lower Madelung potential of surface lattice ions can result in reduced bandgaps, allowing surface ions to absorb and be excited by light of longer wavelengths than the bandgap of the bulk ions. This has been observed for non-transition-metal oxides such as MgO powders[23] and porous Vycor glass.[22] These excitons are thought to be bound to a defect on the surface of the alkaline-earth oxide, while excitons formed by light of energy near the bandgap are essentially free to migrate through the lattice. The excitons trapped at oxide ions on the surface are thought to be in the form $[M^{(n-1)+}O^-]^*$:

$$[M^{n+}O^{-2}] + h\nu \rightarrow [M^{(n-1)+}O^-]^*. \qquad (2)$$

The excitons formed can undergo several routes of decay. Photoluminescence at longer wavelengths can occur by a reverse of the exciton-forming reaction, with excess energy lost in vibrational modes of the crystal:[24]

$$[M^{(n-1)+}O^-]^* \rightarrow [M^{n+}O^{-2}] + h\nu. \qquad (3)$$

In the presence of oxygen the observed photoluminescence is efficiently quenched.[2, 22, 23] Tench and Potts suggested that the complex formed between the exciton and oxygen could form $^1O_2$ by transfer of electronic energy to the adsorbed oxygen molecules. The absorption of oxygen to the exciton results in formation of the O_3^- species:[24]

$$[M^{(n-1)+}O^-]^* + {}^3O_2 \rightarrow [M^{(n-1)+}O_3^-]^* \qquad (4)$$

while reversal of this reaction is suggested to lead to $^1O_2$ formation:

$$[M^{(n-1)+}O_3^-]^* \rightarrow [M^{n+}O^{-2}] + {}^1O_2. \qquad (5)$$

This mode of reactivity may not be open to the irradiated TiO_2 surface[24] in the presence of oxygen at room temperature. At room temperature O_3^- and O^- are not present and O_2^- is the only observed species.

These results provide evidence that singlet oxygen is being formed on non-transition-metal oxide surfaces using broad-band fluorescent light. Although the mechanism of formation is unclear, involvement of lattice defects is likely since oxygen quenches the phosphorescence of illuminated non-transition-metal surfaces.[2, 22, 23] The reactions observed on the non-transition-metal oxides were distinctly different than observed with titanium dioxide, and although titanium dioxide had the greatest photocatalytic activity, singlet oxygen was not detected on that surface.

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