

## Short Communication

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### Evidence for the production of singlet molecular oxygen from the quenching of excited states of dialkyl ketones by molecular oxygen<sup>†</sup>

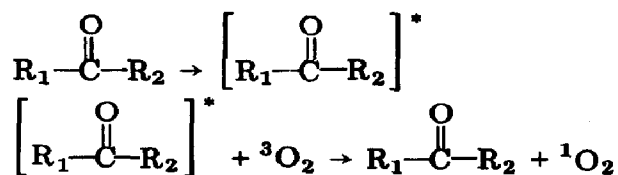
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#### 1. Introduction

It is now recognized that singlet molecular oxygen is the reactive intermediate in many photo-oxidation reactions [1, 2]. The singlet molecular oxygen is produced from the quenching of excited states of organic or inorganic compounds by ground state molecular oxygen [2 - 6]. Up to now there has been no reported experiment concerning the production of singlet molecular oxygen from the excited states of dialkylketones. The numerous photochemical reactions of excited aliphatic ketones in the absence of oxygen, *e.g.* hydrogen abstraction, Norrish type I and II reactions, have been extensively studied [7, 8]. Because of these "background" photochemical reactions, it may be difficult to observe the production of singlet molecular oxygen from the photon-excited dialkylketones. However, this is a problem of considerable practical interest since it has been proposed that the macro-ketone impurities in polymers such as polyethylene and polypropylene are responsible for the photo-oxidation of the polymers [9, 10]. According to the proposed mechanism singlet molecular oxygen is produced by an energy transfer process between an excited macro-ketone and ground state molecular oxygen. Photo-oxidation of the polymer then occurs in which the singlet molecular oxygen reacts with an olefin (as an impurity or as a product of the photochemical changes in the polymer). The purpose of this experiment is to test the proposed mechanism; specifically, we want to observe the production of singlet molecular oxygen from the reaction



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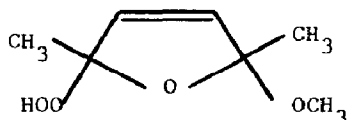
## 2. Experimental

### 2.1. Materials

Aliphatic ketones of highest available purities were obtained from Aldrich and were used without further purification. 2,5-Dimethylfuran (Aldrich, 99%+) was purified twice by passing through an alumina column before use. 1,3-Diphenylisobenzofuran (DPBF) was crystallized once from a methanol-acetone mixture. Aldrich spectrophotometric grade methanol was used directly without purification.

### 2.2. Procedure

A Bausch and Lomb SP200 medium pressure mercury lamp was used as the irradiation source. The 313 nm line from this lamp was isolated using a Corning 7-54 filter and a cell of path length 1 cm containing 0.02% potassium chromate in 0.1% sodium hydroxide solution. After passage through the filters, the 313 nm light was focused onto the front surface of the photolysis compartment (path length 3 cm) containing about 80 ml of a solution which was saturated with oxygen by continuous bubbling. In a typical experiment, the solution was made up of 15 vol.% of an aliphatic ketone, 0.3 M 2,5-dimethylfuran and methanol. This high concentration of dimethylfuran is sufficient to react with more than 99% of the singlet molecular oxygen produced [11], producing compound A which is the characteristic product between singlet molecular oxygen and methanolic 2,5-dimethylfuran [12, 13]:



(A)

After the solution had been irradiated for 12 h the volatile components of the solution were removed. Then NMR and IR spectra of the resulting oil were measured and compared with the reported spectra of A [13]. The quantum yield of production of singlet molecular oxygen from neat 3-pentanone or 2-pentanone was estimated by the difference between the photosensitized bleaching of a  $10^{-4}$  M solution of DPBF in an oxygen or nitrogen saturated ketone solution [14]. The light intensity at 313 nm was then measured by potassium ferrioxalate actinometry.

### 3. Result and discussion

From the NMR spectra of the photolysis product, singlet molecular oxygen is found to be produced when the following oxygenated aliphatic ketone solutions are irradiated: acetone, 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-heptanone and 4-heptanone. When an oxygenated methanolic solution of 2,5-dimethylfuran was irradiated alone, a negligible amount of singlet molecular oxygen was produced. From the NMR signals and the amount of oily liquid produced, it is estimated that the quantum yield of singlet molecular oxygen is relatively constant (within a factor of 3) for the specified ketone solutions. Actual determination of the quantum

yield of singlet molecular oxygen from neat 2-pentanone and 3-pentanone gave values of 0.03 and 0.04 respectively. For 2,4-dimethyl-3-pentanone compound A is not detected among its photolysis products. It is estimated, for this particular ketone, that the quantum yield of production of singlet molecular oxygen cannot be greater than 0.0003.

There are several interesting points which can be deduced from the result. The yield of singlet molecular oxygen is relatively independent of the chain length of the dialkylketone as long as there is no substitution at the carbon atom adjacent to the carbonyl group. Thus, in changing from acetone to heptanone, no substantial change in the yield of singlet molecular oxygen is observed. Secondly, the yield of singlet molecular oxygen from all the ketones used is much smaller than unity (about 0.03). This may be because the efficiency of production of singlet oxygen from the excited state of an aliphatic ketone is intrinsically small or that the deactivation processes available to the excited ketone are so fast that only a small part of the excited state is quenched by oxygen. The second explanation is consistent with the observation of a much smaller yield of singlet molecular oxygen from 2,4-dimethyl-3-pentanone. The branching adjacent to the carbonyl group is expected to increase the rate of cleavage reactions such as the Norrish type I cleavage. Hence the portion of excited 2,4-dimethyl-3-pentanone quenched by molecular oxygen may be much smaller than that for the other ketones studied.

Now let us examine the implication of the present findings for the proposed mechanism of photo-oxidation of polymers such as polyethylene [9, 10]. It is shown here that, as long as there is no alkyl substitution at the carbon atom adjacent to the carbonyl group, the yield of singlet molecular oxygen is relatively independent of the chain length of the aliphatic ketone. The macro-carbonyl impurities found in polymers such as polyethylene generally belong to this class of non-substituted aliphatic ketones. Furthermore, although the yield of singlet oxygen is small in this class of ketones (about 0.03), it is an observable and a substantial quantity when the time of exposure for the photo-oxidation reaction of polymers is taken into consideration. Hence the proposed mechanism of photo-oxidation of polyethylene or polypropylene [9, 10] is quite reasonable in view of the present experiments. These studies also suggest that singlet oxygen may play a much smaller role in the oxidative photo-degradation of polypropylene since the macro-carbonyl moieties in this system (either present initially as impurities or produced during the photo process) would give rise to much smaller yields of singlet oxygen similar to that found with 2,4-dimethyl-3-pentanone.

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