

## OBSERVATION OF $O_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$ CHEMILUMINESCENCE FROM THE SELF-REACTION OF ISOPROPYLPEROXY RADICALS<sup>†</sup>

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### Summary

We report the first direct observation of singlet oxygen product resulting from a gas phase self-reaction of alkylperoxy radicals. The evidence is a rotationally resolved  $O_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$  chemiluminescence spectrum observed in a 12 l integrating sphere reactor containing less than  $10^{14}$  isopropylperoxy radicals per cubic centimeter diluted in helium and  $O_2$  at a total pressure of 80 Pa (0.6 Torr). According to a mechanism proposed by Russell in 1957, the self-reactions of non-tertiary alkylperoxy radicals proceed by formation of a weakly bound dialkyl tetraoxide intermediate which can decompose to yield a carbonyl, an alcohol and  $O_2$ . There are five energetically accessible product state potential energy surfaces. Spin conservation forbids the ground state products, but allows the formation of  $O_2$  in the  $^1\Sigma_g^+$  or  $^1\Delta_g$  states or of  $T_1$  carbonyl. We claim these results to be strong evidence for the occurrence of Russell's mechanism in the gas phase.

### 1. Introduction

Alkylperoxy radicals are well-recognized key intermediates in hydrocarbon oxidation. In addition to many other possible reactions, alkylperoxy radicals undergo bimolecular self-reactions. The latter can be considered as two-step processes involving the reversible formation of a vibrationally excited dialkyl tetraoxide intermediate which can decompose irreversibly according to the following [1 - 6]:



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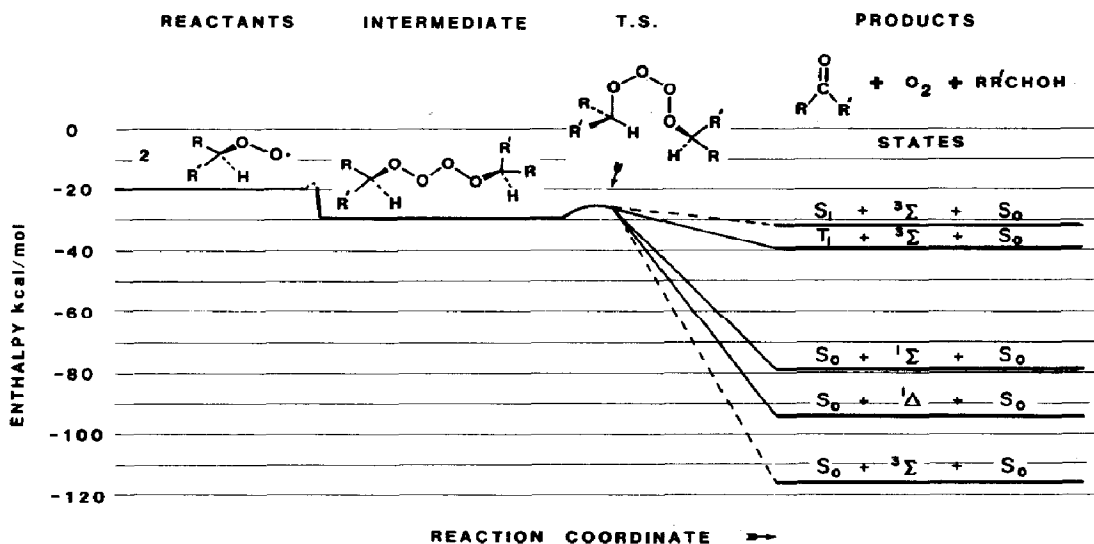
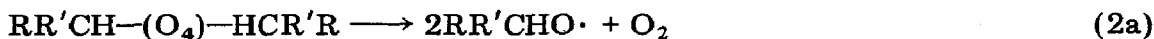
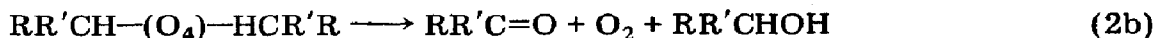


Fig. 1. Reaction coordinate diagram and product states for Russell's mechanism.



$$(\Delta H_{2a} = -21 \text{ kJ mol}^{-1} = -5 \text{ kcal mol}^{-1})$$



$$(\Delta H_{2b} = -405 \text{ kJ mol}^{-1} = -97 \text{ kcal mol}^{-1})$$



Where  $R \equiv$  alkyl, aryl or H, and product path (2b) is blocked if the tetraoxide is formed from two tertiary alkylperoxy radicals. The thermochemistry given is for ground state products and  $R \equiv R' \equiv$  methyl [7]. If the tetraoxide is formed from two different non-tertiary alkylperoxy radicals, reaction (2b) will have two possible pairs of (carbonyl plus alcohol) products.

A concerted mechanism for reaction (2b), proposed by Russell [8], and shown as Fig. 1, has been criticized on the basis of the likelihood of a low entropy of activation for reaching the transition state [9]. Confirmation of Russell's mechanism by product identification is fraught with difficulty because the alkoxy radical products of reaction (2a) can self-react so that final carbonyl and alcohol products from reaction (2a) followed by (3) are indistinguishable from those formed by reaction (2b).

We have previously performed product trapping and analysis experiments on flowing dilute gas phase alkylperoxy radical systems reacting at  $T \geq 200^\circ \text{C}$  [10]. Under these conditions all alkoxy radicals were expected to decompose by unimolecular fragmentation. We found more than 50% of the products to be carbonyls and alcohols having the unaltered carbon skeleton of the starting alkylperoxy radical, in all but one of the cases studied. These results were interpreted as evidence for the occurrence of reaction (2b) by the concerted Russell mechanism [10].

Reaction (2b) is exothermic by approximately  $405 \text{ kJ mol}^{-1}$  ( $97 \text{ kcal mol}^{-1}$ ) [7]. This allows the possibility of forming a given set of chemical products on five different potential energy surfaces. The accessible product states are identified and placed on an energy scale in Fig. 1. The activation energy for the formation of dialkyl tetraoxide is near zero, so that its internal energy is small [2 - 6]. Therefore this intermediate must be formed in its singlet ground state, and the spin-allowed decomposition paths are those giving all singlet products or a pair of triplets. These allowed paths lead to  $\text{O}_2(^1\Delta)$ ,  $\text{O}_2(^1\Sigma)$  and carbonyl  $T_1$  products, and are shown by bold lines in Fig. 1. Spin-forbidden paths are shown by dotted lines. Reaction (2a) is not exothermic enough to form  $^1\text{O}_2$  product, although it is allowed, by spin conservation, to form either  $^1\text{O}_2$  or  $^3\text{O}_2$  plus two doublet alkoxy radicals.

The above considerations have motivated a search for  $^1\text{O}_2$  product in alkylperoxy radical systems. Evidence has been found in solution phase studies via chemical trapping [11], and via the observation of unstructured emission bands at the wavelengths of several known cooperative transitions of the  $\text{O}_2(^1\Delta)$  and  $\text{O}_2(^1\Sigma)$  states [12, 13]. The purpose of this paper is to report the results of a successful search for rotationally resolved  $\text{O}_2(b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-)$  chemiluminescence at 760 - 770 nm in the isopropylperoxy radical system at  $P = 87 \text{ Pa}$  (0.65 Torr).

## 2. Experimental details

Discharge flow reactor techniques were used for these experiments. A schematic diagram of the apparatus is shown as Fig. 2. A cylindrical flow reactor was used to prepare isopropyl radicals ( $\text{iPr}\cdot$ ) from dimethyl ketene via the reaction [14, 15]

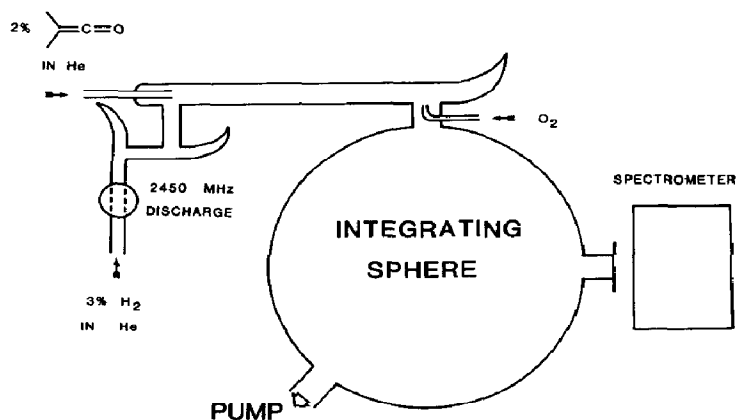


Fig. 2. Experimental apparatus (not to scale).

The effluent gas then entered a 12 l integrating sphere which was internally coated with gold and overcoated with a thin layer of Teflon.

The reactor was pumped by a roots blower backed by a mechanical pump. The measured pumping speed of this combination was  $150 \text{ l s}^{-1}$ , corresponding to an average residence time of the gas in the integrating sphere of 0.08 s.

Hydrogen atoms were made by passing a 3%  $\text{H}_2$ -He mixture through a 100 W 2450 MHz discharge. This gas stream was mixed with a stream of 2% dimethyl ketene in helium. The combined streams flowed 80 cm, then undischarged  $\text{O}_2$  was added and the total flow entered the integrating sphere reactor. The total pressure in the reactor was 80 Pa (0.6 Torr), comprised of 58%  $\text{O}_2$  with most of the remaining 42% being helium. This procedure results in the conversion of isopropyl radical to isopropylperoxy radical:



Typically, we obtain  $\text{H}(^2\text{S})$  concentrations of less than  $10^{14} \text{ atoms cm}^{-3}$ ; thus the upper limit of the  $\text{iPrOO}\cdot$  concentration is  $10^{14} \text{ molecules cm}^{-3}$ .

Light, collected by multiple reflection, exited the reactor by a quartz window and entered a 0.5 m  $f/8.6$  grating monochromator through a 0.2 mm  $\times$  20 mm slit. The detector was a thermoelectrically cooled S-20 photomultiplier operating in a single-photon counting mode. At  $\lambda = 760 \text{ nm}$  the quantum efficiency of the photomultiplier was 1.5% and the dark background was  $2 \text{ counts s}^{-1}$ .

Dimethyl ketene was prepared by thermal decomposition of the dimer 2,2,4,4-tetramethyl-1,3-cyclobutanedione. This was accomplished by passing a stream of helium through a tube containing the dimer at  $80^\circ\text{C}$ . The mixture of helium plus dimer was passed through a quartz tube heated to  $550^\circ\text{C}$  followed by a trap cooled to  $-78^\circ\text{C}$ . The isolated product, dimethyl ketene monomer, was placed in a 60 l stainless steel bulb at a concentration of 2% in helium at a total pressure of  $10^5 \text{ Pa}$  (1 atm). IR spectra of the mixture were obtained periodically and they showed no measurable loss of the monomer concentration after 6 months storage at room temperature.

### 3. Results

The chemiluminescence spectrum, observed when  $\text{H}(^2\text{S})$  atoms, dimethyl ketene and  $\text{O}_2(^3\Sigma)$  flows were present, is shown in Fig. 3(a). The wavelength of the band center, the relative intensities of the P and R branches and the positions of the partially resolved rotational lines in the P branches identify the spectrum as the  $\text{O}_2(\text{b}^1\Sigma_g^+ \rightarrow \text{X}^3\Sigma_g^-)$  transition [16-18]. We attribute most of the spectral intensity to isopropylperoxy radical self-reaction occurring by the concerted Russell mechanism [8].

Of the two low-lying  $^1\text{O}_2$  states, the  $^1\Delta$  is far more difficult to observe. We searched unsuccessfully for measurable spectral intensity at 635 nm, the wavelength of the "dimol" transition,  $2(\text{O}_2(^1\Delta)) \rightarrow 2(\text{O}_2(^3\Sigma)) + h\nu_{635 \text{ nm}}$  [19].

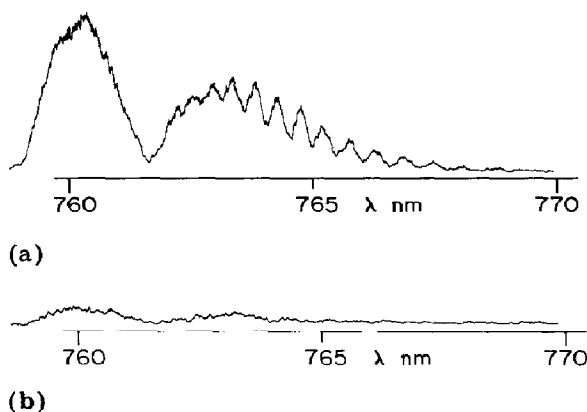


Fig. 3. Chemiluminescence spectra showing the presence of  $O_2(^1\Sigma_g^+)$ : (a) in the presence of isopropylperoxy radicals; (b) in the presence of  $H(^2S)$  and  $O_2(^3\Sigma)$  only.

We did not search for the  $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$  transition at 1270 nm. Thus there is a possibility that the  $O_2(^1\Sigma)$  which we observed was not a primary reaction product but a result of the energy pooling process [20]



In either case the interpretation is the same, that the presence of  $^1O_2$  is evidence for the occurrence of reaction (2b).

Figure 3(b) shows a weak background spectrum also attributed to the presence of  $O_2(^1\Sigma)$  and having an intensity of about 1/10 of that in Fig. 3(a). The latter spectrum was obtained by turning off the flow of dimethyl ketene; all other conditions in the reactor were the same for both spectra. We attribute the presence of  $O_2(^1\Sigma)$  in the background to the reaction sequence



Reaction (7) was studied by Washida *et al.* [21], who reported fractional yields of excited product  $O_2$  of 0.015 in the  $^1\Delta$  state and 0.0003 in the  $^1\Sigma$  state. In preparing isopropylperoxy radicals,  $H(^2S)$  and excess dimethyl ketene were mixed 80 cm upstream of the point of addition of  $O_2(^3\Sigma)$ , so that most, if not all,  $H(^2S)$  will be consumed by reaction (4). Therefore we believe that both the concentration product  $[HO_2][H]$  and the fractional contribution of reaction (7) to the spectrum in Fig. 3(a) were negligible.

In our product analysis work we prepared alkylperoxy radicals by the reactions of alkanes with  $O(^3P)$  or  $Cl(^2P)$  atoms in the presence of  $O_2(^3\Sigma)$  [10]. These methods were found to be inappropriate to the search for  $^1O_2$  product in the self-reactions of alkylperoxy radicals because an  $O_2$  discharge produces high background levels of  $O_2(^1\Delta)$  and  $O_2(^1\Sigma)$  [22], and a  $Cl_2$  discharge produces interference from the  $Cl_2(^3\Pi_u^{0+})$  afterglow [23], and could form  $^1O_2$  by energy transfer.

Reaction (4) was chosen as a source of alkyl radicals for this study because it would form a single product isomer and because the initially formed products would have less internal energy than the products of  $\text{H}(^2\text{S})$  plus olefin reactions [7]. In retrospect, the reactions of  $\text{H}(^2\text{S})$  with cyclopentene or cyclohexene would probably have served as well. The obvious choice, the methyl radical, was not studied because it is known that collisional stabilization of the initially formed methylperoxy radical is very inefficient in the 100 Pa pressure region [24].

#### 4. Discussion

The results of several other investigations are relevant to this work.

Kirsch *et al.* [25] have reported quantitative product analyses and rate constants for the gas phase isopropylperoxy radical system at total pressures of the order of  $10^5$  Pa (1 atm) and  $T = 302$  K. The distribution of the products acetone, isopropanol and isopropyl hydroperoxide was studied as a function of the  $\text{O}_2$  partial pressure. It was concluded that a route to isopropanol existed which did not involve isopropoxy radicals, and that this route was reaction (2b). The reaction rate constant ratio  $k_{2a}/k_{2b}$  was reported as 3/2 at  $T = 302$  K [25].

Nangia and Benson [9] have objected to the Russell mechanism for alkylperoxy radical self-reaction and have proposed an alternative mechanism involving the Criegee intermediate [26, 27] as a chain carrier. (For isopropyl the Criegee intermediate has the empirical formula  $(\text{CH}_3)_2\text{COO}$ ; the structure is left unspecified by convention.) As part of their mechanism, Nangia and Benson have proposed that the Criegee intermediate can undergo bimolecular reaction with an alkylperoxy radical, transferring an oxygen atom, to form a vibrationally excited alkyltrioxy radical. They estimated that the internal energy of the trioxy radical would be sufficient to allow fragmentation, yielding an alkoxy radical plus  $\text{O}_2(^1\Sigma)$  or  $\text{O}_2(^1\Delta)$  [9]. There is no experimental evidence in support of this proposed mechanism. Published reports of the gas phase behavior of Criegee intermediates suggest a very short lifetime toward unimolecular rearrangement or fragmentation [28, 29].

For our conditions, total pressure  $P = 80$  Pa (0.6 Torr), 95% of which is helium or  $\text{O}_2$ , we would not expect  $\text{C}_3$  Criegee intermediates to undergo bimolecular reactions even if they were formed [28, 29]. Niki and coworkers found no evidence that Criegee intermediates were formed in the self-reactions of methylperoxy [30], ethylperoxy [30] and hydroxymethylperoxy [31] radicals. They sought, but did not find, secondary ozonides and their fragmentation products under conditions designed to approximate those used in studying ozone-alkene reactions in which these products were readily detected [30, 31]. Herron *et al.* [32] have given a detailed analysis of the arguments opposing the Nangia and Benson proposal that Criegee intermediates might be involved in the gas phase self-reactions of alkylperoxy radicals.

Indirect evidence for the presence of  $^1\text{O}_2$  in solution phase secondary alkylperoxy radical systems has been reported from chemical trapping experiments [11]. Chemiluminescence experiments have been reported in which a high efficiency filter spectrometer was used to observe unstructured emission bands [12, 13]. These were assigned to the  $^1\text{O}_2$  cooperative transitions involving the compound excited state species:  $^1\Sigma + ^1\Delta$ ;  $^1\Delta + ^1\Delta$ ;  $^1\Delta + ^1\Delta$ ,  $\nu = 1$ ;  $^1\Delta + ^1\Delta$ ,  $\nu = 2$  [12, 13]. The observation of the rotationally resolved  $\text{O}_2(^1\Sigma) \rightarrow \text{O}_2(^3\Sigma)$  transition, in the gas phase, at low pressure, must be considered as stronger evidence than the above.

Our result is consistent with the thermodynamics and the spin conservation rule for alkylperoxy radical self-reaction by Russell's mechanism [7, 8]. It is also consistent with a large body of product analysis work, particularly that of Kirsch *et al.* [25] and a preliminary report from this laboratory [10]. We believe the work reported here to be strong evidence in support of Russell's mechanism. This belief is based on the simplicity of the system studied compared with previous investigations, the certainty of the spectral identification and the fact that the result fits the theoretical expectation that excited  $^1\text{O}_2$  should be formed as a reaction product.

## 5. Final remarks

The first high resolution spectrum of the  $\text{O}_2(\text{b}^1\Sigma_g^+ \rightarrow \text{X}^3\Sigma_g^-)$  transition was reported by Branscomb [16]. The spectrum was excited by an r.f. discharge and showed a rotational temperature of 710 K and a signal-to-noise ratio of approximately 5. The published tracing was obtained from a 30 min photographic plate exposure [16]. We have observed the spectrum of the same transition using the cooled photomultiplier and single-photon counting electronics described above. It is shown as Fig. 4. The rotational temperature of the spectrum matched the ambient temperature of 300 K. The resolution  $\lambda/\Delta\lambda = 20\,000$ , based on the ability to resolve the  $\text{R}_2(16)$  and  $^{\text{R}}\text{Q}_{21}(14)$  lines.

To obtain this spectrum, we passed pure  $\text{O}_2$  with a trace of mercury vapor [22] through the 100 W microwave discharge and then immediately

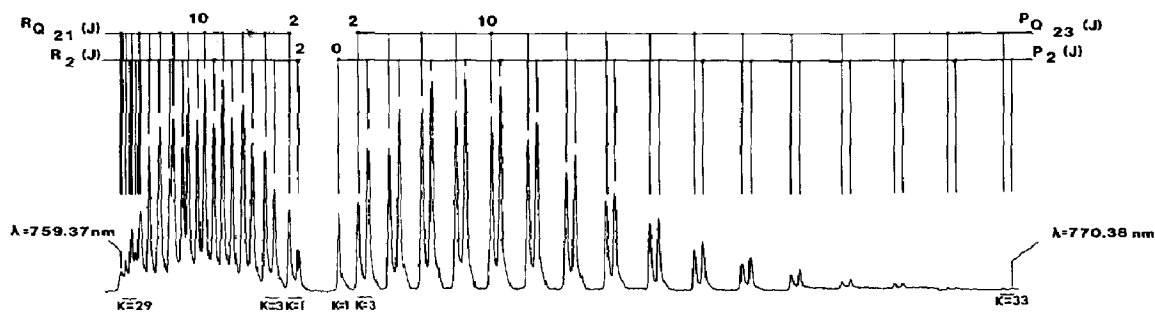


Fig. 4. High resolution emission spectrum of  $\text{O}_2(\text{b}^1\Sigma_g^+ \rightarrow \text{X}^3\Sigma_g^-)$  excited by a discharge through pure  $\text{O}_2$ .

into the integrating sphere. The pressure was 480 Pa (3.6 Torr) and the mean residence time in the sphere was 2.8 s. On the basis of our previous work [33], we expect  $3\% \pm 1\%$  ( $(3.4 \pm 1) \times 10^{15}$  molecules  $\text{cm}^{-3}$ ) of the  $\text{O}_2$  in the observation region to be in the  $^1\Delta$  state. The energy pooling process,  $2(\text{O}_2(^1\Delta)) \rightarrow \text{O}_2(^1\Sigma) + \text{O}_2(^3\Sigma)$  [20], together with quenching,  $\text{O}_2(^1\Sigma) + \text{O}_2(^3\Sigma) \rightarrow \text{O}_2(^1\Delta) + \text{O}_2(^3\Sigma)$  [34], is expected to produce approximately  $2 \times 10^{12}$  molecules  $\text{cm}^{-3}$  of  $\text{O}_2(^1\Sigma)$  under these conditions.

The analysis of  $^1\Sigma \rightarrow ^3\Sigma$  transitions has been discussed by Herzberg [17]. For the ground  $\text{O}_2(^3\Sigma)$  state, the rotational state angular momentum  $K$  interacts with the electron spin to form a total angular momentum  $J$ . Both  $J$  and  $K$  are subject to selection rules. In addition, the selection rule on nuclear spin statistics for homonuclear diatomic molecules forbids the even  $K$  levels in the  $^3\Sigma$  state and the odd  $K$  levels in the  $^1\Sigma$  state. As a result, the spectrum has four subbranches and a pattern of doubled lines known as " $K$  doublets".

Spectra of pure discharged  $\text{O}_2$  were taken using wider spectrometer slit openings than were used for Fig. 4. These showed the gradual merging of the  $K$  doublets. At the same spectrometer slit width used for Fig. 3, we obtained a spectrum matching Fig. 3, but with a much larger signal-to-noise ratio.

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