# REACTION OF ALKOXY RADICALS WITH OXYGEN AS A CLEAN THERMAL SOURCE OF HYDROPEROXYL RADICALS

K.A. SAHETCHIAN, R. RIGNY, A. HEISS and R.I. BEN-AIM Laboratore de Chunie Genérale, Equipe de Recherche Associée au CNR No 457, Université Pierre et Marie Curie, Paris VI, 75230-Paris Cedex-05, France

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From 160 to 240°C and at a pressure of 180 Torr, alkoxy radicals RO react with molecular oxygen and constitute a source of hydroperoxyl radicals, according to the elementary reaction RO +  $O_2 \rightarrow 11O_2$  + product. RO is produced by the dim-heptyl peroxide decomposition with rate constant  $k = 0.67 \pm 0.14 \text{ s}^{-1}$  at 236°C

#### 1. Indroduction

The alkoxy radicals take a prominent part in troposphere chemistry [1] and in combustion of hydrocarbons at low temperatures [2]. However the RO radical behaviour is very diversified. It leads either to isomerisation (or to decomposition) or to a reaction with oxygen according to the equation [1-5].

 $RO + O_2 \rightarrow HO_2 + carbonyl compound$ .

Obviously, RO can also react with various atoms or radicals present in the mixture. Yet, when the concentrations of active centers are low, these quadratic reactions are unlike.

Hoare and Wellington [6] have studied the ditertiarybutyl peroxide decomposition in the presence of formaldehyde. They have detected the formation of tertiarybutanol and have shown that addition of oxygen to the mixture prevents formation of this alcohol.

Alcohol formation is also observed in the last stages of a hydrocarbon's cool oxidation when oxygen is almost consumed [7].

All these experimental features are in agreement with reaction (1), the rate constant which has been determined, for the methoxy radical, by Benson and Golden [8], and Batt and Robinson [9].

Recently, a theoretical estimate has been made for the activation energy and the rate constant of reaction between various alkoxy radicals  $(CH_3O, C_2H_5O, i-PrO,$ 

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*n*-ButO, *t*-ButO) and molecular oxygen [10].

However, formation of the hydroperoxyl radical  $HO_2$  has never been experimentally observed. In this work, we prove that, in a given temperature range and at low concentration, the main reaction for the alkoxy radical is

 $RO + O_2 \rightarrow HO_2 + product$ .

In fact, in these conditions, the peroxide  $CH_3$ -( $CH_2$ )<sub>5</sub> $CH_2$ OOCH<sub>2</sub>( $CH_2$ )<sub>5</sub> $CH_3$  decomposes in the presence of oxygen and gives rise to HO<sub>2</sub> radicals. The concentration measurement of these radicals enables us to determine the rate constant of the diheptyl peroxide decomposition.

### 2. Experimental

The RO radicals are obtained by the diheptyl peroxide ROOR decomposition occurring in a mixture of  $O_2 + 2\%$  CO<sub>2</sub>, in a dynamic system. The experimental device has been previously described [11,12] and used to study the decomposition of heptyl-1 and heptyl-2 hydroperoxides. The gaseous mixture flows through a quartz vessel placed in a thermoregulated oven. The total pressure in the reaction vessel is 180 Torr and the experiments are performed in the temperature range from 160 to  $320^{\circ}$ C. A small sample of the gaseous mixture is taken out, under a pressure of  $\approx$ 0.2 Torr, through a movable quartz microprobe. The gaseous sample extracted comes into contact with the finger of a Dewar (cooled with liquid nitrogen) placed at the center of an EPR cavity.

Heterogeneous reactions of the HO<sub>2</sub> radical on various walls and at several temperatures have been studied [13]. Wall effects are avoided by vessel and probe passivation with boric acid followed by slow combustion of hydrogen at 510°C and 250 Torr [11–14].

The diheptyl peroxide is prepared by the method of Williams and Mosher [15]. It is purified on a Lichroprep Si 60 column (Merck). The mobile phase is a mixture of 25% diethyl ether and 75% heptane. Under these conditions, ROOR is free of any trace of heptyl hydroperoxide or carbonyl compounds, secondary products which might be obtained during the synthesis. We have used high-pressure liquid chromatography (HPLC) and thin layer chromatography (TLC) to check the peroxide purity before reaction and to analyse the peroxides trapped on the cold finger of the dismountable Dewar.

The peroxide concentration (expressed in ROOR molecules per cm<sup>3</sup> of gas) is measured by HPLC. This method of measurement has previously been used for hydroperoxides [16]. It was not possible to carry out a chemical quantitative titration of the double peroxide ROOR. Measurements are made on a Varian 5020 chromatograph with a Lichrosorb RP 18 column and an isocratic regime. The mobile phase is a mixture of 95% methanol and 5% water. With a 2 cm<sup>3</sup> min<sup>-1</sup> flow rate, the heptyl peroxide retention time is 4.3 min. The detection is made by UV absorption at 215 nm.

ROOR, trapped on the cold finger of the dismountable Dewar, is recovered in methanol and its concentration is determined by previous calibration. The gaseous flow rate carrying the peroxide is measured independently. ROOR concentration is of the order of 1.9  $\times$  10<sup>13</sup> molecules cm<sup>-3</sup> in the reaction vessel.

### 3. Results

For our experimental conditions, at temperatures lower than 240°C and for residence times  $\approx 10^{-2}$  s, the EPR spectrum obtained is that of the radical HO<sub>2</sub> [17] represented in fig. 1.

At temperatures higher than 250°C, the EPR spectra are modified. This alteration becomes more and



Fig. 1. EPR spectrum of IIO<sub>2</sub> at 236°C. Power 10 mW, modulation amplitude 8 G, time constant 1 s, scan time 8 min.

more important as the oven temperature increases and appears to be the result of a superposition of  $HO_2$  and  $RO_2$  spectra (fig. 2). This shows that formation of  $RO_2$  has an activation energy higher than formation of  $HO_2$ .

This superposition of radical spectra has previously been observed during the oxidation of propane [18] and methane [19].

Due to the weak concentration of ROOR, the system is chemically simple; so it is obvious that, first, decomposition of ROOR occurs, producing 2RO. Then parallel paths compete:

(i) Isomerisation and/or decomposition of RO, followed by reaction with  $O_2$ , produces  $RO_2$ .

(ii) RO by direct reaction with O<sub>2</sub> produces HO<sub>2</sub>.

Our results are in agreement with a theoretical study of Baldwin et al. [10] who showed that isomerisation or decomposition reactions of RO have an activation



Fig. 2. EPR spectrum of  $HO_2$  and  $RO_2$  superposition at 318°C under identical conditions

energy higher than that of direct reaction with oxygen. At low temperatures (<240°C) the main reactions are.

$$ROOR \xrightarrow{\kappa_1} 2RO, \qquad (1)$$

 $RO + O_2 \xrightarrow{k_2} HO_2 + products,$  (2)

$$HO_2 + HO_2 \xrightarrow{k_3} H_2O_2 + O_2.$$
 (3)

This mechanism is supported by the following remarks: (a) the only peroxidic radical detected is  $HO_2$ ; (b) the  $HO_2$  concentration reaches a maximum and decreases; (c) the formation of  $H_2O_2$  is concomitant with the consumption of ROOR.

At higher temperatures, it is necessary to complete the process with isomerisation and/or decomposition of RO which leads to various products through the peroxidic  $RO_2$  radicals. These reactions are beyond the scope of this paper.

For a temperature of 236°C, where HO<sub>2</sub> radicals alone are present, we have determined the rate constant  $k_1$ . The evolution of HO<sub>2</sub> concentration as a function of time, is represented in fig. 3.

From the previous mechanism and the assumption of a quasi-stationary state of RO, the formation of  $HO_2$  radicals is described by the following differential equation:

 $d[HO_2]/dt = 2k_1[ROOR]_0 \exp(-k_1t) - 2k_3[HO_2]^2$ .

In this equation, we introduce the values [ROOR]  $_0$ = 1.9 × 10<sup>13</sup> molecules cm<sup>-3</sup>, and  $k_3 = 3 × 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [20]. This rate constant is widely used [17,21,22] in the field of combustion and



Fig. 3. Experimental and calculated curves of HO<sub>2</sub> concentration versus residence time (s) for the ROOR decomposition, at 236°C.  $HO_2/10^{12}$  particles cm<sup>-3</sup>, --- experimental curve, --- calculated curve.

explains many experimental results, although studies of reaction (3) near ambient temperature have shown its complexity [23-26]. In a recent work [27] fitted values ranged from  $2.5 \times 10^{-12}$  to  $8.0 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> with a mean of  $4.4 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The higher values of  $k_3$  (>4 × 10<sup>-12</sup>) may be due to the presence of additives (such as water). The best fit between the experimental curve and a calculated one, solution of the above differential equation is obtained for  $k_1 = 0.67$  s<sup>-1</sup>, at 236°C. Taking account of possible values for  $k_3$  ranging from 2 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, the overall uncertainty is estimated to be ±20%. The resultant value of  $k_1$ , at 236°C, is therefore  $k_1 = 0.67 \pm 0.14$  s<sup>-1</sup>.

### 4. Conclusion

This paper describes another application of the method [11,12] we recommended for the determination of decomposition rate constants.

Our simple chemical system enables us to show experimentally that  $HO_2$  radicals are produced by the reaction of alkoxy radicals RO with molecular oxygen.

In our experimental conditions this reaction provides, by a chemical way,  $HO_2$  radicals without any competitive reaction. The diheptyl peroxide decomposition in the presence of oxygen, is therefore a clean source of  $HO_2$  radicals. "The difficulty of finding a controlled and reproducible source of  $HO_2$  radicals" has been mentioned [21]. This system contributes to the solution of this problem and allows the study of some elementary reactions in which the hydroperoxyl radical takes part.

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