# Kinetics of the Reactions between Alkyl Radicals and Molecular Oxygen in Aqueous Solution

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The rate constant for the reaction  $R^* + O_2 \rightarrow ROO^*$  in aqueous solution was determined for 18 alkyl radicals by laser flash photolysis. The values are all at the diffusion-controlled limit and lie in the range  $(1.6 - 4.9) \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. The radicals studied are primary, substituted primary, secondary, and benzyl radicals.

### Introduction

Peroxyalkyl radicals, ROO<sup>•</sup>, are important intermediates in combustion chemistry, radiation chemistry, atmospheric chemistry, and photochemistry.<sup>1</sup> Although reactions of alkyl radicals with oxygen, eq 1, have been extensively studied in the gas phase,<sup>2</sup>

$$\mathbf{R}^{\bullet} + \mathbf{O}_2 \to \mathbf{ROO}^{\bullet} \quad (k_1) \tag{1}$$

mechanistic uncertainty remains. At T < 600 K the reaction is believed to follow the addition process, as in eq 1. At higher temperatures an equilibrium with the excited state, \*RO2\*, becomes more important, leading to alkene:

$$\mathbf{ROO^{\bullet}} \stackrel{a}{\rightleftharpoons} *\mathbf{ROO^{\bullet}} \to *\mathbf{R}_{-H}\mathbf{O}_{2}\mathbf{H} \to \mathbf{R}_{-H} + \mathbf{HO}_{2}^{\bullet} \qquad (2)$$

Relatively few values are available for  $k_1$  in solution. This may be so because the clean generation of the alkyl radicals is possible only for those derived from hydrocarbons with all C-H bonds equivalent. Thus rate constants have been reported for  ${}^{\circ}CH_{3}^{3,4}$  ${}^{\circ}C_{2}H_{5}^{5}$ , c- ${}^{\circ}C_{5}H_{9}^{6}$ , and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.<sup>7,8</sup>

Photohomolysis of organocobalt(III) complexes, RCo- $(dmgH)_2OH_2$  and RCo(cyclam)H<sub>2</sub>O<sup>2+</sup>, affords a method for generating a wide range of R<sup>•</sup> radicals in solution, in a way that is amenable to examination by laser flash photolysis.<sup>9</sup> We have used this technique in combination with either of two chemical schemes to study the reactions of an entire series of alkyl radicals with oxygen.

#### **Experimental Section**

Reagents. Literature methods were used to prepare alkylaquobis(dimethylglyoximato)cobalt(III),<sup>10</sup> alkylaquocobalt(cy-clam) perchlorate<sup>11</sup> (cyclam = 1,4,8,11-tetraazacyclotetradecane), and (R,R,S,S)-nickel(cyclam) perchlorate.<sup>12</sup> Stock solutions of Ni(cyclam)<sup>2+</sup> were prepared in 0.0100 M perchloric acid and standardized spectrophotometrically,  $\epsilon_{448} = 45 \text{ L mol}^{-1} \text{ cm}^{-1.12}$ The reagent ABTS<sup>2-</sup> (2,2'-azinobis(3-ethylbenzthiazoline-6-

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TABLE I: Rate Constants<sup>4</sup> for  $\mathbb{R}^{\bullet} + \mathbb{O}_1 \rightarrow \mathbb{ROO}^{\bullet}$  at 25 °C in Aqueous Solution

R	method <sup>b</sup>	$k_1/10^9 L$ mol <sup>-1</sup> s <sup>-1</sup>	R	method <sup>b</sup>	$k_1/10^9 \text{ L}$ mol <sup>-1</sup> s <sup>-1</sup>
CH3	PR	4.7 (7) <sup>c</sup>	CH <sub>3</sub> OCH <sub>2</sub>	Ni	4.9 (4)
	PR	$0.32(4)^{d}$	CICH <sub>2</sub>	Ni	1.9 (4)
	Ni	3.7°	BrCH <sub>2</sub>	Ni	2.0 (5)
	Α	4.1 (3)	$CH_2CH(CH_3)_2$	Α	3.21 (5)
	Ni	4.1 (15)	$CH_2C(CH_1)_1$	Α	2.65 (9)
C <sub>2</sub> H <sub>5</sub>	PR	2.9 (8) <sup>f</sup>	2-C <sub>3</sub> H <sub>7</sub>	Α·	3.78 (9)
	Ni	2.1 (2)	2-C <sub>4</sub> H <sub>9</sub>	Α	3.2 (Ì)
$1-C_{1}H_{7}$	Ni	3.5 (2)	c-C,H	PR	4.9 (6)8
1-C₄H。	Ni	1.8 (2)		Α	3.5 (1)
1-C <sub>4</sub> H <sub>11</sub>	Ni	3.8 (4)	$2 - C_8 H_{17}$	Α	3.70 (7)
1-CAH	Ni	3.9 (5)	C,H,CH,	PR	2.0 <sup>*</sup> `´
1-C <sub>2</sub> H <sub>15</sub>	Ni	1.6 (2)		Α	2.77 (9)
1-C <sub>8</sub> H <sub>17</sub>	Ni	2.4 (3)			

<sup>a</sup>In 1.0 M HClO<sub>4</sub> (Ni) or 0.1 M HClO<sub>4</sub> (A). <sup>b</sup>PR = pulse radiol-ysis, A = ABTS<sup>2-</sup> method, Ni = Ni(cyclam)<sup>2+</sup> method. <sup>c</sup>Reference 3. <sup>d</sup>Reference 4. <sup>e</sup>Reference 16. <sup>f</sup>Reference 5. <sup>g</sup>Reference 6. <sup>h</sup>Reference 8.

sulfonate)) was oxidized by aqueous bromine to the persistent radical ABTS<sup>•-</sup> ( $\epsilon_{650} = 1.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).<sup>13</sup> Molecular oxygen (99.5%, Fischer) was bubbled into water to saturate it (1.26 mM); this solution was diluted as required for the reactions studied. All solutions were made with water purified by a Milli-Q Millipore reagent water system.

Kinetics. Depending on the method used (see Results) the reaction was followed by the disappearance of ABTS<sup>--</sup> at 650 nm or by the buildup of ROONi(cyclam) $H_2O^{2+}$  at 360 nm. Reactions were initiated by a laser pulse at 490 nm, produced by use of the LD490 dve. The cobaloximes were the major source of R<sup>•</sup>, but the RCo(cyclam)H<sub>2</sub>O<sup>2+</sup> complexes were used where available. Absorbance (D)-time data followed first-order kinetics and were fit by a nonlinear least-squares method to the equation  $D_t = D_{\infty}$ +  $(D_0 - D_\infty) \exp(-k_{\psi}t)$ .

#### Results

Two techniques to determine the rate constant were employed. One method (A) was based on the competition between the reaction of bulk concentrations of  $R^{\bullet}$  (1-2  $\mu$ M) with O<sub>2</sub> (eq 1) and its addition to (and oxidation by)<sup>14</sup> the ABTS<sup>\*-</sup> radical:

$$R^{\bullet} + ABTS^{\bullet-} \rightarrow adduct \quad (k_3) \tag{3}$$

The rate of loss of R<sup>•</sup> is given by

 $-d[R^{\bullet}]/dt = 2k_d[R^{\bullet}]^2 + k_1[R^{\bullet}][O_2] + k_3[R^{\bullet}][ABTS^{\bullet-}]$ (4)

where the first term on the right-hand side refers to  $R^* + R^*$ self-reactions. Since the first term is quite small, the data can

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<sup>805.</sup> (14) Equation 2 is accompanied by an appreciable amount ( $\sim$ 30% for R<sup>•</sup> =  $^{\circ}C_{2}H_{3}$ ) of outer-sphere oxidation to the alkene.



Figure 1. Plots of  $k_{\psi}^{-1}$  versus [Ni(cyclam)<sup>2+</sup>]/[O<sub>2</sub>] for the homolysis of RNi(cyclam)H<sub>2</sub>O<sup>2+</sup> in the presence of oxygen. Kinetic data were obtained in 0.1 M perchloric acid at 25 °C by using the radical precursors RCo(dmgH)<sub>2</sub>OH<sub>2</sub> (for hexyl) and RCo(cyclam)H<sub>2</sub>O<sup>2+</sup> (for methoxymethyl and ethyl).

be (and were) fit to a single exponential<sup>15</sup> with a rate constant given by

$$k_{\psi} = 2k_{\rm d}[{\rm R}^{\bullet}]_{\rm av} + k_1[{\rm O}_2] + k_3[{\rm ABTS}^{\bullet-}]$$
 (5)

Since values of  $k_d$  and  $k_3$  are known,  $k_1$  can be determined. The second method (Ni) is based on the reversible homolysis

of alkylnickel complexes,<sup>16,17</sup> eq 6. First, the radicals produced

$$RNi(cyclam)^{2+} \rightleftharpoons R^{\bullet} + Ni(cyclam)^{2+} \quad (k_6, k_{-6}) \quad (6)$$

in the flash are consumed rapidly  $(t_{1/2} \le 1 \ \mu s)$  in reactions with O<sub>2</sub> (eq 1) and with Ni(cyclam)<sup>2+</sup> (eq -6). Subsequent homolysis of RNi(cyclam)<sup>2+</sup> initiates the sequence of reactions 6, 1, and 7.

$$ROO^{\bullet} + Ni(cyclam)^{2+} \rightarrow ROONi(cyclam)^{2+}$$
(7)

In this scheme the radical R is a steady-state intermediate. The rate law for the formation of  $RO_2^{\bullet}$  is given in eq 8. This equation

$$\frac{d[RO_2^{\bullet}]}{dt} = \frac{k_6[RNi(cyclam)^{2+}]}{1 + k_{-6}[Ni(cyclam)^{2+}]/k_1[O_2]} = k_{\psi}[RNi(cyclam)^{2+}] (8)$$

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can be rearranged to a form showing a linear relationship between  $1/k_{\psi}$  and the ratio of concentrations.  $k_1$  can be calculated from

$$\frac{1}{k_{\psi}} = \frac{1}{k_{6}} + \frac{k_{-6}}{k_{1}k_{6}} \frac{[\text{Ni}(\text{cyclam})^{2+}]}{[\text{O}_{2}]}$$
(9)

the slope of the suggested plot, since  $k_6$  and  $k_{-6}$  are known.<sup>16,17</sup> This provides a useful form in which to depict the data, as shown in Figure 1. In practice a nonlinear least-squares fit of  $k_{\psi}$  according to eq 8 was used to calculate values of  $k_1$ . The least-squares values and their standard deviations are given in Table I.

#### Discussion

The reversibility of the reactions of  $O_2$  with carbon-centerd radicals<sup>18</sup> is expected (and has been observed) only for stabilized radicals such as  $(C_6H_5)_3C^{\circ}$ , cyclohexadienyl, etc. For all the radicals studied in this work the reaction with  $O_2$  can be safely considered irreversible. As expected, we obtained no evidence for the reverse of reaction 1 for any of the radicals examined.

The values of  $k_1$  are at the diffusion-controlled limit for molecules of this size. The range is  $(1.6-4.9) \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. No perceptible trend is seen as the nature of the alkyl radical was varied, nor is one expected in view of the diffusion-controlled character of the reactions. It should be noted that one<sup>4</sup> of the previously determined values for  $O_2 + {}^{\circ}CH_3$  from pulse radiolysis can be safely rejected. In three other cases,  $C_2H_5$ , c- $C_5H_9$ , and  $C_6H_5CH_2$ , pulse radiolytic values are in reasonable agreement with the ones we have determined.

Several rate constants are available for the gas phase. Values of  $k_1/10^9 \text{ L} \text{ mol}^{-1} \text{ s}^{-} 1.2 ({}^{\circ}\text{CH}_3), {}^{19} 1.0 ({}^{\circ}\text{C}_2\text{H}_5), {}^{20} \text{ and } 0.67 (C_6-H_5\text{CH}_2)^{21}$  are smaller than for the solution reactions. This is consistent with related observations<sup>22</sup> that reactions of other radical transients (e.g., H<sup>•</sup>, HO<sup>•</sup>) with gases having low affinity for the solvent (e.g., H<sub>2</sub>, CO, O<sub>2</sub>) occur with rate constants that are higher in the solution phase.

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