# Kinetics of the reaction of IO radicals with HO<sub>2</sub> radicals at 298 K

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The molecular-modulation-UV/visible-absorption-spectroscopy technique has been used to investigate the simultaneous timeresolved behaviour of IO and HO<sub>2</sub> produced by the photolysis of O<sub>3</sub> in the presence of CH<sub>3</sub>OH, I<sub>2</sub>, O<sub>2</sub> and Ar. This has enabled a direct measurement of the rate coefficient for the reaction IO+HO<sub>2</sub>→HOI+O<sub>2</sub> to be made at 760 Torr and 289 K. The value obtained was  $k_5 = (6.4 \pm 0.7) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

### 1. Introduction

The kinetics of reactions of the IO radical have received some attention in recent years [1-7], owing to its importance as an intermediate in the tropospheric oxidation of iodine-containing compound [8-10]. A complete knowledge of its sources and sinks is required in order to calculate its ambient concentration, and to asses its potential importance as an oxidising radical in the lower atmosphere.

IO radicals are produced in the troposphere following the photodissociation of stable iodine-containing molecules such as  $CH_3I$ 

$$CH_{3}I + h\nu \rightarrow CH_{3} + I, \qquad (1)$$

$$I + O_3 \rightarrow IO + O_2 . \tag{2}$$

Potentially important removal routes for tropospheric iodine have been identified as the self-reaction of IO and its reactions with  $NO_2$  and  $HO_2$ , followed by physical removal of the product molecules  $I_2O_2$ , IONO<sub>2</sub> and HOI [8–10]

$$IO+IO \xrightarrow{M} I_2O_2$$
, (3)

 $IO + NO_2 \xrightarrow{M} IONO_2$ , (4)

 $IO+HO_2 \rightarrow HOI+O_2$ . (5)

The kinetics of reactions (3) and (4) have been studied [3-7], but to date, there have been no published measurements of the kinetics of the reaction of IO radicals with HO<sub>2</sub>. In this paper, we report the results of experiments performed to investigate this reaction at 298 K.

### 2. Experimental

Experiments were performed in a 1.2 & quartz reaction vessel, 120 cm in length. The vessel was surrounded by a jacket through which ethanol was circulated, allowing temperature regulation. All experiments were performed at 298 K. The kinetics of the reaction of IO with HO<sub>2</sub> were investigated using the molecular-modulation-UV/visible-absorption-spectroscopy technique, which has been described in some detail in previous publications [4,10].

The radicals were produced by the 253.7 nm modulated photolysis of appropriate flowing gas mixtures, as described below, and were monitored using absorption spectroscopy. IO radicals were monitored at 427.1 nm, corresponding to the band head of the (4, 0) component of the A  ${}^{2}\Pi \rightarrow X {}^{2}\Pi$  transition ( $\sigma$ =3.1×10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> [11], 0.27 nm resolution) using a tungsten lamp. HO<sub>2</sub> radicals were monitored in the broad UV band at 220 nm, using

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a deuterium lamp source ( $\sigma = 3.4 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> [12], 1.1 nm resolution). Modulation frequencies in the range 1.0–3.3 Hz were generally used, and up to 3000 cycles were accumulated in order to get well-averaged absorption-time profiles.

The production of both radicals was initiated by the photolysis of  $O_3$  using 253.7 nm radiation from two low-pressure mercury lamps (Philips TUV 40 W). This resulted in the initial production of both  $O(^1D)$  and  $O(^3P)$  atoms

$$O_3 + h\nu(\lambda = 253.7) \rightarrow O(^1D) + O_2$$
, (6a)

$$\rightarrow O(^{3}P) + O_{2}, \qquad (6b)$$

$$O(^{1}D) + M \rightarrow O(^{3}P) + M.$$
 (7)

In the presence of  $CH_3OH$  and  $O_2$ ,  $HO_2$  radicals were generated by the following scheme:

 $O + CH_3 OH \rightarrow CH_2 OH + OH, \qquad (8)$ 

 $OH + CH_3 OH \rightarrow CH_2 OH + H_2 O, \qquad (9)$ 

$$CH_2OH + O_2 \rightarrow HO_2 + HCHO.$$
 (10)

Addition of  $I_2$  to the system allowed simultaneous production of IO radicals

$$O+I_2 \rightarrow IO+I, \tag{11}$$

$$I + O_3 \rightarrow IO + O_2 . \tag{12}$$

The reaction of ground-state  $O(^{3}P)$  atoms with  $I_{2}$  is about a factor of  $3 \times 10^4$  more rapid than the reaction with CH<sub>3</sub>OH ( $k_{11} = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$  $s^{-1}$  [1],  $k_8 = 5.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  [13]). Since the reaction of  $O(^{1}D)$  with CH<sub>3</sub>OH is expected to be significantly more rapid, Ar was used as a diluent gas in order to minimise the rate of the quenching reaction (7), thereby allowing CH<sub>3</sub>OH to compete favourably with I<sub>2</sub> for reaction with atomic oxygen. Under the conditions of these experiments,  $CH_3OH$  was in large excess over  $I_2$ , to ensure that most of the O(<sup>1</sup>D) reacted with CH<sub>3</sub>OH leading to the production of HO<sub>2</sub>. Most of the  $O(^{3}P)$ , however, reacted with  $I_2$  to produce IO. The presence of high concentrations of CH<sub>3</sub>OH also ensured that reaction (9) was the exclusive reaction for OH radicals.

Experiments were performed with HO<sub>2</sub> in excess over IO. Production rates of HO<sub>2</sub> about a factor of 4 greater than those of IO were achieved using the following concentrations of reagent gases:  $\approx 2.5 \times 10^{14}$  molecule cm<sup>-3</sup> O<sub>3</sub>,  $(3.5-6.5) \times 10^{17}$  molecule cm<sup>-3</sup> CH<sub>3</sub>OH,  $\approx 3 \times 10^{13}$  molecule cm<sup>-3</sup> I<sub>2</sub>,  $\approx 9 \times 10^{16}$ molecule cm<sup>-3</sup> O<sub>2</sub> and  $2.4 \times 10^{19}$  molecule cm<sup>-3</sup> Ar (total pressure is 760 Torr). O<sub>3</sub> was generated by the 184.9 nm photolysis of O<sub>2</sub> (BOC, Breathing Grade) flowing slowly through a Pyrex flask equipped with a "penray" lamp (Ultra Violet Products). CH<sub>3</sub>OH was admitted to the reaction vessel by diverting a proportion of the Ar (Air Products, High Purity) through a jacketted bubbler containing the liquid (Fisons, AR Grade). The temperature of the bubbler could be adjusted in order to vary the concentration of CH<sub>3</sub>OH in the gas flow. I<sub>2</sub> was generated by a flow of Ar over iodine crystals (BDH, Analar Grade) contained in a sintered glass tube immersed in an ice/water bath. The flows of the constituent gases were monitored on pre-calibrated rotameters. The total flow was  $\approx 12 \ \ell \ min^{-1}$ , corresponding to a residence time of 6 s in the vessel.

The concentrations of O<sub>3</sub> and I<sub>2</sub> were determined by conventional absorption spectroscopy ( $\sigma$ (260 nm)=1.06×10<sup>-17</sup> cm<sup>2</sup> molecule<sup>-1</sup> for O<sub>3</sub> [14];  $\sigma$ (500 nm)=2.19×10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup> for I<sub>2</sub> [15]). The concentrations of O<sub>2</sub> and Ar were calculated from the measured flow rates. A knowledge of the vapour pressure of CH<sub>3</sub>OH at the bubbler temperature, and accurate measurement of the proportion of the gas flow through the bubbler, allowed calculation of the CH<sub>3</sub>OH concentration.

### 3. Results

3.1. Photolysis of  $O_3/I_2/O_2/Ar$ : removal of IO in the absence of  $HO_2$ 

Several modulated photolysis experiments were carried out in the absence of  $CH_3OH$ , during which IO radicals were produced by reaction sequence (6), (7), (11) and (2), without simultaneous production of HO<sub>2</sub>. Significant modulated absorption signals due to IO were detected at wavelengths near 427 nm, maximising at a monochromator setting of 427.1 nm (0.27 nm resolution). In the absence of HO<sub>2</sub>, IO removal should be initiated by its rapid self-reaction, which is dominated by an association channel at atmospheric pressure [11]

$$IO + IO \xrightarrow{M} I_2O_2$$
. (3)

As in previous work from this laboratory in which reaction (3) was investigated using the molecularmodulation technique [3,4], the formation of lowvolatility "iodine oxide" products was observed, characterised by a visible fogging of the reaction vessel. This resulted in attenuation of the monitoring beam, which became very severe at shorter wavelengths. Kinetic analysis of the modulated IO waveforms indicated that it was removed about 3 to 4 times more rapidly than could be accounted for by reaction (3) alone  $(k_3 = 5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  $s^{-1}$  [11]), in agreement with our previous work [3,4]. Clearly, IO is removed by additional reactions with  $I_2O_2$  or other  $IO_x$  species, leading to the formation of polymeric products. Consequently, during the experiments to investigate reaction (5) (section 3.3), HO<sub>2</sub> was present in large excess over IO, in order to suppress the flux through reaction (3) to a very low level, thereby eliminating the potential complicating reactions of IO with the products of reaction (3).

## 3.2. Photolysis of $O_3/CH_3OH/O_2/Ar$ : the selfreaction of $HO_2$ at elevated $CH_3OH$ concentrations

The use of high concentrations of CH<sub>3</sub>OH in the experiments to measure  $k_5$  (section 3.3) ensured that HO<sub>2</sub> was present in large excess over IO. Under these conditions, HO<sub>2</sub> is removed mainly by its self-reaction (12), which has been shown previously to be accelerated in the presence of elevated concentrations of CH<sub>3</sub>OH in air at 760 Torr (Andersson et al. [16])

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 . \tag{12}$$

Since the concentrations of CH<sub>3</sub>OH used in this work, (3.5–6.5)×10<sup>17</sup> molecule cm<sup>-3</sup>, were greater than those used by Andersson et al. (up to  $\approx 2.5 \times 10^{17}$ molecule cm<sup>-3</sup>), the production and removal of HO<sub>2</sub> during modulated photolysis in the absence of IO was investigated. A modulated HO<sub>2</sub> absorption waveform obtained with [CH<sub>3</sub>OH]= $5.9 \times 10^{17}$  molecule cm<sup>-3</sup> was analysed using procedures described in detail elsewhere [17]. Removal of HO<sub>2</sub> was well described by a second-order analysis, with  $k_{12}=7.9 \times$  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This is 14% lower than the value  $(9.2\pm3.0)\times10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> extrapolated from the [CH<sub>3</sub>OH]-dependent expression (299 K) of Andersson et al. [16], but lies well within the uncertainty limits. A slightly lower value might be expected since Ar was used as the diluent gas.

The observed steady-state concentration of HO<sub>2</sub> in this experiment also allows calculation of the production rate of HO<sub>2</sub> radicals (and, therefore, O atoms), since it is a balance between production and removal, and the removal rate is known. This production rate is consistent with O<sub>3</sub> photolysis at a rate of  $(6.1\pm0.4)\times10^{-2}$  s<sup>-1</sup>. A further experiment performed in static mode whilst monitoring the removal of O<sub>3</sub> at 260 nm provided a first-order decay rate of  $(6.4\pm0.3)\times10^{-2}$  s<sup>-1</sup>, in excellent agreement with that determined above. The observed rate of removal of  $O_3$  is expected to be equivalent to the elementary photolysis constant,  $k_6$ , since regeneration of  $O_3$  by the association reaction of  $O({}^{3}P)$  atoms and  $O_2$  is only of minor importance under the conditions of these experiments.

# 3.3. Photolysis of $O_3/CH_3OH/I_2/O_2/Ar$ : the reaction of IO radicals with HO<sub>2</sub> radicals

The simultaneous behaviour of IO and HO<sub>2</sub> was investigated by performing pairs of experiments on identical reaction mixtures in which the system was monitored either at 427.1 or 220 nm. These are summarised in table 1. The modulated absorption profiles for IO and HO<sub>2</sub> obtained in experiment 5 with a modulation period of 0.3 s are displayed in fig. 1. The magnitude of the modulated absorption signals obtained for IO and HO<sub>2</sub> was similar, indicating that  $HO_2$  was in excess by about an order of magnitude over IO. Consequently, the behaviour of HO<sub>2</sub> was dominated by its removal by reaction (12), and the timescale for its removal was slow compared with the modulation period. The figure shows that HO<sub>2</sub> had not reached steady state during the "light on" phase, and did not decay away completely during the "light off" phase, indicating that a significant concentration was present throughout the modulation period. In contrast, IO established a steady state rapidly which reduced gradually in the latter part of the "light on" phase. This is typical of a rapid reaction with a species present in large excess, the concentra-

Run	τ <sup>a)</sup>	[O <sub>3</sub> ] <sup>b)</sup>	[CH <sub>3</sub> OH] °)	[I <sub>2</sub> ] <sup>b)</sup>	[O <sub>2</sub> ] <sup>c)</sup>	k5 d)
1	0.6	26.4	34.3	3.39	9.95	6.01
2	0.6	24.6	35.0	3.11	10.00	6.15
3	0.6	23.1	64.2	2.89	9.48	6.68
4	0.6	23.5	62.8	2.99	9.28	6.89
5	0.3	23.5	62.8	2.99	9.28	6.12

Table 1	
Summary of experimental conditions and	determined values of $k_5$

<sup>a)</sup> Modulation period in s. <sup>b)</sup> In 10<sup>13</sup> molecule cm<sup>-3</sup>. <sup>c)</sup> In 10<sup>16</sup> molecule cm<sup>-3</sup>. <sup>d)</sup> In 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Fig. 1. Modulated absorption waveform measured for (a) IO at 427.1 nm, (b) HO<sub>2</sub> at 220 nm (experiment 5). Computed profiles represent the best fit (----) and optimised fits with  $k_5$  fixed at  $3 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (---) and  $9 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (---).

tion of which is gradually increasing. When illumination ceased, IO also decayed rapidly. This behaviour clearly indicates that IO was being removed predominantly by reaction with a "slow" radical which was present in excess, i.e. HO<sub>2</sub>. At its observed concentrations, the self-reaction of IO was only of minor importance, and no complication due to the formation of polymeric iodine oxide products was observed.

The chemical system was simulated using FAC-SIMILE [18] with the simplified chemical scheme listed in table 2. Modulated-absorption profiles generated for IO and  $HO_2$  by the model are shown in fig. 1 along with the experimental data. It was immediately clear that the experimental results could be recreated extremely precisely by the model if reaction (5) was included with a value of  $k_5$  of about  $6 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, with the calculated IO waveform being particularly sensitive to the adopted value of  $k_{s}$ . For experiments performed with a longer modulation period, however (see fig. 2), the IO profiles displayed an unexpected increase in absorption at the end of the modulation cycle, and inclusion of a slow "dark" source of IO in the model was necessary to obtain good fits to the experimental data.

The most probable dark source of IO in this system is the decomposition of the product HOI which accumulates in the reaction vessel. This might produce IO directly, or iodine atoms which would regenerate IO rapidly by reaction (2)

$$HOI + M \rightarrow OH + I + M$$
, (13a)

$$\rightarrow$$
H+IO+M. (13b)

The IO waveforms obtained in experiments 1–4 were well described if reaction (13) was included in the model at a rate of  $k_{13} = 0.06 \pm 0.01 \text{ s}^{-1}$ . Current estimates of  $\Delta H_f$  for HOI suggest, however, that gasphase decomposition is significantly endothermic (ref. [19] and references therein), so a heterogeneous mechanism may need to be invoked. The perturbation to the measured waveforms due to the slow regeneration of IO was a comparatively minor effect, however, and does not greatly influence conclusions concerning the rate of reaction (5).

The calculated behaviour of IO was very sensitive to variation of  $k_5$ , as shown in fig. 1. In contrast, the behaviour of HO<sub>2</sub> was dominated by its self-reaction (12) and was only perturbed slightly by the presence of IO. It was found that non-linear least-squares fitting to the experimental IO waveforms alone allowed optimisation of  $k_5$  and  $\alpha$  (the relative production rate of the two radicals) in each experiment. Inclusion of the HO<sub>2</sub> data in the fitting procedure provided no extra information on these parameters, given that the total radical production rate was already known. However, the calculated HO<sub>2</sub> profiles were always in satisfactory agreement with those obtained experimentally (e.g., see fig. 1). The values of  $k_5$  obtained for each of the five experiments are shown in table 1. The mean of these determinations is

#### Table 2

Simplified chemical scheme for simulating modulated waveforms for IO and HO<sub>2</sub> generated simultaneously

Reaction	Rate parameter	Comment				
 $O_3 + h\nu(\rightarrow O + O_2) \rightarrow 2HO_2$	$6.25 \times 10^{-2} \alpha$	<b>a, b</b> , c)				
$O_3 + h\nu (\rightarrow O + O_2) \rightarrow 2IO$	$6.25 \times 10^{-2} (1-\alpha)$	a, b, c)				
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.7 \times 10^{-12}$ + [CH <sub>3</sub> OH] $8.8 \times 10^{-30}$	d, e)				
$IO + IO \rightarrow I_2O_2$	5.2×10 <sup>-11</sup>	d, f)				
$IO + HO_2 \rightarrow HOI + O_2$	k,	<b>c</b> )				
$HOI \rightarrow \rightarrow IO + HO_2$	k <sub>13</sub>	<b>c</b> )				

\*) In ş<sup>-1</sup>.

<sup>c)</sup>  $\alpha$ ,  $k_5$  and  $k_{13}$  optimised by fitting procedure (see section 3.3).

e) Zero [CH<sub>3</sub>OH] value taken from ref. [11], [CH<sub>3</sub>OH] dependence determined from present experiments (see section 3.2).

<sup>f)</sup> Taken from ref. [11].

<sup>&</sup>lt;sup>b)</sup> Overall radical production rate measured (see section 3.2).

d) In cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.



Fig. 2. Modulated absorption waveform measured for IO at 427.1 nm (experiment 4). Computed profiles represent the best fit (----) and optimised fits with  $k_{13}$  fixed at 0.5 s<sup>-1</sup> (---) and zero (---).

$$k_5 = (6.4 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
  
(T=298 K; error = ±2 $\sigma$ ).

### 4. Discussion

There are no previously published data for  $k_5$ , but work currently in progress at CNRS, Orleans [20], using discharge flow-mass spectroscopy has provided a preliminary value of  $7.3 \times 10^{-11}$  cm<sup>3</sup> mole $cule^{-1} s^{-1}$  at 298 K, in good agreement with the present determination. Although the present experiments were performed for only a limited range of reagent conditions, owing to the necessity of having HO<sub>2</sub> in large excess, we believe the observed behaviour of IO can only be explained by rapid reaction with a "slow" radical which is present only when CH<sub>3</sub>OH is added to the system. Furthermore, modelling studies confirmed that the precise time dependence of IO could only result from reaction with a species displaying the same time dependence as HO<sub>2</sub>. At the high concentrations of CH<sub>3</sub>OH employed, the adduct species, HO2-CH3OH, is expected to be present at a few percent of the concentration of HO<sub>2</sub> [16], and will display an identical time dependence to HO<sub>2</sub>. However, the reaction of IO with HO<sub>2</sub>-CH<sub>3</sub>OH does not appear significant since variation of [CH<sub>3</sub>OH] (and, therefore, [HO<sub>2</sub>-CH<sub>3</sub>OH]) by almost a factor of two had no observable effect on the determined value of  $k_5$ .

Under the conditions appropriate to the marine coastal troposphere, the reaction of IO with HO<sub>2</sub> will compete with reaction with NO<sub>2</sub> and the self-reaction of IO as a removal route for IO radicals, based on the current determination of  $k_5$ , and literature values of  $k_3$  and  $k_4$  (see discussion in ref. [10]). The relative importance of these reactions as sinks for active iodine, however, will be strongly dependent on the photolysis lifetimes of the product molecules HOI, IONO<sub>2</sub> and I<sub>2</sub>O<sub>2</sub>, for which no firm absorption cross sections are presently available from which to estimate photodissociation constants. The regeneration of active iodine from the photolysis of IONO<sub>2</sub> completes a "null cycle" (owing to the rapid subsequent photolysis of NO<sub>3</sub>)

 $I + O_3 \rightarrow IO + O_2 \tag{2}$ 

$$IO + NO_2 \longrightarrow IONO_2$$
 (4)

$$IONO_2 + h\nu \rightarrow 1 + NO_3 \tag{14}$$

$$NO_3 + h\nu \rightarrow NO_2 + O \tag{15}$$

$$O + O_2 \rightarrow O_3 \tag{16}$$

zero

In contrast, the cycles based on the photodissociation of HOI and  $I_2O_2$  lead to a net loss of  $O_3$  and, in the case of the HOI cycle, coupling with the HO<sub>x</sub> chemistry through conversion of HO<sub>2</sub> into OH

total

$$\mathbf{I} + \mathbf{O}_3 \rightarrow \mathbf{IO} + \mathbf{O}_2 \tag{2}$$

 $IO + HO_2 \rightarrow HOI + O_2$  (5)

 $HOI + h\nu \to OH + I \tag{17}$ 

 $HO_2 + O_3 \rightarrow OH + 2O_2$  total

 $(I+O_3 \rightarrow IO+O_2) \times 2 \tag{2}$ 

 $IO + IO \rightarrow I_2O_2$  (3)

 $I_2O_2 + h\nu \rightarrow 2I + O_2 \tag{18}$ 

 $2O_3 \rightarrow 3O_2$  total

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