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Chemical generation of atomic iodine for the chemical oxygen-iodine laser. II. Experimental results

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Abstract

A new method for the chemical generation of atomic iodine intended for use in a chemical oxygen-iodine laser (COIL) was investigated experimentally. The method is based on the fast reaction of hydrogen iodide with chemically produced chlorine atoms. Effects of the initial ratio of reactants and their mixing in a flow of nitrogen were investigated experimentally and interpreted by means of a computational model for the reaction system. The yield of iodine atoms in the nitrogen flow reached 70–100% under optimum experimental conditions. Gain was observed in preliminary experiments on the chemical generation of atomic iodine in a flow of singlet oxygen. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The process of chemical generation of atomic iodine was studied for use in the chemical oxygen–iodine laser (COIL). This laser is the shortest wavelength high-energy chemical laser operating on the electronic transition of the ²P ground term of atomic iodine at 1.315 μ m

$$I({}^{2}P_{1/2}) \to I({}^{2}P_{3/2}) + hv$$
 (1)

Population inversion on this transition is maintained by near resonant energy transfer from metastable excited oxygen, $O_2({}^1\Delta_g)$, to iodine atoms in the ground state

$$I({}^{2}P_{3/2}) + O_{2}({}^{1}\Delta_{g}) \rightarrow I({}^{2}P_{1/2}) + O_{2}({}^{3}\Sigma_{g}^{-})$$

$$k_{2} = 7.6 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}.$$
(2)

In conventional COIL, atomic iodine is produced by dissociation of molecular iodine through pooling processes which consume 4–6 $O_2(^1\Delta_g)$ molecules

$$I_2 + nO_2(^1\Delta_g) \to 2I + nO_2(^3\Sigma_g^-)$$
 $n = 4-6.$ (3)

The energy of $O_2(^1\Delta_g)$ saved by avoiding this process can be utilised for laser pumping and an increase in laser power up to (25%) [1] can be

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achieved. Another drawback of using molecular iodine as a precursor of iodine atoms in COIL is the fast quenching reaction

$$I({}^{2}P_{1/2}) + I_{2} \rightarrow I({}^{2}P_{3/2}) + I_{2}$$

$$k_{4} = 3.5 \times 10^{-11} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}.$$
(4)

Iodine vapour for COIL operation is produced by evaporation of solid or liquid iodine, which is difficult to control due to a time-varying interfacial surface area and high temperature gradients in the bed of solid iodine. In addition, the overall iodine management system must be heated to 80-100 °C to prevent solid iodine precipitation. To avoid or suppress these problems, and to increase the COIL efficiency, other methods of generating atomic iodine have been investigated. Endo et al. [2] produced iodine atoms by dissociating I₂ in a microwave discharge. Pazyuk et al. [3] produced iodine atoms with electrical discharges in alkyl iodine vapours.

In our laboratory, a new method was proposed based on fast chemical reactions of gaseous reactants [4,5]. Experimental results on the chemical generation of iodine atoms obtained on a smallscale device are presented in this paper. The flow conditions in this device are similar to the plenum conditions in a supersonic COIL.

2. Description of the reaction system

The chemical system studied experimentally is based on a two-step reaction process. In the first step, atomic chlorine is formed in the reaction of chlorine dioxide with nitrogen oxide. The chlorine then reacts in the second step with gaseous hydrogen iodide to produce atomic iodine. Most of the kinetic data for this system could be taken from the papers concerned with the investigation of the chemical HCl and HCl/ CO_2 transfer lasers [6] (see also references in our paper [7]).

2.1. Generation of chlorine atoms

Chlorine atoms are produced in the fast exothermic reaction of gaseous chlorine dioxide with nitrogen oxide

$$ClO_2 + 2NO \rightarrow Cl + 2NO_2$$
 (5)

This reaction represents a branched chain reaction system consisting of the following steps [6]:

$$\frac{\text{CIO}_2 + \text{NO} \rightarrow \text{CIO} + \text{NO}_2}{k_6 = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},}$$
(6)

$$ClO + NO \rightarrow Cl + NO_2 k_7 = 1.7 \times 10^{-11} e^{(-120/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
(7)

$$Cl + ClO_2 \to 2ClO k_8 = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
(8)

Reaction (6) initiates the chain. Reaction (8) is the chain-branching step with Cl and ClO as chain carriers. For the fast and efficient course of the whole process, other processes must not exhaust Cl atoms and ClO radicals. Atomic chlorine is the main reaction product for the initial ratio $NO:ClO_2 = 2:1$. ClO radicals are formed predominantly for the ratio 1:1 [6,7]. Chlorine atoms can be subsequently consumed by recombination with third molecules [6,7]. The fastest loss processes for both Cl and ClO are the termolecular reactions with nitrogen dioxide, which is an unavoidable by-product of the reactions (6) and (7).

$$Cl + NO_2 + N_2 \rightarrow ClNO_2 + N_2 k_9 = 1.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$
(9)

$$CINO_2 + Cl \to Cl_2 + NO_2$$

 $k_{10} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$
(10)

$$ClO + NO_2 + N_2 \rightarrow NO_3Cl + N_2$$

 $k_{11} = 1.4 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$
(11)

Because reaction (10) is much faster than (9), it can be assumed that Cl atoms disappear with the effective rate constant of 3×10^{-30} cm⁶ molecule⁻¹ s⁻¹ which is more than 20 times higher than the rate constant for reaction (11). Reactions (9) and (10) can be also considered as the recombination of Cl atoms catalysed by NO₂ and nitrogen.

2.2. Generation of iodine atoms

Iodine atoms are produced by the fast exothermic reaction of chlorine atoms with hydrogen iodide

Cl + HI → HCl(HCl^{*}) + I(²P_{3/2}) + 132 kJ mol⁻¹

$$k_{12} = 1.64 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
 (12)

According to Maylotte et al. [8], about 70% of the reaction exothermicity is transferred into vibrational energy of HCl^{*} molecules.

In the COIL medium, iodine atoms will undergo excitation according to reaction (2). In addition, recombination of iodine atoms takes place in termolecular reaction with molecules of carrier gas $(k_{N2} = 4.2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$, and molecular iodine $(k_{I2} = 3.7 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1})$, respectively. Due to the high concentration of NO₂ in the reaction mixture, iodine atoms are lost primarily in the reactions:

$$I + NO_2 + N_2 \rightarrow INO_2 + N_2 k_{13} = 3.1 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$
(13)

$$I + INO_2 \rightarrow I_2 + NO_2$$

 $k_{14} = 8.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$
(14)

Mathematical modelling, in which instantaneous mixing was assumed, showed that Cl atoms are exhausted from the reaction mixture by the extremely fast reaction (12) provided that HI, CIO_2 and NO are added together at a single point [7]. This results in a deceleration of the chain reaction (5) and to the overall process. The formation of atomic iodine should therefore be faster when HI is admixed at a certain distance downstream from the mixing point of ClO_2 and NO streams [7]. The injection of NO through two injectors separated by some distance in the flow direction was also proposed in order to diminish the loss of chlorine atoms [6]. Optimal conditions for the highest I yield in this arrangement were found from the mathematical modelling [7].

3. Experimental

The experimental investigation was first performed in an environment of nitrogen to study the atomic iodine produced with flow conditions similar to those in COIL, but with non-reactive gas. Experiments were then performed in the flow of reactive singlet oxygen. A small-scale device was designed for the flow conditions that are typical for the region upstream in the nozzle plenum of a supersonic COIL. The experimental setup for measurements that were performed in nitrogen is shown schematically in Fig. 1. The chemical flow reactor 1 is made of stainless steel tube of 10 mm in i.d. Three injectors for the injection of secondary gases into the primary gas are inserted coaxially in the reactor bends. They are movable allowing a change in their position and variable time span between injections of reactants. They are made of stainless steel tube of 5 mm in o.d. with one, two or three rows of holes. The diameter and number of the holes in each injector were calculated to achieve full penetration of each secondary flow into the primary flow. The following flow rates of reactants were used: $(0.1 \text{ mmol ClO}_2 +$ 5 mmol N₂) s^{-1} in the primary flow, (0.1 mmol $NO + 1 \text{ mmol } N_2$) s⁻¹ through the first and secinjector, respectively, and (0.1 mmol ond $HI + 1 \text{ mmol } N_2$) s⁻¹ through the third injector. Twenty-four holes were made in the first injector, 20 holes in the second injector, and 16 holes in the third injector; all holes in the 0.4 mm i.d.

The primary gas flowing into the reactor consisted of 4–10% ClO₂ in nitrogen. A mixture of NO and nitrogen (10% NO) was introduced through a single injector only or through the first and second injectors simultaneously. A mixture of HI and N₂ (with 8–10% HI) was introduced in most experiments through the third injector. The flow rates of secondary gases were measured by the flow meters 6–8 with the calibrated sonic orifices. Flow rates of reactants were 50–240 µmol ClO₂ s⁻¹, 100–600 µmol NO s⁻¹, and 0–500 µmol HI s⁻¹. The pressure in the reactor was 1.5–4 kPa, with a gas velocity 130–160 m s⁻¹. The reactants entered the reactor at room temperature.

Gaseous ClO_2 was produced on site by the reaction of chlorine with sodium chlorite [6]

$$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$$
 (15)

For safety reasons, the partial pressure of ClO_2 should not exceed 4 kPa [6], in special devices 13



Fig. 1. Schematic of small-scale device for atomic iodine generation. 1 -flow reactor, $2 - ClO_2$ generator, 3, 4 -rotameters, 5 -pressure reducer, 6-8 -flow meters, 9 -diagnostic cell, 10 -Ar ion laser, 11 -ISD cell, 12, and 13 -VIS photometry cells.

kPa [9]. Reaction (15) took place in the generator 2 where gaseous chlorine diluted with nitrogen (in the ratio 1:20 to 1:50) passed through the column with NaClO₂ at the room temperature. The generator (a PVC tube 7 or 11 cm in i.d., 1 m long) was filled with either 40% (w/w) aqueous solution or powdered NaClO₂. The flow rate of ClO₂ and residual chlorine, respectively, was determined by chemical analysis of potassium iodide solution (2.5%), in which the exit gas was trapped [10].

The gas mixture from the reactor 1 first entered the optical cell 11 used for the detection of atomic I by the iodine scan diagnostics (ISD) [11]. This diagnostic is based on a narrow band tunable near infrared diode probe laser that monitors the gain or absorption for the $I({}^{2}P_{1/2})-I({}^{2}P_{3/2})$ transition at 1.315 µm. The laser frequency is scanned over the 3–4 hyperfine transition in the iodine atom. The probe beam was double passed through the optical cell 11 (11 mm i.d., 45 mm of inner length) in a direction parallel to the gas flow. The optical cell was close coupled to the reactor because the lifetime of iodine atoms in the gas mixture is short (0.2-1 ms). The longitudinal gas flow through the cell was chosen because of the low flow rate of atomic iodine and the need for sufficient absorption length. The gas velocity downstream of the reactor 1 and through the ISD cell was $80-90 \text{ m s}^{-1}$. The gain/loss data were processed on line with a PC. The atomic iodine flow rate was also determined indirectly from the measured concentration of I_2 molecules that were formed by recombination of iodine atoms. The I2 concentration was measured at some distance from the reactor by VIS absorption photometry at 488 nm. The flow rate of nitrogen dioxide that was formed in the reactor was estimated by the same method (using an absorption cross-section of 2.7×10^{-19} cm²), from the light absorption change upon adding NO to ClO₂. The photometry employed the argon ion laser 10, a beam splitter, two optical cells 12 and 13, two silicon photodiodes, and current amplifiers. The AD converter and PC processed signals on-line from the photodiodes, the gas flow meters 6-8, and the temperature and pressure sensors. The gas transport times were 0.2 ms from the third injector to the entrance of the ISD cell 11, 0.6 ms to the ISD cell exit, 6 ms to the centre of the first I_2 cell, and 93 ms to the second I_2 cell. At the beginning of each experiment, ClO₂ and NO were introduced into the reactor at constant flow rates, then HI was admixed with either a constant or variable flow rate. At the end of each experiment, the HI was shut off first, then ClO₂ flow, and finally the NO flow. This procedure made it possible to determine the contribution of NO_2 and I_2 , respectively, to the light absorption in the detection cells 12 and 13. The temperature was measured by a Ni-NiCr thermocouple (1 mm in o.d. including the Inconel sheath) placed at the beginning of the diagnostic cell 9. The gas exiting the diagnostic cell 9 was exhausted by the rotary pump $(25 \text{ m}^3 \text{ h}^{-1})$ after passing a liquid nitrogen trap.

The production of atomic iodine in a flow of singlet oxygen was performed in the same reactor 1 with the difference that an $O_2({}^1\Delta_g)$ stream was introduced as the primary gas. The oxygen was generated in a small-scale $O_2({}^1\Delta_g)$ jet-type generator. The performance of this generation is described in detail in our earlier paper [12]. The $O_2({}^1\Delta_g)$ concentration was evaluated from 1.27 µm emission in a detection cell placed between the $O_2({}^1\Delta_g)$ generator and the reactor. The ClO₂ + N₂ mixture was introduced in the reactor through the first injector, the NO + N₂ mixture through the second injector, and HI + N₂ mixture through the third injector.

4. Results and discussion

4.1. ClO_2 production

The solid NaClO₂ (50% w/w) was used first for ClO_2 production. The column was filled with 10 dm³ of powdered NaClO₂ through which was

passed 90 $\mu mol~Cl_2$ and 2.5 $mmol~N_2~s^{-1}.$ This yielded 140–150 μ mol ClO₂ s⁻¹ with about 15 μ mol s⁻¹ of residual chlorine. The ClO₂ yield (80-85%) decreased with further increasing chlorine flow rate. The ClO₂ yield also declined with "aging" of the filler, a yield of only 40% was obtained after two months' intermittent use, even though Cl₂ reacted with only 12–15% of the NaClO₂. The reason for this effect, also observed by Arnold [6], is probably caused by a layer of NaCl formed on the surface of the NaClO₂ crystals that hinders chlorine diffusion and so slows down ClO₂ production. When NaClO₂ in the form of 32% solution was used, 1 liter provided 200–250 μ mol ClO₂ s⁻¹ with a yield of 81–85%. This production rate was constant during 5 h of operation, which corresponds to 90% utilisation of the NaClO₂. Water contained in the gas exiting the solution could cause problems in a COIL medium; its amount, however is small by comparison with water vapour produced in the $O_2(^1\Delta_g)$ generator.

4.2. Formation of molecular iodine

Molecular iodine may be formed by the recombination of I atoms and also by other reactions contributing to the VIS photometry signal. The residual chlorine in the ClO_2 flow reacts with HI

$$Cl_2 + 2HI = 2HCl + I_2$$

$$k_{16} = (3.4 \pm 1.7) \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$
(16)

The rate of this reaction was estimated in our earlier investigation [4]. Modelling of the reaction system producing iodine atoms showed that reaction (16) may affect the I_2 concentration measured in the downstream cell 13, while in the upstream cell 12 it may be neglected. The overall rate of atomic iodine production was therefore calculated from the I_2 concentration measured in the upstream cell 12. Another process that could distort the overall rate of atomic iodine formation is the reaction

 $ClO_2 + 2HI \rightarrow I_2 + products$ (17)

The rate constant for reaction (17) was not found in the literature and was therefore estimated

experimentally. Chlorine dioxide (200-250 µmol s^{-1}) mixed with nitrogen was introduced into the reactor 1 as the primary gas, 90–340 μ mol HI s⁻¹ was admixed through the third injector. No atomic iodine was detected in the ISD cell 11, but molecular iodine was measured in both I₂ cells. A rate constant of $k_{17} \cong 3.8 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ was determined. It was found by modelling of the reaction system ClO_2 -NO-HI that reaction (17) does not increase the I2 concentration in the cell 12 if the HI flow rate is lower than the rate of chlorine atom formation, i.e., at $HI/ClO_2 \leq 1$, and simultaneously at $NO/ClO_2 > 1$. These conditions determine when the overall rate of atomic iodine formation may be evaluated from the I_2 flow rate measured in the cell 12.

4.3. Generation of atomic iodine in nitrogen environment

First, atomic iodine generation was studied at different flow rates of reactants. An example of the effect of HI flow rate is shown in Fig. 2. It can be seen that the overall production of atomic iodine (detected by VIS photometry) was rather high and increased with increasing HI flow rate. The atomic iodine yield, however, declined from nearly 100% to 80% with increasing HI flow rate. The production rate calculated from the ISD method was significantly lower. This was caused by a drop in the atomic iodine concentration in the flow direction downstream of the reactor. This was confirmed by the results of our modelling studies calculated for the same experimental conditions (see Fig. 3). The calculated curves demonstrate that the average flow rate of atomic iodine through the ISD cell is substantially lower than the overall rate of I formation, which is approximately equal to twice the value of the I₂ flow rate through the first I_2 cell. The flow rate of atomic iodine measured by the ISD increases with HI flow rate to some limit only (see Fig. 2). This can be explained by the higher rate of I atom formation and recombination at the higher HI flow rates. This results in a greater concentration gradient of atomic iodine downstream of the HI injection point, and a smaller fraction of the I flow rate being detected in the ISD cell compared to the overall production rate.



Fig. 2. Overall rate of atomic iodine production (\circ), and the rate estimated by the ISD (\bullet) and its dependence on HI flow rate; primary flow: 220 µmol ClO₂ s⁻¹ + 2 mmol N₂ s⁻¹, second injector: 375 µmol NO s⁻¹, third injector: HI; total pressure 2–2.9 kPa; distance between injectors: $d_{2-3} = 3.7$ mm, and between third injector and the ISD cell: $d_{3-ISD} = 11$ mm.



Fig. 3. Calculated temporal behaviour of I and I_2 flow rates downstream of the third injector; 220 µmol HI s⁻¹, gas velocity 85 m s⁻¹, and other conditions as in Fig. 2.

$n_{\rm NO}$ (first injector) (µmol s ⁻¹)	$n_{\rm NO}$ (second injector) (µmol s ⁻¹)	$n_{\rm HI}$ (third injector) (µmol s ⁻¹)	$n_{\rm I}^{\rm ISD}$ (µmol s ⁻¹)	$n_{\rm I}^{ m VIS}$ (µmol s ⁻¹)
320	0	100	0	18
200	200	100	8	46
0	420	100	20	75

Effect of the position of NO injection on atomic iodine production measured by ISD (n_1^{ISD}) , and VIS photometry (n_1^{VIS})

Primary flow: 220 μ mol ClO₂ s⁻¹ + 2 mmol N₂ s⁻¹, distance between injectors: $d_{1-2} = 30$ mm, $d_{2-3} = 3.7$ mm, and third injector–ISD cell: $d_{3-ISD} = 20$ mm.

In the next experiments, the effect of the way in which NO was injected into the primary flow on atomic iodine production was studied. Nitrogen oxide was injected into the primary ClO_2 flow either through the first or the second injector, or both injectors simultaneously. The results are summarised in Table 1.

Table 1

The lowest production of atomic iodine was measured when NO was introduced through the first injector only. This is because a high fraction of chlorine atoms recombined before the HI was injected. This was confirmed by the calculated decrease in Cl atom concentration for the experimental conditions. Fig. 4 shows that the calculated yield of Cl atoms was only 5% at a distance of 33.7 mm between the NO and HI injectors. The mea-



Fig. 4. Time history of reactants and reaction products downstream of NO injector calculated for 220 μ mol ClO₂ s⁻¹+ 2 mmol N₂ s⁻¹ in primary flow, and 420 μ mol NO s⁻¹; gas velocity 140 m s⁻¹, and total pressure 2.3 kPa.

sured yield of I atom formation (see Table 1) was higher than the above value, which may be explained by a limited gas mixing rate that extends the concentration profiles.

The rate of I atom formation was much higher when the NO was injected into the primary flow sequentially through the first and second injectors. In this way, ClO radicals are formed mostly downstream of the first injector, and Cl atoms downstream of the second injector (Fig. 5). In this case, the overall process proceeds predominantly by the non-chain mechanism, i.e., without participation of the chain-branching reaction (8). It was



Fig. 5. Time history of reactants and reaction products and I atom production calculated for 220 µmol ClO₂ s⁻¹+ 2 mmol N₂ s⁻¹ in primary flow, 200 µmol NO s⁻¹ (first injector), 200 µmol NO s⁻¹ (second injector), 100 µmol HI s⁻¹ (third injector); total pressure 2.7 kPa; $d_{1-2} = 30$ mm, and $d_{2-3} = 3.7$ mm; gas velocity between first and third injector: 140 m s⁻¹, downstream of third injector: 85 m s⁻¹.

d_{1-2} (mm)	<i>d</i> _{2–3} (mm)	$d_{3-\text{cell 11}} (\text{mm})$	$n_{\rm I}^{\rm ISD}$ (µmol s ⁻¹)	$n_{\rm I}^{\rm VIS} ~(\mu { m mol}~{ m s}^{-1})$
9	23	20	0.5	15
19	13	20	3	35
37	3.7	20	6	54
37	3.7	10	10	55

Table 2 Effect of distance between injectors on atomic iodine flow rate, measured by ISD (n_1^{ISD}) , and VIS photometry (n_1^{VIS})

Primary flow: 240 μ mol ClO₂ s⁻¹, first injector: 220 μ mol NO s⁻¹, second injector: 220 μ mol NO s⁻¹, third injector: 100 μ mol HI s⁻¹, total N₂ 7.2 mmol s⁻¹.

further found experimentally that the rate of I production was not influenced by the distance between the NO injectors (within 8–21 mm). This can be explained by the relatively high stability of CIO radicals downstream of the first NO injector (see Fig. 5).

The highest yield of atomic iodine (see Table 1) was attained when all the NO was introduced through the second injector and HI was injected downstream (3.7 mm). This distance, between the injectors, is close to the optimum corresponding to the calculated maximum concentration of Cl atoms (see Fig. 4).

In other experiments, the NO flow was split between two injectors. The effect of the variable distance between the two injectors is presented in Table 2. These data show the positive effect of a shorter distance between the second NO injector and the HI injector on I atom production in spite of a simultaneously longer distance between the first and second NO injector. This is due to a lower recombination loss rate of Cl atoms upstream of the HI injector. A higher concentration of I atoms in the ISD cell was measured with a shorter distance between the HI injector and the cell, even though the overall rate of I atom formation remained unchanged. This was caused by a lower loss of iodine atoms by recombination reactions upstream of the ISD cell.

The generation of iodine atoms is substantially affected by the initial ratio of the reactants. In the experiments, where all of the NO was introduced through the second injector, the overall yield of atomic iodine was nearly 100% (related to HI) at NO:ClO₂ \cong 1 or 1.5 (see Fig. 6). A substantially lower yield (70% and 45%, respectively) was obtained with NO:ClO₂ ratios equal to 2 and 2.5. This effect can be explained by a different mecha-



Fig. 6. Dependence of the overall flow rate of atomic iodine (measured in cell 12) on HI flow rate at 220 μ mol ClO₂ s⁻¹, and various NO flow rate: 205 μ mol s⁻¹ (\bigstar), 330 μ mol s⁻¹ (\circ), 440 μ mol s⁻¹ (\bullet), 560 μ mol s⁻¹ (\triangle); for other conditions see Fig. 2.

nism of Cl atom formation for the different experimental conditions. At NO:ClO₂ \geq 2, chlorine atoms are formed very rapidly by the chainbranching mechanism (6)–(8), and their fast recombination occurs before HI admixing. This takes place in the regions with an excess of ClO₂ and NO, and insufficient HI concentration. In the case of the smaller ratio NO:ClO₂ \cong 1, more stable ClO radicals are formed being in equilibrium with Cl atoms and ClOO radicals according to

$$ClO + ClO \leftrightarrow Cl + ClOO$$
 (18)

The equilibrium is strongly shifted to the left $(k_{17} = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [13], $k_{-17} =$

 1.0×10^{-11} cm³ molecule⁻¹ s⁻¹) [6]. In the presence of HI, chlorine atoms are rapidly consumed in the reaction (12), and further Cl atoms and ClOO radicals are formed in the reaction (18). The excessive ClOO radicals then provide Cl atoms in the reaction [6]

$$ClOO + N_2 \rightarrow Cl + O_2 + N_2$$

$$k_{18} = 1.34 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
(19)

Our previous modelling results have shown [7] that the formation of atomic chlorine by the chain mechanism (6)–(8) prevails at NO/ClO₂ \cong 2 and proceeds much faster than the non-chain process (Eqs. (6), (18), and (19)) which occurs predominantly at NO/ClO₂ \cong 1. In a real system with a limited rate of Cl and HI mixing, the recombination loss of Cl atoms is higher in the first case, which is characterised by a high local rate of Cl atom production.

In some experiments, the order of NO and HI injection into the primary ClO₂ flow was reversed. A more uniform HI concentration in the region of NO admixing was expected and consequently, regions with fast generation of Cl atoms and insufficient HI concentration might be minimised. This could reduce the recombination loss of Cl atoms. On the other hand, some ClO₂ and HI might be consumed by the direct formation of molecular iodine (Eq. (17)). When HI (10–220 μ mol s⁻¹) was injected into the primary flow with ClO₂ (240 μ mol s⁻¹) before NO, and NO (280 μ mol s⁻¹) was admixed 20 mm downstream, the rate of atomic iodine formation estimated by both detection techniques was about the same as in the case when NO was admixed 3.7 mm upstream the HI injector. Also in the configuration with two NO

injectors, no significant difference in the iodine atom production between the "reverse order" $(NO_I-HI-NO_{II})$ and the "normal order" $(NO_I-NO_{II}-HI)$ of injectors was found, if a short distance (3.7 mm) between the NO_{II} and HI injectors was maintained. Both arrangements are suitable for the effective generation of iodine atoms owing to a low loss of chlorine atoms.

In all experiments the gas temperature measured in the diagnostic cell was higher than the inlet temperature (20 °C) due to exothermic reactions. A steep temperature rise was observed after ClO_2 was mixed with NO. The temperature change was smaller at the HI admixing. The gas temperature in the diagnostic cell was between 80 and 120 °C.

A few preliminary experiments were performed with chemically generated atomic iodine in the presence of a singlet oxygen flow. Gas exiting the singlet oxygen generator (not diluted with any buffer gas) was introduced into the iodine reactor as the primary flow. In the first experiments, ClO_2 diluted with nitrogen was introduced through the first injector, NO through the second injector, and HI through the third injector. Nitrogen was introduced into the reactor only in mixtures with ClO₂, NO, and HI, respectively. In the experiment with a short distance (10 mm) between the HI injector and the ISD cell, the formation rate of atomic iodine detected by both experimental methods was nearly the same regardless of the $O_2(^{1}\Delta_g)$ presence (see Table 3). It appears that the $O_2(^{1}\Delta_g)$ did not change the reaction kinetics. At a longer distance (33 mm) between the HI injector and the ISD cell, a substantial fraction of the iodine atoms in the nitrogen flow recombined upstream of the ISD cell. This was gleaned from the fact that the ISD signal was 4.4 times lower

Table 3										
Generation	of atomic	iodine	either i	n nit	rogen	or	a mixture	with	singlet	oxygen

d _{3–ISD} (mm)	$n_{N_2}^{tot}$ (mmol s ⁻¹)	$\binom{n_{\mathrm{O}_2(\Delta)}}{(\mathrm{mmol}\ \mathrm{s}^{-1})}$	$n_{O_2(\Sigma)}$ (mmol s ⁻¹)	n _{NO} (μmol s ⁻¹)	N _{HI} (μmol s ⁻¹)	n _I ^{ISD} (μmol s ⁻¹)	$n_{ m I}^{ m VIS}$ (µmol s ⁻¹)
10	4.2	_	_	166	145	22	70
10	4.1	0.39	1.9	166	135	20	70
33	4.6	_	_	159	155	5	70
33	4.5	0.39	1.9	159	145	24	70

Primary flow: no or $O_2({}^1\Delta_g) + O_2({}^3\Sigma_g^-)$, first injector: 130 µmol ClO₂ s⁻¹ + 1.25 mmol N₂ s⁻¹, second injector: NO + N₂, third injector: HI + N₂, $d_{2-3} = 3.7$ mm.

than in the previous case. In the presence of singlet oxygen, this signal increased 4.8 times due to I_2 dissociation by $O_2(^1\Delta_g)$. The overall flow rate of iodine was the same in all cases. The observed production of atomic iodine in the ground state even in the presence of $O_2({}^1\Delta_g)$ was explained by a low $[O_2(^1\Delta_g)]/[\text{total }O_2]$ ratio in the reactor (about 15-20%) which was near the threshold value necessary for population inversion in atomic iodine. This low ratio was caused by a high $O_2(^1\Delta_g)$ quenching loss upstream of the iodine reactor due to a high pressure (3-4.5 kPa) and the absence of gas dilution. The reason for this high pressure was the small cross-section of the reactor (0.59 cm^2) , and the high flow rates of secondary gases.

A substantial reduction in $O_2(^1\Delta_g)$ loss was achieved by introducing the ClO₂ and N₂ mixture into the $O_2(^1\Delta_g)$ flow close to the generator exit, instead of into the reactor through the first injector. The volume between the $O_2(^1\Delta_g)$ generator and the iodine reactor was reduced, and the flow rates of the other reactants were reduced to minimise the pressure loss inside the iodine reactor. These modifications helped to increase the $O_2(^1\Delta_g)$ yield to 40-45% at the iodine reactor entrance. Under these conditions, gain on the 3-4 hyperfine transition in the iodine atom was observed (see curve 1 in Fig. 7). The curve 2 in Fig. 7 represents the absorption curve recorded with similar flow rates of reactants but with no $O_2({}^1\Delta_g)$ in the primary flow.

In the experiments with atomic iodine in nitrogen the gas temperature in the ISD cell was 81 ± 13 °C. The temperature was calculated from the Gaussian full width after the deconvolution of the Voigt profile of the absorption-frequency curves [11]. The temperature measured by a thermocouple in the I_2 cell 12 was 58 °C. In a flow of $O_2(^{1}\Delta_g)$, the temperature in the ISD cell was 117 ± 22 °C, and the temperature measured by the thermocouple in the I₂ cell was 180 °C. The temperature increase in the flow direction observed in this case may be ascribed primarily to the exothermic quenching of I* atoms by water molecules. Further processes that can lead to higher temperatures in the $O_2({}^1\Delta_g)$ experiments are the $O_2({}^1\Delta_g)$ self-quenching and pooling reactions.



Fig. 7. Absorption/emission (gain) curve for atomic iodine recorded for primary flow of either 30 µmol ClO₂ s⁻¹ + 2.5 mmol N₂ s⁻¹ (curve 2), or 30 µmol ClO₂ s⁻¹ + 2.5 mmol N₂ s⁻¹ + 0.9 mmol O₂(¹ Δ_g) s⁻¹ + 1.4 mmol O₂(³ Σ_g) s⁻¹ (curve 1); 225 µmol NO s⁻¹ (second injector), 30 µmol HI s⁻¹ (third injector); $d_{2-3} = 3.7$ mm, $d_{3-ISD} = 11$ mm; total pressure 1.8 kPa.

5. Conclusions

A new method for the chemical generation of atomic iodine in COIL devices was studied experimentally. It is based on the chemical production of chlorine atoms and their subsequent reaction with gaseous hydrogen iodide. Effects of the initial ratio of reactants and the way in which mixing in a flow of nitrogen occurs were studied and interpreted by means of a kinetic model for the reaction system. Concentrations of atomic iodine were determined by two independent techniques: the iodine scan diagnostics, and the absorption photometry for molecular iodine (formed by recombination of iodine atoms). The yield of atomic iodine generated in the nitrogen environment was rather high (70-100%), with optimum conditions. In preliminary experiments performed in the presence of singlet oxygen, gain on the 3-4 transition in iodine atom was measured. A detailed investigation of this system is under way. Finally, the chemical generation of atomic iodine is planned directly for implementation on a supersonic COIL.

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