

# Kinetic Study of the Reaction between Fe and O<sub>3</sub> under Mesospheric Conditions

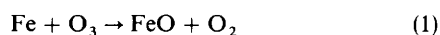
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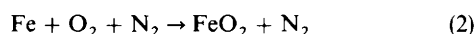
Detailed observations of the layer of atomic iron in the mesosphere have been made in the last four years. However, there is almost no information about the gas-phase chemistry of neutral iron which is necessary to understand the characteristic features of the layer. In this paper, a study of the reaction  $\text{Fe} + \text{O}_3 \rightarrow \text{FeO} + \text{O}_2$  is reported. The reaction was investigated by the pulsed photodissociation at 193.3 nm of ferrocene vapour to produce Fe atoms in an excess of O<sub>3</sub> and N<sub>2</sub> bath gas, followed either by time-resolved laser-induced fluorescence spectroscopy of atomic Fe at 248.3 nm [ $\text{Fe}(x^5\text{F}_5^0\text{--}a^5\text{D}_4)$ ], or by time-resolved chemiluminescence from the 'orange bands' of FeO at  $\lambda = 590 \pm 5$  nm [ $\text{FeO}(^5\Delta_7\text{--}X^5\Delta_1)$ ]. The rate coefficient is given in the Arrhenius form by  $k(189 < T/\text{K} < 359) = (3.44 \pm 0.76) \times 10^{-10} \exp[-(1210 \pm 420)\text{J mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted uncertainties are  $2\sigma$ . This result is compared with the predictions of long-range capture theory, and contrasted with the analogous reactions of other metal atoms with O<sub>3</sub>. The title reaction is then demonstrated to be the most rapid oxidation process of atomic iron in the atmosphere between 65 and 100 km. Furthermore, it is shown that this reaction may make a significant contribution to the night-time production of O<sub>2</sub>(b<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) in the upper atmosphere below 90 km.

The layer of atomic Fe in the mesosphere was first observed in 1976 by photometric measurement of the twilight emission at 386.0 nm [ $\text{Fe}(z^5\text{D}_4^0\text{--}a^5\text{D}_4)$ ].<sup>1</sup> In the last four years, lidar (laser radar) systems operating on the atomic Fe transition at 372.0 nm [ $\text{Fe}(z^5\text{F}_5^0\text{--}a^5\text{D}_4)$ ] have revealed the characteristics of this layer in detail.<sup>2–4</sup> Compared with the much more studied Na layer, the column abundance of the iron layer is larger by a factor of *ca.* 2. This was unexpected because the major source of both metals is believed to be meteoric ablation,<sup>5</sup> and the relative abundance of Fe to Na in meteoritic minerals is *ca.* 8.<sup>6</sup> The peak height of the iron layer is also *ca.* 5 km lower at 85–88 km, the layer is *ca.* 25% narrower, and it has a smaller scale-height on the underside, of only about 1 km.

In order to understand these differences between Fe and Na in the upper atmosphere, an obvious starting point is to contrast the pertinent gas-phase chemistries of these metals. Laboratory studies over the past decade have revealed a substantial amount about the chemistry of sodium species, enabling models to be developed which are now in very good agreement with the observed features of the Na layer.<sup>5,7</sup> However, with the exception of an upper limit for the rate constant of the reaction between Fe and O<sub>2</sub> at 300 K,<sup>8</sup> there appear to have been no studies of the likely atmospheric reactions of iron species at low temperatures. Thus, we will report here an investigation of the reaction



followed by a study of the recombination reaction



in a later paper.<sup>9</sup> By analogy with the chemistry of Na,<sup>5</sup> reaction (1) is likely to be the most rapid reaction undergone by freshly ablated Fe atoms in the mesosphere.

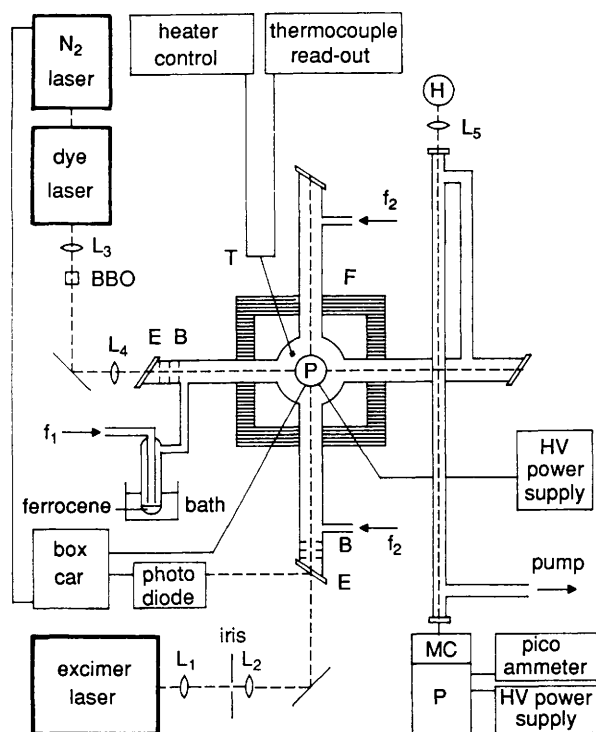
FeO(<sup>5</sup>Δ<sub>4</sub>) has a large bond energy of  $402 \pm 8 \text{ kJ mol}^{-1}$ .<sup>10</sup> Thus, reaction (1) is sufficiently exothermic [ $\Delta H_0^\circ(1) = -301 \pm 8 \text{ kJ mol}^{-1}$ ] to populate several excited electronic states of FeO. In fact, emission from the infrared, orange and blue systems of FeO has been observed in Fe–O<sub>3</sub> diffusion flames.<sup>11</sup> West and Broida<sup>11</sup> determined a photon yield for the orange bands (500–700 nm) of *ca.* 2% in a diffusion flame at 700 K, and at a total pressure of 1.2 Torr. These

workers<sup>11</sup> assigned a system of FeO(<sup>5</sup>Σ<sup>+</sup>/<sup>5</sup>Π–X<sup>5</sup>Σ<sup>+</sup>) transitions to account for the orange bands. However, subsequent work employing laser photoelectron spectrometry of FeO<sup>–</sup>,<sup>12</sup> and laser-induced fluorescence studies of the orange system combined with observation of the infrared emission from an FeO discharge<sup>13</sup> have demonstrated that the ground state of FeO is in fact a <sup>5</sup>Δ state. The nature of the excited electronic states associated with the orange bands is not as well established.<sup>14</sup> These states appear to comprise a severely perturbed <sup>5</sup>Δ state,<sup>15</sup> and an extensive number of additional states, probably arising from a <sup>5</sup>Σ<sup>+</sup> state.<sup>16</sup> West and Broida<sup>11</sup> also determined that the radiative lifetimes of the excited electronic state(s) giving rise to the orange system are  $450 \pm 100 \text{ ns}$ . Thus, time-resolved molecular chemiluminescence should be a suitable tool for studying the kinetics of reaction (1).

In the present paper we will report the determination of  $k_1(T)$  over a significant temperature range, including temperatures applicable to the upper atmosphere, so that the atmospheric importance of reaction (1) can be examined. This study will also provide a test of several theoretical formalisms for calculating the rate coefficients of fast reactions governed by long-range attractive forces between neutral species.

## Experimental

Reaction (1) was investigated by the pulsed photolysis of ferrocene [dicyclopentadienyl iron, Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] to produce atomic Fe in an excess of O<sub>3</sub> and N<sub>2</sub> bath gas. The reaction was then monitored either by time-resolved laser-induced fluorescence (LIF) spectroscopy of the atomic Fe, or by time-resolved chemiluminescence from the product FeO. Fig. 1 is a schematic diagram of the experimental system employed. The reaction was initiated and then monitored spectroscopically in the central cylindrical chamber of the stainless-steel reactor, which has been described in detail elsewhere.<sup>17</sup> Four horizontal side-arms attached to this chamber provided the optical coupling for the lasers into and out of the central chamber. These side-arms also carried the flows of ferrocene and O<sub>3</sub>, diluted in N<sub>2</sub>, into the chamber, and served as an exit for the gas flows to the vacuum pump. A fifth, vertical, side-arm provided the optical coupling to the photomultiplier tube which monitored the LIF or chemiluminescence signals.



**Fig. 1** Block diagram of the pulsed laser photolysis system with time-resolved monitoring of the reaction by laser-induced fluorescence. Components are identified as follows: B, baffle to exclude scattered laser light; BBO,  $\beta$ -barium borate frequency-doubling crystal; E, Suprasil end-window at the Brewster angle; F, furnace around the central chamber of the reactor; f<sub>1</sub>, flow of pure N<sub>2</sub> (5 sccm); f<sub>2</sub>, flow of O<sub>3</sub> and N<sub>2</sub> (195 sccm); H, low-pressure mercury lamp; L<sub>1</sub>, Suprasil lens, ( $f = 50$  cm); L<sub>2</sub>, Suprasil lens ( $f = 30$  cm); L<sub>3</sub> = Suprasil lens ( $f = 10$  cm); L<sub>4</sub>, Suprasil lens ( $f = 30$  cm); L<sub>5</sub>, Suprasil lens ( $f = 5$  cm); MC, monochromator; P, photomultiplier tube; T, thermocouple in the central chamber of the reactor.

Powdered ferrocene was placed in a glass trap which was usually immersed in an ice-bath. The vapour pressure of ferrocene at 273 K is  $1.6 \times 10^{13}$  molecules cm<sup>-3</sup>.<sup>18</sup> This vapour was entrained in a flow of N<sub>2</sub> and carried into the central chamber, where it mixed with the flow of O<sub>3</sub> in N<sub>2</sub>. It was therefore diluted to a concentration of ca.  $4.0 \times 10^{11}$  molecules cm<sup>-3</sup>, before being photolysed with an ArF excimer laser at 193.3 nm (Questek, Model 2110, pulse energy 5 mJ, pulse rate 4 Hz). The excimer beam was shaped by a system of lenses and a pin-hole, and then loosely focused through the chamber.

For the time-resolved LIF experiments, the resulting Fe atoms were probed at 248.3 nm [ $\text{Fe}(x^5\text{F}_5^0 - a^5\text{D}_4)$ ] using a nitrogen-pumped dye laser (Laser Photonics, Models LN1000/LN107, laser dye Coumarin 500, pulse energy = 240  $\mu\text{J}$ ; bandwidth = 0.03 nm), frequency-doubled with a BBO crystal (Inrad Corp.) to give a pulse energy at 248.3 nm of ca. 10  $\mu\text{J}$ . The diameter of the dye laser was set to be ca. 80% of that of the excimer, and the two lasers crossed orthogonally in the centre of the chamber. The time-resolved LIF signal was measured by a photomultiplier tube (Thorn EMI Gencom Inc., Model 9816QB) after passing through an interference filter centred at 250 nm (Microcoatings, Model ML3-250, f.w.h.m. = 10 nm), and was then recorded using a gated integrator (Stanford Research Systems, Model SR250) interfaced to a microcomputer.

For the time-resolved chemiluminescence experiments, the dye laser was switched off and the gated integrator replaced by a fast photon-counting system comprising an emitter-follower (Thorn EMI, Model Aped-II) and a multi-channel

scaler (EG&G Ortec, Model ACE-MCS) interfaced to a microcomputer. The chemiluminescence signal from the orange bands [ $\text{FeO}(^5\Delta_1 - X^5\Delta_1)$ ] was then measured by time-resolved photon counting after passing through an interference filter at  $\lambda = 590 \pm 5$  nm (Oriol Corp.).

Reaction (1) was studied at low total pressures (5–18 Torr) in order to minimise the turnover time of the gas mixture in the central chamber (0.5–1.6 s), thus preventing excessive loss of ferrocene vapour and O<sub>3</sub> on the chamber walls. The O<sub>3</sub> concentration was monitored down-stream of the reactor by optical absorption of the 253.7 nm line from a low-pressure mercury lamp. This was measured in a 1 m long absorption cell with a 0.9 nm resolution monochromator (Optometrics Corp., Model MC1-02) coupled to a photomultiplier tube. The ozone absorption cross-section at 298 K was taken to be  $1.143 \times 10^{-17}$  cm<sup>2</sup> from an average of several recent determinations.<sup>19</sup> Although ferrocene absorbs relatively strongly at 254 nm,<sup>20</sup> the gas-phase concentrations of ferrocene employed were too small to compete with the absorption due to O<sub>3</sub>. Iron pentacarbonyl, Fe(CO)<sub>5</sub>, was employed initially as a photolytic precursor of atomic Fe. However, the higher concentrations of this precursor that were required to produce a satisfactory yield of Fe atoms interfered with the O<sub>3</sub> absorption measurements. When high levels of either Fe(CO)<sub>5</sub> or ferrocene were added to the reactor, there was evidence from the absorption measurements that a reaction occurred with O<sub>3</sub>, although this appeared to be limited by the short turnover times of the gas mixture in the reactor and was much less rapid in the case of ferrocene. The rapid reaction between Fe(CO)<sub>5</sub> and some gas-phase oxidants has been noted previously.<sup>8</sup>

## Materials

N<sub>2</sub>, 99.9999% purity (Air Products) was used without further purification. O<sub>3</sub> was made by passing O<sub>2</sub>, 99.999% pure (Air Products), through a commercial ozoniser (Clearwater Tech, model M-1500). The resulting 5–8% O<sub>3</sub>–O<sub>2</sub> mixture was collected on silica gel at 156 K, and the O<sub>2</sub> then pumped off at 195 K until a >50% O<sub>3</sub>–O<sub>2</sub> mixture was degassed from the gel. Ferrocene (Aldrich, 98%) was purified by pumping on the sample in the glass trap at 77 K for several hours prior to kinetic experiments.

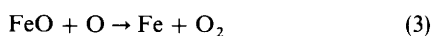
## Results

The dissociation energy of ferrocene to produce atomic Fe( $a^5\text{D}_4$ ) is 749.7 kJ mol<sup>-1</sup>,<sup>21</sup> so that the photolysis of ferrocene to yield atomic Fe requires at least two photons at 193.3 nm. In fact, the absorption of three or four photons at 193.3 nm has been shown to yield predominantly ions such as  $\text{Fe}(\text{C}_2\text{H}_5)^+$  and  $\text{Fe}^+$ .<sup>21</sup> We investigated the yield of Fe atoms, measured by LIF at 248.3 nm [ $\text{Fe}(x^5\text{F}_5^0 - a^5\text{D}_4)$ ], as a function of the photolysis laser pulse energy at 193.3 nm. The laser fluence was varied over the range  $(7\text{--}42) \times 10^{15}$  photons cm<sup>-2</sup> pulse<sup>-1</sup>, where the pulse width is ca. 7 ns. The atomic Fe yield was observed to be only slightly dependent on the laser fluence over this range. This probably indicates that the absorption of the first two photons is nearly saturated at these laser fluences. The relative atomic Fe yield may also be reduced by the increasing yield of ionic over neutral photolysis products.<sup>21</sup>

Since the two-photon photolysis of ferrocene to give atomic Fe leaves the products with 488 kJ mol<sup>-1</sup> of excess energy,<sup>21</sup> a significant fraction of the atomic Fe was probably produced in excited states, by analogy with the photolysis of Fe(CO)<sub>5</sub>.<sup>22,23</sup> However, the low-lying excited states of Fe, and even the higher spin-orbit multiplets of the ground-state

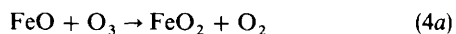
$\text{Fe}(a^5D_i)$ , are quenched rather rapidly by  $\text{N}_2$ .<sup>22,23</sup> For example, at the lowest bath-gas pressure employed in the present study (5 Torr), excited states such as  $\text{Fe}(a^5F_1)$ ,  $a^3F_1$  and  $a^5P_3$  have a lifetime, with respect to quenching by  $\text{N}_2$ , of less than  $1 \mu\text{s}$ .<sup>23</sup> Also, the ground-state multiplet  $\text{Fe}(a^5D_3)$  has a lifetime of  $7 \mu\text{s}$  with respect to collisional quenching to  $\text{Fe}(a^5D_4)$ ,<sup>22,23</sup> so that a Boltzmann equilibrium between the ground-state multiplets would have been established rapidly<sup>22</sup> on the timescale of the chemical reaction between Fe and  $\text{O}_3$  (see below). Thus, the reactions of the individual multiplets could not be observed independently in this system. The separation of the  $i = 3$  and 4 levels of  $\text{Fe}(a^5D_i)$  is only  $416 \text{ cm}^{-1}$ , whereas the  $i = 2, 1$  and 0 multiplets are 704, 888 and  $978 \text{ cm}^{-1}$  above the lowest  $i = 4$  level, respectively.<sup>24</sup> Hence, over the temperature range of 190 to 357 K at which  $k_1(T)$  was determined, the Boltzmann fraction of  $\text{Fe}(a^5D_i)$  in  $i = 3$  varied from 3.2 to 12.7%, with essentially the rest in  $i = 4$ .

The excimer laser energy was limited in order to keep the photolysis of  $\text{O}_3$  to less than 1%.<sup>19</sup> One reason for this is because the reaction



probably proceeds at close to the collision number. This can be seen by consideration of the reverse reaction, i.e.  $\text{Fe} + \text{O}_2$ , which has been studied at temperatures above 1000 K. Fontijn and Kurzius<sup>25</sup> obtained  $k_{-3}$  (1600 K) =  $(3.6 \pm 1.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , in very good accord with the Arrhenius expression  $k_{-3}$  ( $1000 < T/\text{K} < 2500$ ) =  $2.1 \times 10^{-10} \exp[-(84.6 \pm 10.2 \text{ kJ mol}^{-1})/RT]$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from Akhmadov *et al.*<sup>26</sup> It appears that this activation energy must be nearly equal to  $\Delta H_0^0(-3)$ , since this would imply that  $D_0(\text{Fe}-\text{O}) = 408 \pm 10 \text{ kJ mol}^{-1}$  which is very close to the current literature value<sup>10</sup> of  $402 \pm 8 \text{ kJ mol}^{-1}$  for the bond energy of FeO. If we assume that these energies are indeed equal, and take the molecular parameters for FeO from ref. 13, then detailed balancing of reaction (3) indicates that  $k_3$  (300 K) =  $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Thus, if the laser photolysis of  $\text{O}_3$  in the present experiments had been significant so that the resulting ratio of  $[\text{O}]:[\text{O}_3]$  was large enough, reaction (3) would probably have caused significant regeneration of atomic Fe and  $k_1$  would then have been underestimated.

Another source of error in studies of the reactions between metal atoms and  $\text{O}_3$  can arise from the recycling of the metal oxide by a reaction such as (4b):



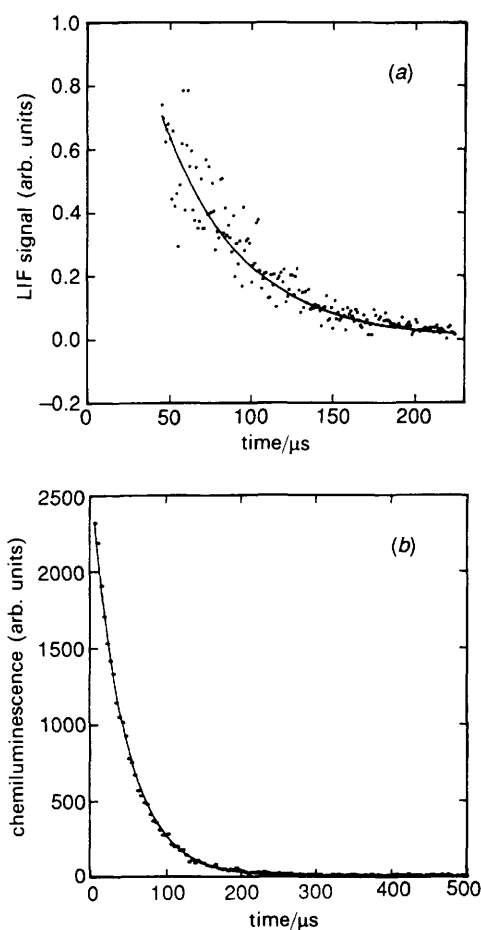
The analogous reaction of NaO does indeed give rise to a significant artifact when studying the reaction between Na and  $\text{O}_3$ .<sup>27-29</sup> However, in the case of FeO reaction (4b) appears to be endothermic,  $\Delta H_0^0(4b) = 11 \pm 8 \text{ kJ mol}^{-1}$ ,<sup>10</sup> and so this reaction should not be fast enough at the low temperatures of the present study to affect the measurement of  $k_1$ . It should be noted that if we take our recent *ab initio* estimate for  $D_0(\text{Fe}-\text{O}_2) \approx 180 \text{ kJ mol}^{-1}$ ,<sup>9</sup> then  $\Delta H_0^0(4a) \approx -170 \text{ kJ mol}^{-1}$  and so this channel of reaction (4) is probably the major removal process for FeO in these experiments.

Under the conditions of the present study, where the concentration of  $\text{O}_3$  was always well in excess of the concentration of Fe atoms resulting from the pulsed photolysis of ferrocene vapour, the loss of Fe atoms should be described by the pseudo-first-order decay coefficient,  $k'$ , where

$$k' = k_{\text{diff, Fe}} + k_1[\text{O}_3] + k_2[\text{O}_2][\text{N}_2] \quad (I)$$

The term  $k_{\text{diff, Fe}}$  describes diffusion of the Fe atoms out of the volume defined by the dye laser beam and within the field of view of the photomultiplier tube.<sup>17</sup> The third term accounts for the loss of Fe by reaction (2). In fact, the ratio of  $[\text{O}_3]:[\text{O}_2]$  in the central chamber varied from 1:1 at reactor temperatures below 320 K, down to 1:2.5 at the highest temperature of 357 K. We have recently shown<sup>9</sup> that  $k_2(T)$  is very slow at these low temperatures, so that this term contributed less than ca. 0.005% to  $k'$  over the range of bath-gas pressures employed in the present study, and could therefore be neglected. The observed decays of the LIF signal were of a simple exponential form and were well fitted to the expression  $A \exp(-k't)$ , as shown in Fig. 2(a).

In the experiments where chemiluminescence was monitored, the emission from excited  $\text{FeO}(^5\Delta_i)$  not only provides evidence of the reaction product, but can also be used as a time-resolved spectroscopic marker of the atomic Fe concentration. This is because the  $\text{O}_3$  concentration is in a large excess over the Fe, so that the intensity of the chemiluminescence is only proportional to the Fe atom concentration. In addition, the radiative lifetime of the orange bands of FeO is  $450 \pm 100 \text{ ns}$ ,<sup>11</sup> which is much faster than the chemical time-constants. A typical decay of the chemiluminescence signal,



**Fig. 2** (a) Time-resolved profile of the laser-induced fluorescence signal from atomic Fe at 248.3 nm [ $\text{Fe}(x^5F_0^o - a^5D_4)$ ], following the pulsed photolysis at 193.3 nm of ferrocene vapour in the presence of  $\text{O}_3$  and  $\text{N}_2$ ;  $[\text{O}_3] = 1.26 \times 10^{14} \text{ molecule cm}^{-3}$ ,  $[\text{N}_2] = 2.60 \times 10^{17} \text{ molecule cm}^{-3}$ ,  $T = 192 \text{ K}$ , excimer laser fluence at 193.3 nm is ca.  $1 \times 10^{16} \text{ photons cm}^{-2} \text{ pulse}^{-1}$ . The solid line is a fit to the form  $A \exp(-k't)$ . (b) Time-resolved profile of chemiluminescence from the orange bands of FeO at  $\lambda = 590 \pm 5 \text{ nm}$  [ $\text{FeO}(^5\Delta_i - X^5\Delta_i)$ ];  $[\text{O}_3] = 1.27 \times 10^{14} \text{ molecule cm}^{-3}$ ,  $[\text{N}_2] = 2.84 \times 10^{17} \text{ molecule cm}^{-3}$ ,  $T = 196 \text{ K}$ . The solid line is a fit to the form  $A \exp(-k't) + B$ .

including a fit to the form  $A \exp(-k') + B$ , is illustrated in Fig. 2(b). Note that both the decays in Fig. 2 were measured at the lowest temperatures of the present study, where the signal-to-noise tended to be somewhat reduced because of the significant loss of ferrocene vapour to the cold chamber walls.

It should be noted that if  $k_{4a}$  were small, and the degree of photolysis of  $O_3$  were large enough to make reaction (3) significant, then the Fe atom concentration would have reached a steady state after an initially rapid decay, and this steady-state concentration would have slowly decreased at longer times owing to diffusion out of the volume defined by the excimer laser. None of the time-resolved decays in the present study, such as those shown in Fig. 2, exhibited evidence of such a steady state, and this is further evidence that recycling of FeO to Fe was not significant.

Plots of  $k'$  versus  $[O_3]$  are illustrated in Fig. 3 for a selection of the temperatures at which reaction (1) was studied. Two sets of plots, one derived from time-resolved LIF and the other from time-resolved chemiluminescence measurements, are illustrated in Fig. 3(a) and (b). Both sets of plots exhibit a clear linear dependence of  $k'$  on  $[O_3]$ . The intercepts of these plots yield values of  $k_{diff, Fe}$  which are in sensible accord<sup>17</sup> with the diffusional loss of Fe atoms from the volume of the excimer laser beam. The slopes of these plots thus yield  $k_1$  as a function of temperature, and the results are listed in Table 1 with the pressure at which each measurement of  $k_1(T)$  was made. The upper temperature limit at which reaction (1) could be studied was constrained by the

**Table 1** Experimental determination of  $k_1(Fe + O_3 \rightarrow FeO + O_2)$  as a function of temperature

T/K	$k_1/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	technique <sup>a</sup>	pressure/Torr
190	$1.58 \pm 0.16$	L	14.9
192	$1.64 \pm 0.16$	L	5.2
196	$1.71 \pm 0.04$	C	5.8
218	$1.55 \pm 0.06$	C	12.7
238	$1.89 \pm 0.02$	C	9.5
262	$2.35 \pm 0.10$	L	11.5
263	$1.82 \pm 0.10$	C	5.5
271	$2.20 \pm 0.16$	C	10.5
326	$2.35 \pm 0.28$	L	17.2
293	$1.92 \pm 0.12$	L	16.1
293	$1.85 \pm 0.06$	C	16.5
293	$2.00 \pm 0.16$	C	10.5
320	$2.16 \pm 0.18$	C	7.0
327	$2.12 \pm 0.22$	L	13.8
328	$2.13 \pm 0.04$	C	13.8
357	$2.24 \pm 0.08$	C	12.5
358	$2.52 \pm 0.24$	L	12.3

Quoted uncertainty is  $2\sigma$ . <sup>a</sup> L = laser-induced fluorescence of atomic Fe at 248.3 nm [ $Fe(x^5F_5^0 - a^5D_4)$ ]; C = chemiluminescence from the orange bands of FeO at  $\lambda = 590 \pm 5 \text{ nm}$  [ $FeO(^5\Delta_1 - X^5\Delta_1)$ ].

decomposition of  $O_3$  in the central chamber becoming too rapid, compared with the residence time of the gas mixture in the reactor. The lower limit was set by the use of solid  $CO_2$  as a refrigerant.

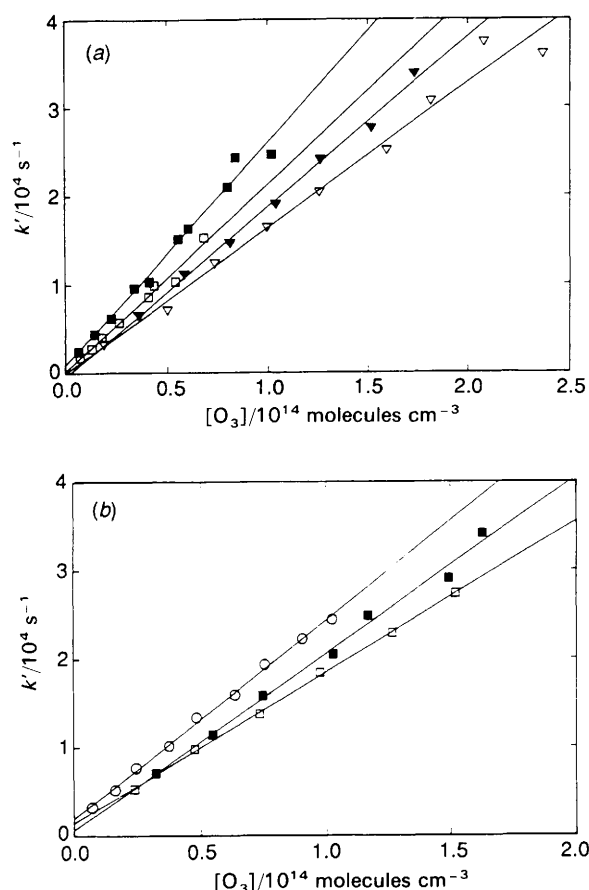
An Arrhenius plot for reaction (1) is shown in Fig. 4. A fit of the data to the Arrhenius form, by means of a linear regression, yields

$$k_1(189 < T/K < 359) = (3.44 \pm 0.76) \times 10^{-10} \times \exp[-(1210 \pm 420) \text{ J mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{II})$$

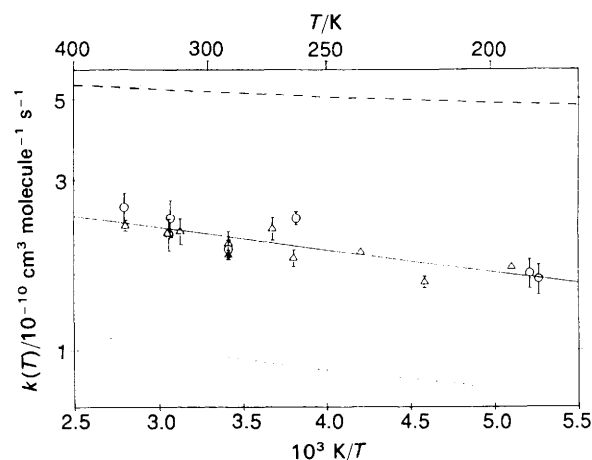
where the uncertainties are at the  $2\sigma$  level. The small temperature dependence of  $k_1$  may be emphasised by employing the common alternative expression

$$k_1(189 < T/K < 359) = (2.11 \pm 0.43) \times 10^{-10} (T/298 \text{ K})^{0.56 \pm 0.20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{II})$$

We consider that systematic errors, particularly those associated with determining the concentration of  $O_3$ , are contained



**Fig. 3** Selected plots of  $k'$  against  $[O_3]$  over the experimental temperature range for the reaction  $Fe + O_3 \rightarrow FeO + O_2$ : (a) time-resolved LIF measurements of atomic Fe at 248.3 nm [ $Fe(x^5F_5^0 - a^5D_4)$ ];  $\nabla$ , 192,  $\blacktriangledown$ , 293,  $\square$ , 327 and  $\blacksquare$ , 358 K. (b) Time-resolved molecular chemiluminescence measurements of the orange bands of FeO at  $\lambda = 590 \pm 5 \text{ nm}$  [ $FeO(^5\Delta_1 - X^5\Delta_1)$ ];  $\square$ , 196,  $\blacksquare$ , 293 and  $\circ$ , 357 K.



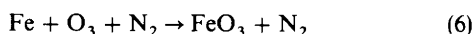
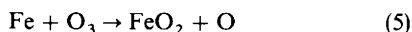
**Fig. 4** Arrhenius plots for the reaction  $Fe + O_3 \rightarrow FeO + O_2$ , comparing the results from the present experimental study with (---) the predictions of the harpoon mechanism (ref. 33) and (---) the modified harpoon mechanism (ref. 37). The solid line through the experimental points is a linear regression fit.  $\Delta$ , Chemiluminescence,  $FeO(^5\Delta_1 - X^5\Delta_1)$ ;  $\circ$ , LIF,  $Fe(x^5F_5^0 - a^5D_4)$ .



within the quoted limits. It is clear from inspection of Fig. 4 (or Table 1) that the values of  $k_1(T)$  obtained by time-resolved LIF and time-resolved chemiluminescence are in excellent agreement with each other.

### Discussion

Reaction (1) has thus been studied both by monitoring the disappearance of Fe atoms, and by observing chemiluminescence from the product FeO. Although the chemiluminescence from  $\text{FeO}(^5\Delta_1\text{-X}^5\Delta_1)$  confirms that FeO is formed by reaction (1), the diffusion flame study of West and Broida<sup>11</sup> found that production of excited FeO (in emitting states) only accounted for *ca.* 2% of the consumption of Fe. The remaining products could have been dark excited states of FeO, or ground-state  $\text{FeO}(\text{X}^5\Delta_1)$ . In addition, there are two other possible reaction channels:



We have recently estimated that the  $\text{FeO}_2(^7\text{A}_1)$  ground state has a bond energy  $D_0(\text{Fe}-\text{O}_2)$  of *ca.* 180 kJ mol<sup>-1</sup>.<sup>9</sup> Thus, reaction (5) is exothermic by only *ca.* 80 kJ mol<sup>-1</sup>, considerably less than  $\Delta H_f^\circ(1) = -301 \pm 8$  kJ mol<sup>-1</sup> for production of  $\text{FeO}(\text{X}^5\Delta_1)$ .<sup>10</sup> Furthermore, it is known that the products of the reactions  $\text{Na} + \text{O}_3$ <sup>28,29</sup> and  $\text{Ca} + \text{O}_3$ <sup>30,31</sup> are the metal monoxides, rather than the superoxides. Hence, we assume that reaction (5) is a minor removal process for atomic Fe compared with reaction (1). Reaction (6) would require a recombination rate coefficient greater than 10<sup>-27</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, and would also have to be at the high-pressure limit, in order to contribute significantly to the removal of atomic Fe in this study. These conditions seem highly unlikely to be the case. In any event, inspection of Table 1 reveals no evidence of a pressure dependence in  $k_1(T)$ .

Eqn. (III) demonstrates that reaction (1) proceeds essentially at the collision number, with a very small *T* dependence. In Fig. 5, the Arrhenius plots of reaction (1) and the analogous reactions of Na and Ca are compared. The three reactions have very similar *T* dependences and the rate coefficients decrease in the order Na > Ca > Fe. This is in the reverse order of the ionization energies of these metal atoms, in accord with the original proposal by Kolb and Elgin<sup>32</sup> that the reaction  $\text{Na} + \text{O}_3$  proceeds *via* the harpoon or electron-jump mechanism. The rate coefficient for the simple

harpoon mechanism is given by<sup>33</sup>

$$k(T) = \pi R_c^2 (8k_B T / \pi \mu)^{1/2} \quad (IV)$$

where  $\mu$  is the reduced mass of the reactants,  $k_B$  is the Boltzmann constant, and  $R_c$  is the charge-transfer distance determined from the simple relationship<sup>33</sup>

$$R_c = e^2 / [4\pi\epsilon_0(E_i - E_{ea})] \quad (V)$$

where  $e$  is the electronic charge,  $E_i$  is the ionisation energy of atomic Fe, and  $E_{ea}$  is the electron affinity of  $\text{O}_3$ . If we adopt the adiabatic electron affinity of  $\text{O}_3$  (since this has been accurately measured<sup>34</sup>) and the ionisation energy of Fe<sup>34,35</sup> that are both listed in Table 2, then  $R_c = 2.49$  Å. This value of  $R_c$  is probably an upper limit since the (smaller) vertical electron affinity should really be applied in this calculation. This is because the charge transfer occurs on a much shorter time-scale than the nuclear motions of the approaching reactants.<sup>36</sup>

It should also be noted, however, that atomic Fe has a moderately large polarizability (Table 2) and so there is a significant attractive dispersion force between Fe and  $\text{O}_3$  at longer range than  $R_c$ . In this case, the maximum impact parameter may be largely determined by the orbiting criterion on the effective potential surface,<sup>33</sup> and the modified harpoon mechanism of Gislason<sup>37</sup> is then more appropriate. The long-range interaction is governed by the  $C_6/R^6$  potential,<sup>38</sup> where

$$C_6 = C_6^{\text{disp}} + C_6^{\text{ind}} \quad (VI)$$

The London formula may be conveniently used to estimate the dispersion coefficient,<sup>38</sup>

$$C_6^{\text{disp}} = (3/2)\alpha_1\alpha_2(E_{i,1}E_{i,2}/E_{i,1} + E_{i,2}) \quad (VII)$$

where  $\alpha$  and  $E_i$  are the polarizability and ionisation energy of each collision partner. Using the data listed in Table 2 yields  $C_6^{\text{disp}} = 3.1 \times 10^{-17}$  J Å<sup>6</sup> molecule<sup>-1</sup>. The dipole-induced dipole coefficient,<sup>37</sup>

$$C_6^{\text{ind}} = (\mu_1)^2\alpha_2/(4\pi\epsilon_0)^2 \quad (VIII)$$

is only  $2.4 \times 10^{-19}$  J Å<sup>6</sup> molecule<sup>-1</sup> because of the small dipole moment,  $\mu_1$ , of  $\text{O}_3$ , and thus hardly contributes to the overall  $C_6$  coefficient. In the modified harpoon mechanism,<sup>37</sup> if  $2C_6/R_c^2 > k_B T$  [which is the case for reaction (1)], then the rate coefficient is essentially given by the orbiting criterion:<sup>33</sup>

$$k(T) = \pi(2C_6/k_B T)^{1/3}(8k_B T/\pi\mu)^{1/2}\Gamma(2/3) \quad (IX)$$

Eqn. (IX) should actually determine the upper limit to the rate coefficient, since it assumes that every collision that surmounts the centrifugal barrier on the effective potential will then orbit until an electron transfer occurs at closer range, thereby ensuring a successful reaction.

The rate coefficients predicted by eqn. (IV) and (IX) for reaction (1) are compared with the experimental results in Fig. 4. This shows that the modified harpoon mechanism [eqn. (IX)] does indeed provide an upper limit to the rate constant, overpredicting  $k_1(T)$  by about a factor of 2. Although the  $T^{1/2}$  dependence of the simple harpoon model

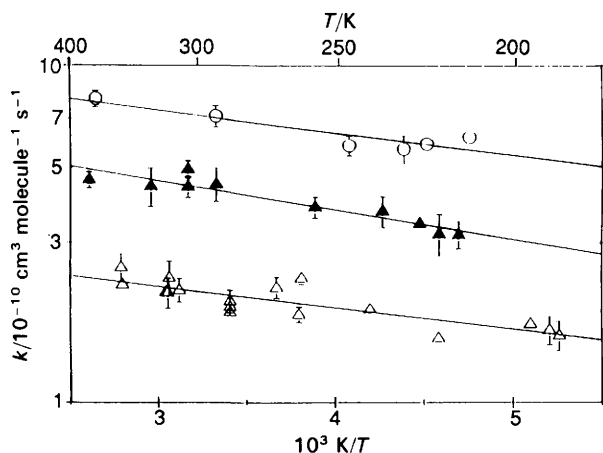


Fig. 5 Arrhenius plots  $\Delta$ , for the reaction  $\text{Fe} + \text{O}_3 \rightarrow \text{FeO} + \text{O}_3$  from the present study, and the analogous reactions of  $\bigcirc$ , Na (ref. 27) and  $\blacktriangle$ , Ca (ref. 30). The solid lines illustrate linear regression fits through each data set.

Table 2 Molecular parameters for the harpoon model calculations

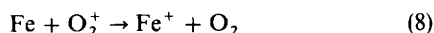
parameter	Fe	$\text{O}_3$
$\mu/\text{D}^a$	—	0.53 <sup>b</sup>
$\alpha/10^{-24} \text{ cm}^3$	8.4 <sup>b</sup>	3.2 <sup>b</sup>
$E_i/\text{eV}$	7.87 <sup>c</sup>	12.4 <sup>c</sup>
$E_{ea}/\text{eV}$	—	2.10 <sup>c</sup>

<sup>a</sup> 1 D (Debye)  $\approx 3.33564 \times 10^{-30}$  C m. <sup>b</sup> Ref. 35. <sup>c</sup> Ref. 34.

[eqn. (IV)] is in good agreement with the experimental result of  $T^{(0.56 \pm 0.20)}$  [eqn. (III)], this model underpredicts the experimental rate coefficient by about a factor of 2. The likely reason for this is that  $R_c$  is underestimated. The calculation of  $R_c$  from eqn. (V) assumes that the charge transfer occurs at a sufficiently large distance that the reactants and resulting ions can be approximated by point charges. However, the ionization energy of atomic Fe is relatively large, so that the electron jump at  $R_c = 2.49$  Å is really a close-range charge transfer to form the  $\text{Fe}^+ \cdots \text{O}_3^-$  ion-pair.<sup>27</sup> The  $\text{O}_3^-$  then presumably undergoes field-induced dissociation to  $\text{O}^-$  and  $\text{O}_2$  in the very strong electric field of the  $\text{Fe}^+$  ion.<sup>39</sup> The physical size of the  $\text{O}_3$ , in particular, and the close-range orbital interactions between the reactants, indicate that the use of eqn. (V) to estimate the cross-section is unrealistic. In fact, we have shown previously<sup>27</sup> that the electron transferred from the metal atom to the  $\text{O}_3$  most probably goes into a  $b_1$  orbital where most of the electron density is on the terminal oxygen atoms. This implies that during a collision the interaction between the Fe atom and either of the terminal oxygens should allow the charge transfer to take place, thus enhancing the total reaction cross-section.

### Atmospheric Implications

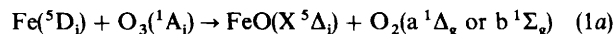
The importance of reaction (1) in the upper atmosphere can most easily be explored by comparing the first-order rates of loss of atomic Fe by this reaction and three other pathways. These are recombination with  $\text{O}_2$  [reaction (2)], and charge exchange with the most abundant positive ions in the mesosphere,<sup>1,40</sup>



The rates of reactions (1), (2), (7) and (8) are plotted in Fig. 6 as a function of altitude between 65 and 110 km, for night-time conditions. In the daytime, the rates of reactions (7) and (8) will increase by about a factor of 10 because of the enhancement in the concentrations of  $\text{NO}^+$  and  $\text{O}_2^+$  due to photo-ionization.<sup>5,40</sup> Indeed, atomic Fe itself will be photo-ionised in the mesosphere with a coefficient estimated by Swider<sup>41</sup> to be *ca.*  $5 \times 10^{-7} \text{ s}^{-1}$ . Inspection of Fig. 6 indi-

cates that this is not a competitive process. Reaction (1) is clearly the most rapid process for removal of atomic Fe between 65 and 105 km, *i.e.* in the mesosphere and lower thermosphere. However, Fig. 6 also shows that reaction (1) is most competitive compared to these other processes at *ca.* 87 km, which is where the peak of the Fe layer tends to occur.<sup>2-4</sup> We have demonstrated above that reaction (3) probably proceeds at close to the collision number, and this reaction recycles FeO back to Fe. Thus, to a first approximation the appearance of atomic Fe in the upper atmosphere should be controlled by the ratio of O to  $\text{O}_3$ . Indeed, at the peak of the Fe layer the ratio  $[\text{O}] : [\text{O}_3]$  is more than  $500 : 1$ ,<sup>43</sup> and the rate of reaction (1) is more than  $10^5$  times faster than the other removal processes in Fig. 6. However, even though the  $[\text{O}] : [\text{O}_3]$  ratio is even larger at higher altitudes, the formation of  $\text{Fe}^+$  by reactions (7) and (8) becomes much more competitive as a removal process for atomic Fe compared with reaction (1). Indeed, between 87 and 100 km the relative rates of these respective processes change from *ca.*  $2 \times 10^{-5}$  to  $10^{-2}$ , and so formation of  $\text{Fe}^+$  most probably controls the topside of the layer. The underside of the Fe layer often exhibits a sharp gradient (or small negative scale-height) just below 80 km,<sup>3,4</sup> which is where the atomic O concentration also decreases markedly so that at 75 km the ratio  $[\text{O}] : [\text{O}_3]$  is less than  $10^{-2} : 1$ .<sup>32</sup> Thus, more than 99% of atomic Fe will be converted to FeO below 80 km. Of course, the atmospheric chemistry of iron is almost certainly more complex. For instance, by analogy with our recent model of the mesospheric sodium layer,<sup>7</sup> it is likely that FeO then recombines with trace atmospheric species such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$  to form the more stable iron-containing molecules  $\text{Fe}(\text{OH})_2$  and  $\text{FeCO}_3$ .

Finally, we consider the possible role of reaction (1) as a source of excited  $\text{O}_2$  in the upper atmosphere at night. If FeO is formed in the ground state ( $X^5\Delta_i$ ), or in one of its low-lying quintuplet states,<sup>44</sup> and the spin multiplicity of reaction (1) is preserved, then excited singlet  $\text{O}_2$  will be produced:



There are two ways in which the formation of singlet  $\text{O}_2$  could be avoided. The first would be the production of a state of FeO of different spin multiplicity, since this might allow formation of  $\text{O}_2(X^3\Sigma_g^-)$  as an adiabatic product. However, although there is some theoretical<sup>44</sup> and experimental<sup>45</sup> evidence for a low-lying  $^7\Sigma^+$  state of FeO, there does not appear to be evidence that  $\text{FeO}(^7\Sigma^+)$  is formed in reaction (1), and so we assume in the following discussion that it is a minor product. Secondly, the reaction could be significantly non-adiabatic. However, although reactions between metal atoms and oxidants such as  $\text{N}_2\text{O}$  sometimes involve non-adiabatic transitions with respect to spin, these transitions tend to have a low probability and do not form the major reaction channels.<sup>46</sup> We assume that this is also the case here.

The peak atmospheric concentration of atomic Fe, at a height of *ca.* 87 km, is typically  $1.5 \times 10^4 \text{ atom cm}^{-3}$ .<sup>3,4</sup> Taking  $k_1(200 \text{ K}) = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from eqn. (III), and  $[\text{O}_3] = 5 \times 10^8 \text{ cm}^{-3}$ ,<sup>43</sup> then the upper limit to the production of singlet  $\text{O}_2$  is *ca.*  $2 \times 10^3 \text{ molecule cm}^{-3} \text{ s}^{-1}$ . Emission from  $\text{O}_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$  gives rise to the infrared atmospheric bands at *ca.* 1270 nm.<sup>40,47,48</sup> At 87 km, the volume emission from these bands at night-time is typically  $4 \times 10^4 \text{ photons cm}^{-3} \text{ s}^{-1}$ ,<sup>48</sup> which implies<sup>40,47</sup> that the concentration of  $\text{O}_2(a^1\Delta_g)$  is *ca.*  $2 \times 10^8 \text{ molecule cm}^{-3}$ . Since spontaneous emission and physical quenching appear to be the dominant removal processes of  $\text{O}_2(a^1\Delta_g)$  in the upper atmosphere,<sup>40,47</sup> it then follows that the rate of night-time production of  $\text{O}_2(a^1\Delta_g)$  is *ca.*  $5 \times 10^4 \text{ molecule cm}^{-3} \text{ s}^{-1}$  at 87 km. Thus, if reaction (1a) produces  $\text{O}_2(a^1\Delta_g)$  exclu-

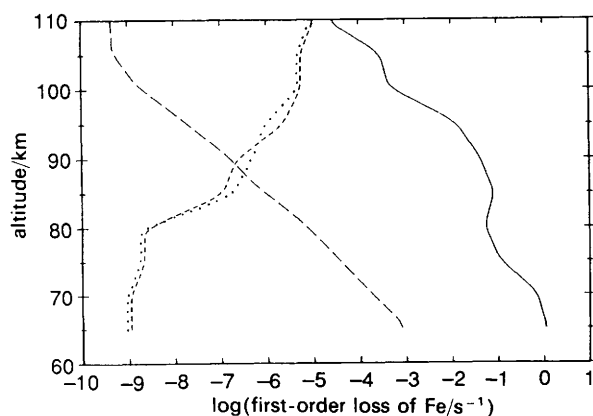


Fig. 6 Vertical profile in the earth's atmosphere between 65 and 110 km, depicting the first-order rates of loss of Fe atoms due to reaction with (—)  $\text{O}_3$  (this study), (---)  $\text{O}_2$  (ref. 9), and charge exchange with (---)  $\text{O}_2^+$  and (····)  $\text{NO}^+$  (ref. 40). The atmospheric concentrations of the trace species  $\text{O}_3$ ,  $\text{NO}^+$  and  $\text{O}_2^+$  are taken from a recent model (ref. 5 and 7), and the dependence of the pressure and temperature with altitude are from ref. 42. The conditions are for December, 40° N.

sively, this would account for only up to 4% of the total production, and does not appear to be significant.

A similar calculation can be performed for emission from  $O_2(b^1\Sigma_g \rightarrow X^3\Sigma_g^-)$ , which produces the atmospheric bands at 761.9 nm.<sup>40,47,48</sup> The night-time emission of these bands is ca. 500 photons  $cm^{-3} s^{-1}$  at 87 km,<sup>48</sup> which implies a night-time  $O_2(b^1\Sigma_g)$  concentration of ca. 6000 molecule  $cm^{-3}$ , and a production rate of 2000 molecule  $cm^{-3} s^{-1}$ . Thus, if reaction (1a) only produces  $O_2(b^1\Sigma_g)$ , this would account for a major fraction of the  $O_2(b^1\Sigma_g)$  formed at this altitude. Indeed, profiles of the  $O_2(b^1\Sigma_g \rightarrow X^3\Sigma_g^-)$  nightglow emission, made by rocket-borne photometers, often reveal a small secondary peak between 85 and 90 km that is distinct from the primary emission peak at ca. 95 km.<sup>48</sup> The calculations presented here, therefore, indicate that reactions between metal atoms of meteoric origin and  $O_3$  may be a source of  $O_2(b^1\Sigma_g)$  that is significant in the night-time mesosphere below 90 km. However, it should be stressed that this possibility requires that the yield of  $O_2(b^1\Sigma_g)$  from these types of reactions is high. Further laboratory experiments will be required to determine this.

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