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Fast-flow study of the C + NO and $C + O_2$ reactions

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Abstract

The C + NO and C + O_2 reactions were studied, at room temperature, in a low-pressure fast-flow reactor. C atoms were obtained from the reaction of CBr₄ or CCl₄ with potassium atoms and probed by their VUV resonance fluorescence. For C + NO, the overall rate constant was determined as $(5.4 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and for C + O_2 as $(2.5 \pm 0.4) \times 10^{-11}$ cm³ molecule s⁻¹. For the C + NO reaction, yielding N(²D, ⁴S) + CO and O(³P) + CN, the atomic products were also probed by their VUV resonance fluorescence. The [N(²D) + N(⁴S)]/[O(³P)] branching ratio was estimated as 1.5 ± 0.3 . © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Atomic carbon reactions are involved in combustion as well as in the interstellar medium for those exhibiting no barrier in the entrance channel. However, for many of them, there are still uncertainties about the overall rate constants and the product branching ratios, mainly because the generation of ground-state carbon atoms clean of other reactive species is not easy. This is the case for C + NO and $C + O_2$ whose channel exothermicities are hereafter given with respect to ground-state products:

$$C(^{3}P) + NO(^{2}\Pi) \rightarrow N(^{4}S) + CO(^{1}\Sigma^{+}),$$

$$\Delta_{r}H^{o}_{298} = -4.62 \text{ eV}, \qquad (1a)$$

$$\rightarrow N(^{2}D) + CO(^{1}\Sigma^{+}), \quad \Delta_{r}H^{o}_{298} = -2.24 \text{ eV}, \qquad (1b)$$

$$\rightarrow N(^{2}P) + CO(^{1}\Sigma^{+}), \quad \Delta_{r}H^{o}_{298} = -1.05 \text{ eV},$$
(1c)

→ O(³P) + CN(²Σ⁺),
$$\Delta_{r}H_{298}^{o} = -1.24 \text{ eV},$$
(1d)

$$C({}^{3}P) + O_{2}({}^{3}\Sigma^{-}) \rightarrow O({}^{3}P) + CO({}^{1}\Sigma^{+}),$$

$$\Delta_{r}H_{298}^{o} = -5.99 \text{ eV}, \qquad (2a)$$

$$\rightarrow O({}^{1}D) + CO({}^{1}\Sigma^{+}), \quad \Delta_{r}H_{298}^{o} = -4.02 \text{ eV}.$$

For C + NO, the reported values of the overall rate constant at 300 K, expressed in units of 10^{-11} cm³ molecule⁻¹ s⁻¹, are: 4.8 ± 0.8 [1], 1.6 ± 0.2 [2], 2.7 ± 0.2 [3]. A first study in a shock tube, over the temperature range 2720–3810 K, found no temperature dependence of the rate constant at a value of 3.3 ± 1.2 [4]. A further shock tube study, over the range 1550–4050 K, again found no temperature dependence of the rate constant at a value of 7.7 ± 3.5 [5]. In the latter study, the product branching ratio

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could be determined in the temperature range 2430–4040 K, as 60% for the CO + N product channel and thus 40% for CN + O. For C + O₂, the reported rate constants at 300 K, expressed in units of 10^{-11} cm³ molecule⁻¹ s⁻¹, are the following: 2.6 ± 0.3 [1], 4.7 ± 0.3 [2], 1.6 ± 0.2 [3], 4.68 [6]. The latter value has been obtained by the CRESU technique from experiments in the temperature range 27–295 K for which the rate coefficient fitted the expression 4.68 $\times 10^{-11} (T/298 \text{ K})^{-0.40}$. No value at temperatures exceeding room temperature is available. In a crossed beam experiment in our laboratory, Costes and Naulin found no potential energy barrier for the C + O₂ reaction [7].

A theoretical study by Halvick et al. [8] reported no potential energy barrier for the collinear approach of C towards the N atom of NO for the C + NO \rightarrow CN + O channel. Later. Persson et al. [9] calculated the potential energy profiles for either approach towards the N and O atom. In both cases, they found no potential energy barrier. However, they pointed out that although the absence of a barrier to the formation of CON by the approach of C towards O would allow the formation of CO + N in a direct process, this channel is entropically disfavoured with respect to the initial formation of CNO, then isomerising to NCO ($^{2}\Pi$) which further dissociates into $N(^{2}D) + CO(X^{1}\Sigma^{+})$. In a further study of this group [10], the rate coefficients for the N(²D) + CO(¹ Σ^+) and $O({}^{3}P) + CN({}^{2}\Sigma^{+})$ productions were calculated over the temperature range 200-4500 K. The branching ratio for CO + N was found not to depart significantly from 0.6 over the whole temperature range, in good agreement with Dean et al.'s experimental results [5]. The sum of their rate coefficient expressions for the two product channels leads to an overall rate constant of 7.8×10^{-11} cm³ molecule⁻¹ s^{-1} at 4500 K, again in agreement with Dean et al.'s values. Unfortunately, at 300 K, the calculated overall rate constant amounts to 12.36×10^{-11} cm³ molecule⁻¹ s⁻¹, far in excess of any experimental value. Since the reaction is barrierless, capture models were used by Beghin et al. [11] to calculate the C + NO rate coefficient over the temperature range 50-500 K. According to these calculations, the rate coefficient should increase from 3.43×10^{-11} cm³ molecule⁻¹ s⁻¹, at 300 K, to 13.6×10^{-11} cm³ molecule⁻¹ s⁻¹, at 50 K.

The C + NO and C + O_2 kinetics were studied, at room temperature, in a fast-flow reactor. C atoms were obtained by the successive abstractions of Br or Cl atoms from CBr₄ or CCl₄ by K atoms and detected by their VUV fluorescence. In the case of C + NO, an estimation of the branching ratio between N + CO and CN + O was made from the detection of N(⁴S), N(²D) and O(³P) by their VUV resonance fluorescence.

2. Experimental

2.1. Fast-flow reactor

The fast-flow reactor has been described in detail elsewhere [12] and only a brief description is thus given. It consisted of a hollowed-out stainless-steel block, in which a 36 mm inner-diameter Teflon tube was inserted, with four perpendicular optical ports for chemiluminescence and laser-induced fluorescence detection. The flow velocity in the reactor was 26.5 m s⁻¹, with He (> 99.995%) as carrier gas, at a total pressure of 2.0 Torr. C atoms were obtained by the successive abstractions of halogen atoms from CCl_4 or CBr_4 by atomic potassium vapour in a microfurnace ending into a nozzle. A glass tube introduced the halogenated compound between the furnace and the nozzle exit. The whole device mixing C atoms escaping from a nozzle with NO or O_2 slid along the Teflon inner wall of the reactor. The distance between the window detection and the nozzle exit could vary over the range 0-100 mm with a 0.5 mm precision.

Atoms were detected by their resonance fluorescence. Atom excitation was achieved with the microwave discharge lamp previously used to probe the atomic products of the CH + NO reaction [12]. The flowing gas mixture previously used to get intense emission lines of N, H and O atoms also gave C emission lines owing to CO and CO₂ impurities. The general procedure for atomic detection has also been detailed previously [12]. We would only mention that the conditions of the presently reported experiments ensure the linear dependence of the atomic fluorescence versus both the lamp emission intensity and the C, N and O atom concentrations. For C(³P), the transitions at 156.11 nm ($2p^{3^3}D^0 \leftrightarrow 2p^{2^3}P$) and at

2.2. Source of C atoms

C atoms were produced in the reactant injector nozzle from the $CBr_4 + 4K \rightarrow C + 4KBr$ or $CCl_4 + 4K \rightarrow C + 4KCl$ overall reactions resulting from the successive elementary steps:

$$CBr_4 + K \rightarrow CBr_3 + KBr,$$

$$\Delta_z H_{000}^o = -1.50 + 0.30 \text{ eV},$$
(3a)

$$CBr_3 + K \rightarrow CBr_2 + KBr$$
, (3b)

 $CBr_2 + K \rightarrow CBr + KBr$,

$$\Delta_{\rm r} H_{298}^{\rm o}(3{\rm b}) + \Delta_{\rm r} H_{298}^{\rm o}(3{\rm c}) = -1.15 \pm 0.3 \text{ eV},$$
(3c)

$$CBr + K \rightarrow C + KBr,$$

$$\Delta_{r} H_{298}^{o} = -1.15 \pm 0.3 \text{ eV},$$

$$CCl + K \rightarrow CCl + KCl$$
(3d)

$$\Delta_r H_{208}^o = -1.32 \pm 0.10 \text{ eV}, \qquad (4a)$$

$$\operatorname{CCl}_3 + \mathrm{K} \to \operatorname{CCl}_2 + \mathrm{KCl},$$

$$\Delta_{\rm r} H_{298}^{\rm o} = -1.0 \pm 0.10 \text{ eV}, \qquad (4b)$$

$$\operatorname{CCl}_2 + \mathrm{K} \to \operatorname{CCl} + \mathrm{KCl},$$

$$\Delta_{\rm r} H_{298}^{\rm o} = -1.21 \pm 0.10 \,\,{\rm eV}\,,\tag{4c}$$

CCl + K → C + KCl,

$$\Delta_{\rm r} H_{298}^{\rm o} = -0.30 \pm 0.10 \text{ eV}.$$
 (4d)

Whatever the microfurnace temperature, an excess of potassium atoms [K] > 20 ($[CCl_4]$, $[CBr_4]$), was used. CBr_2 , CBr or CCl radicals and C atoms were probed while varying the different parameters such as the oven temperature, the halomethane flow and the corresponding carrier gas flows. CBr_2 radical evolution was followed by the Br_2^* chemiluminescence at 292 nm given by the $CBr_2 + O \rightarrow CO + Br_2^*$ reaction. The evolution of CBr was followed via the $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ chemiluminescence at 387 nm given by $CBr + N \rightarrow CN(B, A, X) + Br$. The CCl radical was followed by the same chemiluminescent reaction or by LIF using the $A^2\Delta \leftarrow X^2\Pi$ transition near 278 nm. C atoms were detected by their VUV fluorescence. All these chemiluminescent

reactions will be detailed in a further article. The variations of the CBr₂, CBr and C signals with the distance between the end of the glass tube injecting the halomethane in the K vapour and the nozzle aperture are given in Fig. 1. In this figure, signals have been normalised to their maximum. The decrease of C atoms was due to the wall removal. The C production efficiency was very similar for CBr₄ and CCl_4 , but, in the case of CBr_4 , the limiting step should be either the second or the third Br abstraction, while in the case of CCl_{4} it should be the last Cl abstraction. The chemical lifetime of CBr in the oven was found to be smaller than that of CCl for similar conditions, so that the production of C_2 by C + CBr is smaller than that by C + CCl. Actually, the reactions $C_2 + NO \rightarrow C + NCO$, $C_2O + N$, and $C_2 + O_2 \rightarrow C + CO_2$, $C_2O + O$ could interfere in the atom probing either for the atomic carbon decay as well as for the N and O product branching of C + NO. The relative importance of C_2 thus was estimated. For that purpose, C2 was produced from C_2Cl_4 at a concentration equivalent to that of C atoms from CCl_4 and then compared to C_2 as a product of subsequent reactions of C atoms. This comparison was made through the CN chemiluminescence from the $C_2 + NO \rightarrow CO + CN$ reaction [13,14]. In the conditions used for the C pseudofirst-order decay determination, C2 was found at concentrations three orders of magnitude lower than



Fig. 1. Evolutions of CBr_2 , CBr and C with the distance between the glass tube injecting CBr_4 in K vapour and the nozzle (see Fig. 1 in Ref. [12]).



Fig. 2. Examples of the C fluorescence decay with NO added in excess.

that of C so that its influence on C decay measurements could be neglected. In the conditions used for the determination of the C + NO product branching, the halomethane concentration was increased so that the C₂ concentration was only two orders of magnitude lower than that of C. It was still of no influence in the estimation of the C + NO product branching from the N and O atom probing, not only because the C_2 concentration remained much lower than that of C but also because the $C_2 + NO$ reaction was found to produce mainly CO + CN. Another difficulty was the overlapping of C fluorescence lines by the CO(A¹ $\Pi_{\mu} \rightarrow X^{1}\Sigma^{+})$ chemiluminescence. For the CO(A¹ Π_{u}) state, lying at 8.02 eV above $CO(X^{1}\Sigma^{+})$, only the reactions $CBr + O \rightarrow CO +$ Br, exoergic by 8.2 eV, and $C_2 + O_2 \rightarrow CO + CO$, exoergic by 10.8 eV, could contribute to the observed chemiluminescence, in addition to the C + O $+ M \rightarrow CO + M$ reaction. To minimise these chemiluminescent reactions, we used low CBr_4 or CCl₄ concentrations with the maximum distance between the end of the glass tube and the nozzle aperture. Under these conditions, the C partial pressure was below 0.005 mTorr with a negligible amount of CBr (CCl) and C₂ radicals. In the case of the $C + O_2$ reaction, we could not completely eliminate the CO chemiluminescence from $C_2 + O_2$ which remained one order of magnitude smaller than the C fluorescence. Each scan was thus recorded with and without the lamp to subtract the CO chemiluminescence from the C fluorescence. NO (99.90%) and O_2 (99.90%) were used directly from the cylinders without further purification. CBr_4 (99%) and CCl_4 (99.5%) were also used without further purification.

3. Overall rate constants of the C + NO and C + O₂ reactions

The pseudo-first-order decays of atomic carbon fluorescence were monitored at different concentrations of NO and O_2 . Owing to the time needed to achieve the mixing of reactants, the decay became exponential at 3 cm from the nozzle through which escaped C atoms (Fig. 2). The pseudo-first-order rate constants were corrected for radial and axial diffusion using Keyser's formula:

$$k_{\rm cor} = k_{\rm obs} \left[1 + \left(\frac{a^2}{48D} + \frac{D}{v^2} \right) k_{\rm obs} \right],$$

where k_{obs} is the observed first-order rate constant, *a* the radius of the reactor, *v* the average flow velocity, *D* the diffusion coefficient of C atoms, equal to $860/P \text{ cm}^2 \text{ s}^{-1}$, where *P* is the total pressure in Torr [3].

For C + NO, an overall rate constant of $(5.4 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ was found (Fig. 3). For C + O₂, it was $(2.5 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Fig. 4).

With the reactor used in the present study, Dorthe et al. [3] had previously found for C + NO a value of $(2.7 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and for C + O₂ a value of $(1.6 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Atomic carbon decay was followed then



Fig. 3. Plot of the pseudo-first-order rate constant of the C+NO reaction against NO concentration.

via the CS(a³Π) chemiluminescence from C + OCS \rightarrow CS(a³Π) + CO, observed when OCS was added to NO. The discrepancy between the two sets of experiments is ascribed to the fact that CS(a³Π) being long-lived, has a chemiluminescence decay which is slower than that of atomic carbon. Our new determinations are consistent with the values reported by Husain and Young [1]: (4.8 ± 0.8) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for C + NO and (2.6 ± 0.3) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for C + O₂.

4. Product channels of C + NO

For the C + NO reaction, the N(4 S), N(2 D), O(3 P) atomic products were also probed. However, the situation was rather complex because $N(^{2}D)$ could be converted by inelastic collisions into $N(^4S)$ and removed by reactive collisions with NO to give $O + N_2$, as occurred for $N(^4S)$ for which the rate constant at 300 K [15] has been determined as 3.65×10^{-11} cm³ molecule⁻¹ s⁻¹. Furthermore, the $N(^{2}D)$ fluorescence line was partially overlapped by the CO chemiluminescence from C + O + M while our lamp/detection system gave smaller signals for O and N atoms than for C atoms. To enhance the signal from N and O atoms, higher concentrations of CCl_4 or CBr_4 were used. As a consequence, the C_2 concentration increased and CCl or CBr radicals were not completely removed. Using the CN chemiluminescence given by $C_2 + NO$, we checked that the concentration of C_2 was two orders of magnitude lower than that of C, by comparison with C_2 ob-



Fig. 4. Plot of the pseudo-first-order rate constant of the $C+O_2$ reaction against O_2 concentration.



Fig. 5. Relative evolutions of $C({}^{3}P)$, $N({}^{4}S)$, $N({}^{2}D)$ and $O({}^{3}P)$.

tained from C_2Cl_4 . In the latter case, we did not observe N atom production from $C_2 + NO \rightarrow C_2O$ + N and the C production from $C_2 + NO \rightarrow NCO$ + C was at least 50 times smaller than that of the C directly obtained from CBr₄, thus suggesting that CN + CO is the main product channel of the $C_2 +$ NO reaction. It can be concluded that C₂ did not actually interfere with our atomic product measurements of the C + NO reaction. The CCl and CBr radicals could also react with NO with a rate constant similar ¹ to that of C atoms and give O atoms but not N atoms. As their concentrations are at least 10 times lower than the C concentration, they could only slightly interfere with the O atoms from C + NO. Typical atom kinetics are given in Fig. 5, the intensities are normalised on the initial C atomic concentration. If N is removed by NO to yield $N_2 + O$, the removal of O by $O + NO + M \rightarrow NO_2$ + M is negligible. The observed O decay is thus due to the wall removal. From the evolution of the stationary concentrations of N and O atoms, we estimate their nascent branching ratio to $N(^{2}D)$ + $N(^{4}S) = 60 + 20\%$ and $O(^{3}P) = 40 + 20\%$, in good agreement with the results of Dean et al. [5] in the 2570-3790 K range and with theoretical calculations [10]. There is no doubt that $N(^{2}D)$, and $O(^{3}P)$ are primary products, as predicted by Persson et al. [9]. The direct production of $N(^4S)$ remains questionable.

 $^{^{-1}}k(\text{CCI} + \text{NO}, 298 \text{ K}) = 3.7 \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ and} k(\text{CBr} + \text{NO}, 298 \text{ K}) = 2.16 \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}, \text{ see} \text{Refs. [16,17], respectively.}$

The nascent electronic branching between $N(^2D)$ and $N(^4S)$ is difficult to estimate since we could not evaluate the effective contribution of the relaxation from $N(^2D)$ to $N(^4S)$ to the observed relative stationary concentrations of N atoms. It appears, however, that the nascent electronic branching must be largely in favour of $N(^2D)$ as suggested by theoreticians who discarded the pathway leading to $N(^4S)$ [9].

5. Conclusions

The new C + NO and C + O₂ rate constant values obtained in our fast-flow reactor from the direct detection of C atoms are found closer to Husain and Young's values than those previously reported from experiments where C atoms were not directly probed. The product branching ratio of C + NO is found to be ~ $60 \pm 20\%$ for CO + N and thus ~ $40 \pm 20\%$ for CN + O. For the C + NO \rightarrow CO + N channel, the electronic branching between N(²D) and N(⁴S) appears largely in favour of N(²D).

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