PRODUCT CHANNELS OF THE $N_2(A\,^3\Sigma_u^+) + O_2$ INTERACTION

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Products of the $N_2(A) + O_2$ reaction were measured in a discharge-flow reactor. N_2O accounts for only (2 ± 0.5)% of the reaction, contrary to recent reports, and O-atoms for (65 ± 10)% if $N_2(A)$ is quantitatively produced from Ar^* with excess N_2. This assumption is examined and specific $N_2(A) + O_2$ rate parameters are estimated.

1. Introduction

Although the overall rate of the title reaction is now very well known [1–3], its product channels are much less well characterized. Five sets of products are energetically allowed

$$N_2(A) + O_2 \rightarrow N_2(X) + O_2^* + \leqslant 5.1\ \text{eV}, \qquad (1)$$

$$\rightarrow N_2(X) + 2O(^3P) + 1.1\ \text{eV}, \qquad (2)$$

$$\rightarrow N_2O(X) + O(^3P) + 2.8\ \text{eV}, \qquad (3a)$$

$$\rightarrow N_2O(X) + O(^1D) + 0.79\ \text{eV}, \qquad (3b)$$

$$\rightarrow NO(X) + NO(X) + 4.3\ \text{eV}, \qquad (4)$$

$$\rightarrow NO_2(^2A_1) + N(^4S) + 0.95\ \text{eV}. \qquad (5)$$

Here, (1) is excitation transfer to any accessible state of O_2 below the dissociation limit, (2) is dissociative excitation transfer leading to the production of two ground-state oxygen atoms, and (3), (4), and (5) are reactive channels, (3) being O-atom transfer to form N_2O, (4) a four-center reaction to form two NO, and (5) an unlikely rearrangement in which two bonds are broken and two others formed. There is no experimental evidence for either (4) or (5). The former should lead to subsequent NO γ-band emission as a result of $N_2(A)$ + NO excitation transfer. This has not been observed, hence both (4) and (5) are neglected in the ensuing discussion.

The identification and quantitative measurement of channels (1) to (3) are of interest not only as a fundamental problem of excitation-transfer and reactivity in a simple system, but also have important applications in upper atmosphere science. Reaction (3) represents a potential high-altitude source of N_2O whose infrared chemiluminescence, photolysis, and reaction with $O(^1D)$ can provide substantial source terms of infared radiation and of NO_x [4,5]. Zipf's [1] finding of 60 ± 20% N_2O formation per $N_2(A)$ reaction has been the only direct experimental contribution, so far, to the question of product channel identity apart from qualitative observations of O-atom formation [6]. Zipf's [1] experimental work was based on spectroscopic and mass spectrometric analysis of a repetitively pulsed, very slowly pumped discharge-afterglow system where cumulative impurity side reactions are not ruled out. We have, therefore, undertaken to measure both O-atom and N_2O-production in a rapidly pumped discharge-flow system, where there is less opportunity for such interference, because the reaction occurs well downstream of the active discharge.

2. Experimental

The apparatus was a slightly modified version of one used previously (see fig. 1 of ref. [2]). The main modification was the addition of a twelve-liter glass bulb connected to the flow tube 5 cm downstream from the vacuum UV resonance fluorescence detection cell. After being filled slowly (≈20 min) to within 2% of flow tube pressure (2 Torr) in the course of an experiment or of a dynamic calibration, this bulb was isolated and connected to an evacuated, 107 cm long, 0.4 cm i.d. col-

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lection tube of either 304 stainless steel or quartz of $\approx$15 cm^3 volume. One end of this tube was then immersed in liquid helium to cryopump the entire gas sample. Following pumpdown to $\lesssim$0.02 Torr, the collection tube was isolated from the bulb, heated to $\approx$150°C, and the gas sample, now at $\approx$3 atm pressure, was analyzed for N_2O using electron capture gas chromatography (Perkin–Elmer, model Sigma-3, N_2 carrier gas, 4 ft. carbosieve-S column at 150°C, with 5 cm^3 sample valve). For each gas sample, up to 12 successive chromatograms were run in order to guard against incomplete mixing in the long tube. The accuracy and sensitivity of the GC analysis of N_2O are estimated to be ±10% and 4 ppb, respectively. This sensitivity corresponds to a detection limit of 2×10^8 cm^{-3} in the flow tube.

Laser-induced fluorescence (LIF) detection of $N_2(A)$ was carried out as before [2]. The $O(^3P)$ concentration was measured by resonance fluorescence [2], calibrated absolutely using small, measured additions of NO to excess N-atoms produced in a microwave discharge in flowing N_2/Ar mixtures. Another microwave discharge in flowing He at 1.5 Torr containing a trace of O_2 served as the VUV resonance lamp. The monochromator slit widths were set at 1 mm, and the photomultiplier signal was pulse counted for 10 s intervals. The detection limit was in the range $(5-10) \times 10^8$ cm^{-3} ($S/N = 1$).

The N_2O collection and detection system was carefully checked using both static and dynamic calibrations. In the former, five separate calibration mixtures were prepared in the 0 to 500 part per billon (ppb) range and analyzed repeatedly under various conditions of inlet system temperature. These points are shown in fig. 1. More importantly, dynamic calibrations were performed which were the exact equivalent of $N_2(A) + O_2$ reaction experiments, except that the Ar* discharge was off and that known small flows of N_2O greatly diluted with O_2 were added to Ar/N_2 mixtures. The final gas composition closely duplicated that of the reaction mixtures, i.e. 80% Ar, 20% N_2, 0.6% O_2, and 100–300 ppb N_2O corresponding to a 20–60% yield of N_2O in the $N_2(A) + O_2$ reaction. Two such dynamic calibrations were carried out using the stainless steel and one using the quartz collection tube to make sure that there was no loss of N_2O in the collection procedure. From the corresponding points in fig. 1, it is clear that there was no N_2O loss, since static and dynamic calibration points agree to within $\approx$±10%. Dynamic blank calibrations without added N_2O were also run and gave no N_2O signal as expected.

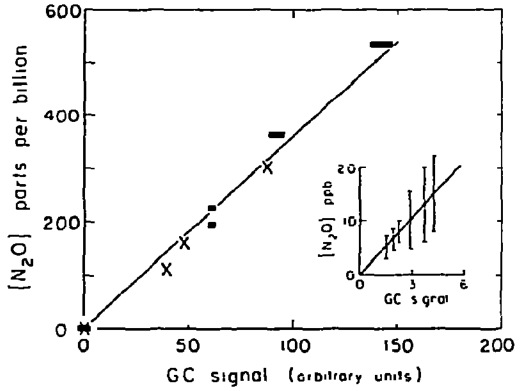

Fig. 1. Gas chromatographic calibration and measurement of [N_2O] ▬, static calibrations represent two to five analyses, each consisting of three to six chromatograms, X, dynamic calibration experiments where each point represents 14–16 consecutive chromatograms The inset shows the calibration line and the six GC measurements of N_2O product from $N_2(A) + O_2$, where each analysis represents 10–12 consecutive chromatograms

Total pressure ($\approx$2 Torr), flow velocity ($v \approx 40$ m s^{-1} except lower in N + NO titrations for O-atom calibration), and gas purification were as described earlier [2].

3. Results and discussions

The principal experiments consisted of the simultaneous collection of twelve-liter samples for N_2O analysis and of O-atom concentration measurement by VUV resonance fluorescence. LIF measurements of $N_2(A)$ and of its removal by added O_2 were also carried out at various times to ascertain that $N_2(A, v = 0, 1, 2)$ LIF signals were comparable to those observed before [2]. The absolute $Ar(^3P_{2,0})$ concentration was measured indirectly by reaction with excess O_2 in the absence of added N_2 under otherwise closely matched experimental conditions. In six experiments, [$Ar(^3P_{2,0})$] was found to be $(3.2 \pm 0.5) \times 10^{10}$ cm^{-3} where it is assumed that O_2 dissociation and dissociative excitation together produce a quantitative yield of O-atoms detected downstream as $O(^3P)$ [7]. In 17 experiments, the $O(^3P)$ yield from $Ar^* + O_2$ was compared quantitatively with that obtained under conditions of identical Ar^* generation, but with excess N_2 interposed upstream of the O_2 mixing inlet, replacing an equal flow of added Ar. These experiments gave a ratio of 0.66 ± 0.10 for O-atoms formed with N_2 interposition, i.e. for $N_2(A) + O_2$, as against without N_2, i.e. for $Ar^* + O_2$. The key experiment, viz. N_2O analysis, was carried out six times and gave the unexpected result of only (2 ± 0.5)% fractional yield of N_2O from $N_2(A) + O_2$ on the assumption, further discussed below, that the $Ar^* + N_2$ reaction ultimately produces $N_2(A)$ in quantitative yield. The $[N_2O]$ measurements are shown in the expanded scale inset of fig. 1.

Before these yields are interpreted in terms of the relative rates of channels (1) to (3), several assumptions inherent in our interpretation must be discussed.

(1) The dissociation of O_2 by reaction with Ar^* was reported by Breckenridge and Miller [7] using electron spin resonance detection of both $Ar(^3P_2)$ and $O(^3P_2)$. In their experiments, as in ours, any $O(^1D_2)$ formed would be rapidly quenched and detected as $O(^3P)$. Although little quantitative information was presented [7], the dissociation was considered to be quantitative, as would reasonably be expected, considering the energetics of the reaction and the many available dissociative states. Balamuta and Golde [8] have recently determined the relative magnitude of the $O(^3P) + O(^3P)$, $O(^3P) + O(^1D)$, and $O(^3P) + O(^1S)$ channels to be 46 : 52 : 2 by resonance fluorescence detection of $O(^3P)$ in the presence or absence of scavenger species such as H_2O.

(2) The comparison of O-atom yields from $Ar^* + O_2$ and $N_2(A) + O_2$ assumes the equivalence of the reactive species concentration apart from the completeness of the Ar^* to $N_2(A)$ transfer. Since O_2 was added through the movable injector which was retracted to just above the $N_2(A)$ or Ar^* inlet (see fig. 1 of ref. [2]), whereas N_2 was added ≈2 ms flow time upstream, the loss processes for Ar^* and $N_2(A)$ in this intermediate region must be compared. For $N_2(A)$ in Ar, we assume diffusion controlled wall deactivation which, in lowest mode diffusion and laminar flow, gives an effective first-order rate constant of $3.66\,D/r^2 = 176\ s^{-1}$ at 2 Torr [9], setting $D_0 = 150\ cm^2\ s^{-1}$ at 1 Torr pressure [10]. For Ar^* in Ar, the corresponding diffusion coefficient is much smaller, $D_0 = 50\ cm^2\ s^{-1}$ [11], but there are two-body and three-body gas-phase quenching processes that add 96 and 57 s^{-1}, respectively, for a total of 210 s^{-1}, which is 34 s^{-1} faster than the $N_2(A)$ loss rate. This corresponds to a 7% greater loss of Ar^* over the 2 ms flow time. Considering the large uncertainties in these loss rates, this difference is neglected.

(3) If N_2O is formed by reaction of $N_2(A)$ and the latter has a radial concentration gradient in keeping with its rapid surface loss, the initial N_2O concentration will reflect that gradient [9]. In 40 cm distance and 10 ms flow time from the reaction zone to the N_2O sampling point at a diffusion coefficient of ≈75 $cm^2\ s^{-1}$, these gradients will have largely disappeared, particularly since both at the O_2 addition point and at the GC sampling point, there are right angle bends in the main flow. Any underestimate of N_2O due to sampling near the wall of the flow tube must be less than ≈10% and probably much less so.

(4) The most serious assumption in our analysis pertains to the ultimate yield of $N_2(A)$ in the $Ar^* + N_2$ reaction. Although this same technique has been used for some time as a source of $N_2(A)$ (see ref. [12] for a recent review), the details of the primary energy transfer and subsequent radiative and collisional cascade are still in some question. The reported ratio of initially populated N_2, C to B states, has risen over the years from 1 : 6 [13] to 1 : 1 [14] to 1 : 0.25 [15] and recently to essentially 1 : 0 [16]. Sadeghi and Setser [16] now claim that only $N_2(C\,^3\Pi_u)$ is formed in the collisional energy transfer. This is followed by the rapid radiative transition to $N_2(B\,^3\Pi_g)$ and then by further radiative and collisional processes to lower triplet states. If $N_2(C)$ is indeed the only initial product, its vibrational distribution [17] of approximately 75% $v = 0$, 20% $v = 1$, and 5% $v = 2$ leads to a vibrational distribution in $N_2(B)$ of 49% $v = 0$, 27% $v = 1$, 13% $v = 2$, 6% $v = 3$, 3% $v = 4$, and 1% $v = 5$ [18] and of much smaller amounts in higher levels. If the subsequent population of $N_2(A)$ were controlled by purely radiative cascade (N_2 first positive emission), its vibrational distribution would be 45% $v = 0$, 31% $v = 1$, 12% $v = 2$, 6% $v = 3$, 3% $v = 4$, 1.4% $v = 5$, and 0.8% $v = 6$, based on the known transition probabilities [18]. Under our experimental conditions, although the C → B transition is entirely radiative ($\tau_R \approx 37$ ns), the B → A transition is not. Sadeghi and Setser [19] and Rotem et al. [20] have shown that the N_2 B, $W(^3\Delta_u)$, and A states are collisionally coupled and that the $B \rightleftharpoons W$ coupling rate con-

stants are nearly gas kinetic for N_2 as a collision partner and quite fast even for Ar collisions. For N_2 (B, v = 2–5) whose radiative lifetime, τ_R, is ≈ 6 μs, the corresponding collisional interconversion times range from ≈ 0.4 μs at $v = 2$ to ≈ 0.2 μs at $v = 5$ [20], i.e. the N_2(B) distribution will be further relaxed to lower v. The rapid B $\rightleftharpoons$ W interconversion and the close energy match of the B and W states for low v rules out any storage of N_2^* in a metastable form, say N_2(W), on the time scale of our experiments. In the ≈ 2 ms between $Ar^* + N_2$ mixing and reaction of $N_2^* + O_2$, interconversion plus B $\rightarrow$ A radiation should lead to N_2(A) in low v-levels in very large yield. The further vibrational relaxation of N_2(A, v = 1–3) is probably slow, i.e. $\tau_v \approx 2$ ms for $v = 3$ and $\gtrsim 100$ ms for $v = 2$ [21], and it is reported to occur in $\Delta v = 2$ steps, which may explain why the $v = 0$ and 1 levels are highly populated while $v \geqslant 2$ are present in much smaller concentrations. This does not rule out the possibility that a small fraction of the initial N_2(C) population may end up in as yet not fully characterized metastable states. However, the known kinetic and radiative properties of the B state require a large yield of N_2(A), in agreement with earlier studies [21], which reported N_2(A) concentrations of $\approx 10^{10}$ cm^{-3} under similar experimental conditions.

The possibility of N-atom production in the Ar^* + N_2 process is as yet unresolved, but there is indirect experimental evidence [22] for the formation of $\lesssim 30\%$ N(^{4}S). This interesting question is under investigation in our laboratory and elsewhere [22].

Finally, our results of relative O-atom and N_2O yields are interpreted in terms of reaction channels (1), (2), and (3) under two sets of assumptions (A) assuming quantitative conversion of Ar^* to N_2(A, v = 0, 1, 2); (B) assuming 80% conversion to N_2(A, v = 0, 1, 2) plus 20% dissociation of N_2, i.e. 33% N(^{4}S) yield. For case (A), the fractions of N_2(A) reacting to give O_2^*, O + O, and N_2O + O are 0.33 ± 0.10, 0.65 ± 0.10, and 0.02 ± 0.005, respectively. Specific rate constants can be assigned only approximately, since the overall rate constant for N_2(A, v = 1) is considerably larger than that for v = 0, 3.9×10^{-12} versus 2.5×10^{-12} cm^3 s^{-1} [1], and nothing is known regarding the v-dependence of product channels. Using a weighted average k_{total} of 3×10^{-12}, $k_{1,\text{av}} \approx 1 \times 10^{-12}$, $k_{2,\text{av}} \approx 2 \times 10^{-12}$, and $k_{3,\text{av}} \approx 6 \times 10^{-14}$ cm^3 s^{-1}.

For case B, neglecting the slow reaction of N(^{4}S) with O_2, the fractions are 0.16 ± 0.13, 0.81 ± 0.13, and 0.025 ± 0.006, and the k-values are correspondingly somewhat different. In either case, the large O-atom yield seems to require a non-vertical transition of N_2, A $\rightarrow$ X, since a vertical transition from A, v' = 0, would yield X, v'' = 5 or 6 with insufficient energy release (4.8 to 4.5 eV) to dissociate O_2. This restriction is relatively weak, however, since O_2-dissociation is nearly thermoneutral for the (4, 0) transition for which the Franck–Condon factor is only slightly smaller than for v'' = 5, and since dissociation is exothermic for a vertical transition from A, v' = 1 to X, v'' = 3.

The discrepancy between our and Zipf's [1] results suggests that other reactions among discharge products were responsible for his large N_2O yields, including, perhaps $N + NO_2 \rightarrow N_2O + O$ [23], since N-oxides were prominently observed in the mass spectra of those experiments. In view of the magnitude of this discrepancy, further verification by an independent experimental method is desirable.

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