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Oxidation of CO by N_2O between 1076 and 1228 K: Determination of the Rate Constant of the Exchange Reaction

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New measurements of the rate constant of the direct reaction of CO with N_2O are reported with the principal purpose of removing some of the remaining discrepancies on its value. Experiments were performed at lower temperatures (1076–1228 K) and lower pressure (~15 Torr) than those prevailing in most of previous works, by using a static reactor. It is shown that, under these experimental conditions, the reaction proceeds essentially according to the direct reaction $CO + N_2O \rightarrow CO_2 + N_2$ (1). The previously proposed "wet" mechanism is not significant under our experimental conditions. It has to be taken into account, however, to describe the observed production and consumption of molecular oxygen. The Arrhenius expression derived from these experiments is $k_1 = 10^{14.4\pm0.3} \exp[-(46 \pm 2)\ \text{kcal mol}^{-1}/RT]\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. A detailed analysis of the results shows that the uncertainties in side reactions do not greatly influence the value of k_1. A critical discussion of the data reported in the literature is presented. In spite of remaining uncertainties in the reaction mechanism, the present results, obtained in a low-temperature range, show that the low activation energy values of reaction 1, reported in several works performed at higher temperatures, are highly unlikely.

Introduction

The reaction of CO with N_2O has been extensively investigated recently. This reaction is important in N_2O–hydrocarbon flames, and one of its interests is related to its possible laser applications[1,2] as a source of vibrationally excited CO_2 at $T > 1500$ K. The interaction of carbon monoxide with nitrous oxide is generally presented as proceeding via two simultaneous channels: (1) the highly exothermic direct reaction

$$CO + N_2O \rightarrow CO_2 + N_2 \quad \Delta H^\circ = -87\ \text{kcal mol}^{-1} \quad (1)$$

and (2) a set of reactions, initiated by the decomposition of N_2O.

Large discrepancies remain about the published rate constants of reaction 1.[3-6] Four quantitative investigations have been carried out in shock tubes at high pressure and high temperature. Lin and Bauer[3] proposed $k_1 = 10^{11.04} \exp(-23/RT)$ cm^3 mol^{-1} s^{-1} at a total gas concentration of approximately 3×10^{-5} mol cm^{-3} and in the temperature range 1320–1900 K. Milks and Matula,[4] with nearly the same experimental conditions, reported $k_1 = 10^{11.32} \exp(-17.3/RT)$ cm^3 mol^{-1} s^{-1}. Zaslonko et al.[5] drew $k_1 = 10^{14.85} \exp(-53/RT)$ cm^3 mol^{-1} s^{-1} from a study at higher pressure (~7 atm) and in the temperature range 1500–2000 K, and recently, Fujii et al.[6] obtained $k_1 = 10^{11.5} \exp(-20/RT)$ cm^3 mol^{-1} s^{-1} between 1350 and 2100 K and about 2.5-atm total pressure. (In all these expressions R is in kcal mol^{-1} K^{-1}.)

Simultaneously, the mechanism of reaction 1 was discussed: according to Coleman et al.[7] and Borisov et al.,[8,9] the reaction between CO and N_2O could proceed only via a wet mechanism involving impurities such as H_2 or H_2O. Alternatively, several authors[5,10-16] suggest, for the direct reaction at high temperatures, a large contribution of vibrationally excited molecules of CO_2, N_2O, CO, or N_2.

In a previous paper[17] we derived the rate constant expression $k_1 = 10^{13.7\pm0.4} \exp[(-44 \pm 3)/RT]$cm^3 mol^{-1} s^{-1}, from measurements of the critical ignition pressure, between 1060 and 1228 K, using the thermal theory of explosion and assuming the generally accepted mechanism. The activation energy is close to that measured by Zaslonko.[5]

All the results are summarized in Figure 1, which clearly demonstrates the discrepancies in both the activation energy and the rate constant.

We present in this paper new measurements of the rate constant k_1, using an experimental method different from those that have been used so far. Moreover, the reaction was studied in the slow reaction regime at lower temperatures (1076–1228 K) and pressure (~15 Torr) than those used in previous studies.

The experimental results were analyzed on the basis of a mechanism involving the direct reaction 1, the reactions subsequent to the decomposition of N_2O and the "wet" mechanism which allowed us to estimate the contribution of hydrogenated impurities. A sensitivity analysis of the value of k_1, derived from simulations, regarding the uncertainties in both the mechanism and reaction rate constants is also reported, and the discrepancies among the results reported in the literature are critically discussed.

Experimental Section

The measurements were performed by the static method, using a conventional gas handling apparatus.[18] Gas mixtures were introduced through an electromagnetic valve (opening time 30 ms, closing time 20 ms) into the reactor, a quartz cylinder, 60 mm in diameter and 100 mm long, previously outgassed to 5×10^{-5} Torr and maintained in a furnace. The temperature was stabilized to within ±1 K and was measured with a chromel–alumel thermocouple (0.25 mm in diameter) set at the center of the reactor. Pressure changes during the reaction were monitored by a piezo-electric transducer (sensitivity 0.04 Torr) connected to a strip-chart recorder. When the reaction had proceeded for the desired time, a second electromagnetic valve was opened and the gases were allowed to expand from the reactor into a vessel

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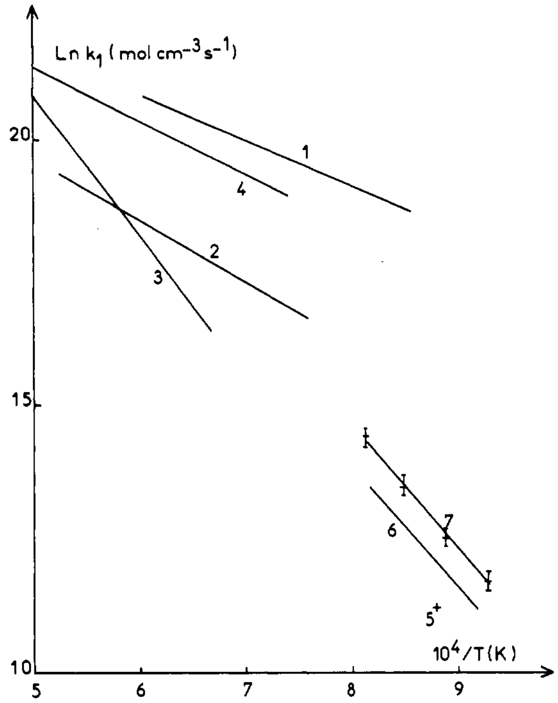

Figure 1. Arrhenius plots of the rate constant k_1: (1) Milks and Matula;[4] (2) Lin and Bauer;[3] (3) Zaslonko;[5] (4) Fujii et al.;[6] (5) Borisov;[28] (6) ref 17; (7) this work. The experimental points correspond to the rate constant values of column C, Table II. The bars correspond to the experimental errors (±20%) and do not take into account uncertainties on the reaction mechanism.

at room temperature. Both valves were driven by an electronic timer. The gases were analyzed by gas chromatography, using helium as the carrier gas and a Porapak-Q column at a temperature of 30 °C.

Nitrous oxide and carbon monoxide were obtained from l'Air Liquide (N_2O purity, 99.995%; H_2O, 20 ppm; H_2, 1 ppm; CO purity, 99.995%; H_2O, 5 ppm; H_2, 1 ppm). N_2O was outgassed at 77 K and distilled at low temperature for removing traces of H_2O. CO was also cooled at 77 K to trap out any condensable gases, particularly H_2O.

The reaction was studied between 1076 and 1228 K at a total gas concentration of 2×10^{-7} mol cm^{-3} (approximately 15 Torr). All experiments were carried out with an initial gas composition consisting of 50% N_2O and 50% CO. The gas composition (N_2O, N_2, NO, O_2, CO, and CO_2) was determined for different reaction times. Generally, 10–15 determinations of gas composition were performed for analyzing the whole reaction kinetics. Any variations of pressure and temperature were recorded simultaneously. The chromatographic column we used did not allow O_2 to be separated from CO. Oxygen concentrations could nevertheless be determined from total pressure measurements: during the reaction, the total pressure P was given by the following equation, obtained by considering the conservation of the numbers of C and N atoms: $P = P_i + P_{O_2} + {}^1/_2 P_{NO}$, where P_i was the initial total pressure. The concentration of oxygen was therefore easily calculated from the measurements of pressure variation, and the concentration of CO was then deduced from the peak corresponding to CO + O_2, by subtracting the O_2 concentration. A few analyses of gas compositions, performed by mass spectrometry, have confirmed the gas chromatographic determinations.

Results

The kinetics of the reaction were determined at four different temperatures between 1076 and 1228 K. The temperature always remained constant over all of the reaction time, indicating that the reaction was slow compared to heat exchange with the walls.

The time dependence of the total pressure during the reaction is represented in Figure 2. The pressure always went through a maximum, the final value always being larger than the initial one. This variation was small since it never exceeded 4% of the total gas pressure. It could nevertheless be measured accurately, since our experiments were carried out without diluent gas, by using a very sensitive pressure transducer.

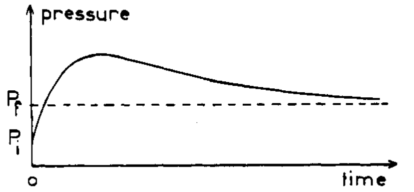

Figure 2. Pressure–time profile of the reaction. T = 1228 K; P_i = initial total pressure = 15.65 Torr; P_f = final total pressure = 15.89 Torr.

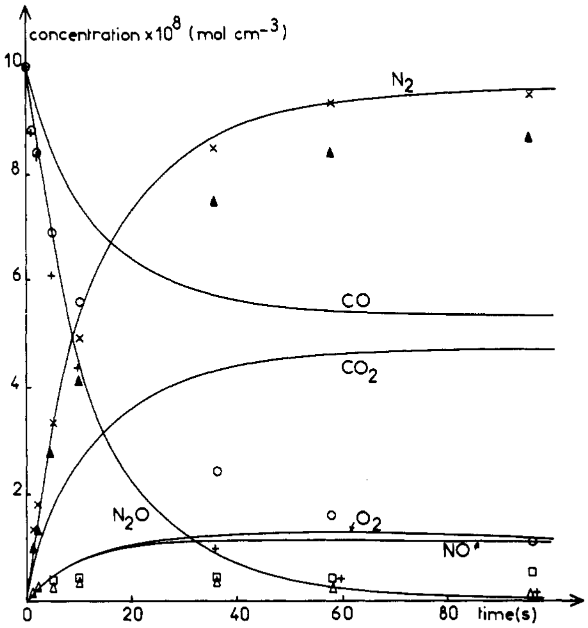

Figure 3. Time dependence of the concentration of reactants and products at T = 1179 K ($[CO]_i = 1.01 \times 10^{-7}$ mol cm^{-3}; $[N_2O]_i = 1.0 \times 10^{-7}$ mol cm^{-3}; $[H_2O]_i = 2.5 \times 10^{-12}$ mol cm^{-3}; $[H_2]_i = 2 \times 10^{-13}$ mol cm^{-3}): +, N_2O; ○, CO; ×, N_2; ▲, CO_2; △, O_2; □, NO. Solid lines correspond to concentrations calculated with the rate constants given in column A, Table II.

An example of the time dependence of the concentration of reactants and products is given in Figure 3, which shows the simultaneous and monotonous increase of CO_2 and N_2 and the decrease of N_2O and CO. O_2 goes through a maximum and cancels out at completion. NO increases rapidly at the beginning of the reaction before reaching a stationary value.

Analysis of Experimental Data

The experimental data were simulated on the basis of a mechanism including the direct reaction 1 of CO with N_2O, the set of reactions initiated by N_2O decomposition, and the set of reactions involving hydrogenated impurities such as H_2 and H_2O. The values used for the rate constants of reactions 3–7, 9, and 11–33 are from the literature (see Table I). k_2 and k_8 were determined under the same experimental conditions (reactor, temperature, and pressure range) as those used in the present study.[18,19]

The kinetic differential equations were integrated by using a program (written by V. Nowak et al. from Heidelberg University, F.R.G.) incorporating recently developed techniques from com-

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TABLE I: Mechanism and Literature Rate Constants Used in the Simulations[a]

	reaction	A	b	E/kcal mol^{-1}	ref
1	$CO + N_2O \rightarrow CO_2 + N_2$[d]				
2	$N_2O + M \rightarrow N_2 + O + M$	4.6×10^{14}	0	51.3[b]	18, 19
−2	$N_2 + O + M \rightarrow N_2O + M$	5.0×10^{13}	0	21.4	20
3	$N_2O + O \rightarrow 2NO$	$k_3/k_4 = 0.5$			20, 21
4	$N_2O + O \rightarrow N_2 + O_2$	1.0×10^{14}	0	28.2	22
5	$O + NO + M \rightarrow NO_2 + M$	1.1×10^{15}	0	−1.9	20
6	$NO_2 + O \rightarrow NO + O_2$	1.0×10^{13}	0	0.6	20
−6	$NO + O_2 \rightarrow NO_2 + O$	1.7×10^{12}	0	46.5	20
7	$NO + N_2O \rightarrow NO_2 + N_2$	2.0×10^{14}	0	50	23
8	$O + wall \rightarrow {}^1/_2O_2$	40			18, 19
9	$NO_2 + CO \rightarrow CO_2 + NO$	1.2×10^{13}	0	32	24
10	$O + CO + M \rightarrow CO_2 + M$	4.1×10^{14}			25[c]
11	$CO + O_2 \rightarrow CO_2 + O$	2.5×10^{12}	0	48	25
−11	$CO_2 + O \rightarrow CO + O_2$	1.7×10^{13}	0	52.6	25
12	$O + O + M \rightarrow O_2 + M$	1.0×10^{17}	−1	0	25
13	$O + H_2O \rightarrow OH + OH$	1.5×10^{10}	1.14	17	25
−13	$OH + OH \rightarrow O + H_2O$	3.4×10^{13}	0	5	26
14	$CO + OH \rightarrow CO_2 + H$	4.4×10^{6}	1.5	−0.7	25
−14	$CO_2 + H \rightarrow CO + OH$	1.6×10^{14}	0	26	25
15	$N_2O + H \rightarrow N_2 + OH$	7.6×10^{13}	0	15	25
16	$H + O_2 \rightarrow OH + O$	1.2×10^{17}	−0.91	16	25
−16	$OH + O \rightarrow H + O_2$	1.8×10^{13}	0	0	25
17	$NO_2 + H \rightarrow NO + OH$	3.5×10^{14}	0	1.5	25
−17	$NO + OH \rightarrow NO_2 + H$	10^{14}	0	30	*e*
18	$O + H_2 \rightarrow H + OH$	1.5×10^{7}	2	7.5	25
−18	$H + OH \rightarrow O + H_2$	8.3×10^{9}	1	7	27
19	$OH + H_2 \rightarrow H_2O + H$	1.0×10^{8}	1.6	3.3	25
20	$N_2O + H \rightarrow NH + NO$	6.3×10^{14}	0	29	ref in 9
−20	$NH + NO \rightarrow N_2O + H$	1.1×10^{12}	0	0.46	25
21	$NH + N_2O \rightarrow N_2 + HNO$	3.2×10^{12}	0	3	ref in 9
22	$HNO + H \rightarrow H_2 + NO$	5.0×10^{12}	0	0	ref in 9
−22	$H_2 + NO \rightarrow HNO + H$	1.4×10^{13}	0	54.9	20
23	$HNO + OH \rightarrow H_2O + NO$	3.6×10^{13}			20
−23	$H_2O + NO \rightarrow HNO + OH$	2.4×10^{6}			20
24	$H + O_2 + M \rightarrow HO_2 + M$	7.0×10^{17}	−0.8	0	25
−24	$HO_2 + M \rightarrow H + O_2 + M$	2.1×10^{15}	0	46	27
25	$H + HO_2 \rightarrow H_2 + O_2$	2.5×10^{13}	0	0.7	25
−25	$H_2 + O_2 \rightarrow H + NO_2$	5.5×10^{13}	0	58	27
26	$H + HO_2 \rightarrow OH + OH$	1.5×10^{14}	0	1	25
−26	$OH + OH \rightarrow H + HO_2$	1.2×10^{13}	0	40	27
27	$H + HO_2 \rightarrow H_2O + O$	1.0×10^{13}			27
−27	$H_2O + O \rightarrow H + HO_2$	5.0×10^{11}	0.5	54	27
28	$OH + NO + M \rightarrow HNO_2 + M$	1.0×10^{16}	0	−1.6	ref in 9
−28	$HNO_2 + M \rightarrow OH + NO + M$	1.0×10^{13}	0	45	ref in 9
29	$H + OH + M \rightarrow H_2O + M$	2.2×10^{22}	−2	0	27
30	$H + H + M \rightarrow H_2 + M$	2.6×10^{18}	−1	0	27
31	$H + NO + M \rightarrow HNO + M$	5.4×10^{15}	0	−0.6	20
−31	$HNO + M \rightarrow H + NO + M$	3.0×10^{16}	0	49	20
32	$O + HO_2 \rightarrow OH + O_2$	2.0×10^{13}	0	0	25
33	$OH + HO_2 \rightarrow H_2O + O_2$	2.0×10^{13}	0	0	25

[a] Rate constants are expressed as $k = AT^b \exp(-E/RT)$, in cm mol s. Reactions with activation energies higher than 60 kcal mol^{-1} are too slow and are not included in the mechanism. [b] Determined for $[M] = 2 \times 10^{-7}$ mol cm^{-3}. The nature of all gases present in the system is taken into account according to ref 19. [c] This rate constant was adjusted either by increasing the literature value or by including an heterogeneous contribution (see text). [d] Values of the rate constants were adjusted. [e] Estimated (see ref 20).

puter science and numerical analysis. Calculations were carried out on an IBM 43/81 computer. The values of k_1 and k_{10} were adjusted to obtain the best fit between experimental and computed concentration curves.

The reaction mechanism and rate constant values that are reported in Table I do not give a good fit of the experimental data by using the literature value of k_{10}[25] (see Table II). If k_1 is adjusted to preferentially fit the N_2O and N_2 concentration profiles, the computed CO and CO_2 concentrations are respectively largely above and below the experimental points as shown in Figure 3. On the contrary, if the priority for the fit is given to CO and CO_2, the reverse situation is obtained for N_2O and N_2, and in that case, even the fits on CO and CO_2 are not satisfactory. The values of k_1 corresponding to these two situations are given in columns A and B, respectively, of Table II. They are different by about a factor of 4.

TABLE II: Results of Simulations[a]

	mechanism and rate constants of Table I		mechanism of Table I; k_2 and k_{10} values different from those of Table I	
	attempted N_2O profile fit	attempted CO profile fit		
	A	B	C	D
k_2	value of ref 19[c]	value of ref 19[c]	value of ref 19[c]	${}^1/_2$(value of ref 19[c])
k_{10}	4×10^{14} (lit.)	4×10^{14} (lit.)	2×10^{16}[b]	1.0×10^{15}[b]
k_1(1076 K)[d]	8.0×10^{4}	3.0×10^{5}	1.2×10^{5}	1.5×10^{5}
k_1(1128 K)[d]	1.7×10^{5}	7.1×10^{5}	2.7×10^{5}	3.4×10^{5}
k_1(1179 K)[d]	4.0×10^{5}	1.8×10^{6}	7.0×10^{5}	9.0×10^{5}
k_1(1228 K)[d]	1.1×10^{6}	4.8×10^{6}	1.8×10^{6}	2.4×10^{6}

[a] Rate constants are in cm mol s units. In all the simulations $[H_2O]_i = 2.5 \times 10^{-12}$ mol cm^{-3} and $[H_2]_i = 2 \times 10^{-13}$ mol cm^{-3}. (These values are considered as upper limits of the hydrogenated species initial concentrations). [b] The literature value can be maintained if an heterogeneous contribution is included for reaction 10 (see text). [c] See Table I. [d] Adjusted.

A much better fit should be obtained by introducing an additional consumption of CO by oxygen species since, as shown

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(25) *Combustion Chemistry*; Gardiner, Jr., W. C., Ed.; Springer-Verlag: Berlin, 1984.

in Figure 3, the calculated concentrations of CO, O_2, and NO are too high at all stages of the reaction. Such reactions are essentially reaction 10 between CO and atomic oxygen and reaction 11 between CO and molecular oxygen. The rate constant of reaction 11 is now well-known: the reaction is slow and its contribution is negligible. There is some agreement on a value of k_{10} of about 4×10^{14} cm^6 mol^{-2} s^{-1}. However, the uncertainty on this value is still large. We have therefore chosen to increase k_{10} to introduce an additional consumption of CO. A fairly good fit for all species can be obtained (Figure 4), but k_{10} has to be increased by a factor of 50. The corresponding values of k_1 are given in column C of Table II. The same result can be obtained by including an heterogeneous reaction between CO and O atoms (see Discussion).

A better fit, compared to the situation shown in Figure 3, should also be obtained by decreasing the contribution of N_2O decomposition. However, as already emphasized, the kinetics of this reaction was investigated under exactly the same experimental conditions[18,19] as those prevailing in this work, and therefore, only a small uncertainty is expected on the value of k_2. The sensitivity to k_2 was tested by decreasing its value by a factor of 2, which can be considered as an extreme limit of uncertainty. An acceptable fit could be obtained (though not as good as in the preceding case), and k_{10} is now increased by a factor of only 2.5 compared to the accepted literature value, which is probably within the uncertainties on this rate constant. The corresponding values of k_1, given in column D of Table II, are close to those obtained in the preceding case (column C).

Since there are always uncertainties on the amount of impurities contained in the gases, particularly H_2 and H_2O which are involved in the wet mechanism, we have tested the sensitivity of the simulations to these concentrations. The concentration of H_2 ($\sim$1 ppm) is fairly well-known and can be considered to be constant in all experiments. The concentration of H_2O, however, for which an upper limit of 12 ppm has been estimated, is more uncertain, and its concentration was varied in these kinetic simulations: calculated concentrations of CO and CO_2 can be driven close to experimental values, compared again to the situation shown in Figure 3, by increasing the concentration of water. However, this concentration had to be increased to 50 times the estimated upper limit. Moreover, the concentration profiles of all species were very badly reproduced by these simulations.

If we consider that the "wet" mechanism was the only process responsible for the reaction between N_2 and CO, according to the Borisov assumption,[8,9] then it requires the concentration of H_2O to be 2 orders of magnitude larger than the estimated upper limit, in order to obtain a fit that is not even acceptable. Thus, the hypothesis of a wet mechanism that would be sufficient cannot be retained. On the other hand, neglecting the wet mechanism all together (reactions 13–33) would result in a k_1 value by 10% larger than the values reported in column C of Table II. In addition, multiplying the water concentration by a factor of 3 results in an effect of similar amplitude. Therefore, the values of k_1 are not significantly affected by the uncertainties on the rate constants of the reactions involved in this mechanism and by those on the concentrations of impurities.

Discussion

The analysis of the experimental results shows that, whatever the uncertainties about the reaction mechanism and rate constants are, the direct reaction 1 is the principal process responsible for the reaction between N_2O and CO. The "wet" mechanism, postulated by Borisov,[8,9] could only be important at much higher concentrations of hydrogenated impurities. Under our experimental conditions, the inclusion of these impurities in the reaction mechanism does not significantly influence the derived value of k_1. However, the reactions of hydrogenated species are necessary to account for the molecular oxygen concentration profile. In particular, the decrease of O_2 concentration in the later stages of the reaction can only be explained by the occurence of reaction 16 and to a lesser extent reaction 24, since the direct reaction of CO with O_2 is too slow.

The principal difficulty in the analysis of our results is the necessity of increasing by a factor of 50 the rate constant k_{10} for the reaction of CO with oxygen atoms (or by a factor of 2.5 if an error of a factor of 2 on k_2 is assumed), in order to reach an acceptable fit for both N_2O and CO (or N_2 and CO_2). It should be mentioned that several authors also found it necessary to overestimate the value of k_{10} in their study of the CO–N_2O reaction. Lin and Bauer[3] and Milks and Matula[4] used a value as high as 4×10^{16} cm^6 mol^{-2} s^{-1}, while the value used by Fujii[6] was close to 10^{15} cm^6 mol^{-2} s^{-1} around 1300 K.

Even though the value of k_{10}, and particularly its dependence upon the nature of the third body, is not precisely known, there is obviously a difficulty with this reaction in most of the studies of the N_2O–CO system. It seems that there is an additional consumption of CO missing in the reaction mechanism generally used. A possible reason for the necessity of using such high values for k_{10} might arise from a contribution of heterogeneous processes at the reactor walls, particularly at the low pressure used in the present work. Reaction 10 is indeed very slow under our experimental conditions, and a heterogeneous contribution to this third-body reaction is not unlikely, since the diffusion rate of oxygen atoms to the walls is faster than the reaction itself (when $k_{10} = 4 \times 10^{14}$ cm^6 mol^{-2} s^{-1}). This possibility of a heterogeneous reaction between CO and O atoms was tested by adding to the mechanism the following reactions:

$$\mathrm{O} + \mathrm{wall} \rightarrow \mathrm{O(s)} \qquad (34)$$

$$\mathrm{CO} + \mathrm{O(s)} \rightarrow \mathrm{CO_2} \qquad (35)$$

Keeping the literature value for k_{10}, a good fit of experimental data is obtained for $k_{34} = 120$ s^{-1} and $k_{35} = 0.014$ s^{-1}. The same values of k_1 as those reported in column C of Table II were obtained.

It is important to estimate to what extent the uncertainties, concerning the reaction mechanism discussed above, influence the values of k_1 that are obtainable from our experimental results.

The reaction mechanism and rate constants, given in Table I, yield two sets of values for k_1, corresponding to the cases given in columns A and B of Table II. These two sets of values can be considered as the extreme limits of the k_1 values that can be derived from the present work. Indeed, any attempt to improve the fitting of experimental data results in new values of k_1 which fall within these limits.

It should be pointed out that the concentration profile of N_2O is very well fitted in all the cases we have considered in Table I, except of course in the case corresponding to column B of Table II where the priority of the fitting was given to CO. This can be understood since the chemistry of N_2O, limited to the three significant reactions 1, 2, and 3 + 4, can be fairly well described, while the chemistry of CO, as shown above, seems more uncertain. Reaction 1 is the principal process responsible for the disappearance of N_2O, and the decomposition rate constant k_2 is well-characterized, since it was measured under the same conditions as those used in the present study. The largest uncertainty concerns the reaction of oxygen atoms with N_2O, since their concentration is strongly dependent on the reaction mechanism used and on the value of k_{10}. However, the contribution of this last reaction to the consumption of N_2O is always limited to less than 30%. Therefore, by giving the priority to the fitting of N_2O, the resulting values of k_1 are not very sensitive to the reaction mechanism chosen for the consumption of CO and to the value of the rate constant k_{10}. This is illustrated in columns A and C of Table II (Figures 3 and 4), where the values of k_1 are not different by more than 50%.

It should be noted that the value of k_2 that we have used, which was determined under the experimental conditions used in this work,[19] is about an order of magnitude larger than the value obtained from the recommended rate expression.[25] However, this

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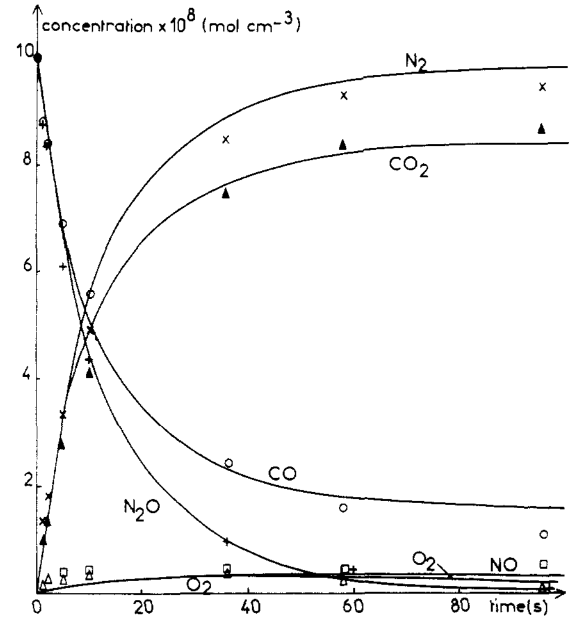

Figure 4. Time dependence of the concentration of reactants and products at T = 1179 K ($[CO]_i = 1.01 \times 10^{-7}$ mol cm^{-3}; $[N_2O]_i = 1.0 \times 10^{-7}$ mol cm^{-3}; $[H_2O]_i = 2.5 \times 10^{-12}$ mol cm^{-3}; $[H_2]_i = 2 \times 10^{-13}$ mol cm^{-3}): +, N_2O; ○, CO; ×, N_2; ▲, CO_2; △, O_2; □, NO. Solid lines correspond to concentrations calculated with the rate constants given in column C, Table II.

rate expression applies to temperature and gas concentration ranges much higher than those prevailing in this work. It was shown in our study of k_2[19] that the bimolecular rate constant and the activation energy are dependent on the total gas concentration, the reaction still being in the falloff regime. Therefore, a linear extrapolation of the Arrhenius expression from higher pressures and temperatures is not correct. Moreover, this recommended expression holds for argon used as the third body while Endo et al.[29] showed that the rate constant is 3–4 times higher for M = N_2O.

In addition, we have shown that an error on k_2 as large as a factor of 2 does not change the derived value of k_1 by more than 25–30% (Table II). If the low value of k_2[25] is used in simulations, our experimental data cannot be fitted since, in such a case, the contribution of reaction 2 is negligible and the calculated concentration profiles of N_2O and CO are very close to each other. Attempting to fit CO leaves k_1 unchanged within 20%, while an attempt to fit N_2O results in an increase of k_1 by a factor of 2–3. This shows again that an error on k_2 does not result in a dramatic error on k_1, compared to the scatter of the literature data.

For the above reasons, we conclude that reliable values of k_1 can be drawn from this work, is spite of the remaining uncertainties. The best values of k_1 are certainly close to those given in column C of Table II, with an uncertainty estimated to be about 50% for each of these values. The corresponding Arrhenius expression is

$$k_1 = 10^{14.4\pm0.3} \exp[-(46 \pm 2) \text{ kcal mol}^{-1}/RT] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

As discussed above, the principal sources of errors are from uncertainties in the reaction mechanism. The discussion also shows that these uncertainties should be smaller than the interval between the extreme limits given in columns A and B of Table II, since the best value of k_1 is likely to be closer to the lower limit corresponding to a correct fit for N_2O.

The preexponential factor in this expression appears somewhat too high. This may result from the limited temperature range of this study and from the fact that the Arrhenius expression may not be the most appropriate for the description of the temperature dependence of reaction 1. However, the present results do not allow us to propose a better expression.

The Arrhenius expression is plotted in Figure 1 for comparison with other data reported in the literature. The present results are in fairly good agreement with those reported in our previous work,[17] obtained in the same range of temperature by using a completely different method (analysis of the critical ignition pressure). In particular, the activation energies are the same within experimental errors. The rate constants are different by a factor of about 2, but such a discrepancy is not really significant considering the large uncertainties quoted in ref 17. The method used in this last study gave better information on the temperature dependence than on the absolute values of rate constants. In the same range of temperature, the value of k_1 obtained at 1140 K by Borisov[28] is slightly smaller than our values.

All other studies have been performed at high temperature in shock tubes. The rate constants reported by Lin and Bauer[3] and by Zaslonsko[5] fall roughly on the extrapolation of our Arrhenius plot to high temperatures. Taking into account the very different experimental conditions, this can be considered as fairly good agreement. The Arrhenius expression reported by Zalonsko[5] is reasonably close to ours, and its extrapolation to low temperatures agrees well with the Borisov value.[28] However, the activation energy of 23 kcal·mol^{-1} reported by Lin and Bauer[3] seems too small. The extrapolation of their Arrhenius expression to lower temperatures yields values of k_1 10–20 times higher than ours. As discussed above, such a difference is not reasonable. Even if our estimated uncertainty of 50% was too small, it is not conceivable that we have made an error larger than a factor of 2 or 3. Indeed, if it seems possible to measure an apparent rate constant larger than the actual value, because some important reactions have been neglected, the contrary is generally not possible, except in the case of chain reactions regenerating the reactants. In addition, the kinetic analysis of Lin and Bauer[3] does not seem satisfactory since they had to use a negative activation energy as large as −23 kcal mol^{-1} for reaction 10, while only a slightly negative value is expected.[25]

As shown in Figure 1, the situation is even worse with the results reported by Milks and Matula[4] and more recently by Fujii et al.[6] The rate constants are higher than all other data, and the activation energies are as low as those of Lin and Bauer[3]. The extrapolation of their results at low temperature yields rate constant values about 2 orders of magnitude higher than other data. As shown above, such high values are not acceptable, considering the results of the present study. No explanation can be given for such discrepancies, except for the possible presence of high concentrations of hydrogenated impurities.

Conclusion

The kinetic data on reaction 1 presented in this paper are the first obtained in a low-temperature range by a direct method. In spite of the remaining uncertainties, the set of low-temperature data presented in Figure 1 may now be regarded with confidence.

These data are important since the results obtained at high temperature alone do not allow any recommendation to be made, due to their large discrepancies. On the contrary, all the data presented in Figure 1 now give a fairly good idea of the kinetic parameters required to account for reaction 1. In particular, these results show that the activation energy cannot be smaller than about 42 kcal mol^{-1} and that the most probable value is around 46 kcal mol^{-1}.

However, the discrepancies and the uncertainties are still important, and further investigations are necessary. Particular emphasis should be placed on seeking new experimental conditions, which would result in a simpler analysis of the reaction mechanism and would allow more direct methods to be used to monitor the reaction.

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