Rate Constant and Activation Energy of the Exchange Reaction $CO + N_2O \rightarrow CO_2 + CO_2$ N₂ in the Temperature Range 1060–1220 K. Application of the Thermal Explosion Theory to a System with Two Parallel Reactions

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The rate constant of the exchange reaction $CO + N_2O \rightarrow CO_2 + N_2$ has been derived from measurements of the critical ignition pressure in the temperature range 1060-1220 K, using the thermal theory of explosion extended to systems with several parallel reactions. The expression of this constant $k = 10^{13.7} \exp(-44 (\pm 3 \text{ kcal mol}^{-1})/RT)$ $cm^3 mol^{-1} s^{-1}$ is in good agreement with recent results obtained at high temperatures in shock tubes and therefore provides good confidence in the activation energy value of this reaction.

Introduction

The reaction of CO with N₂O is generally presented as proceeding via two simultaneous channels: (i) the highly exothermic exchange reaction of CO with N_2O^{1-3}

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

and (ii) the set of reactions initiated by the decomposition of N₂O

 $N_2O + M \rightarrow N_2 + O + M$ $\Delta H = +39 \text{ kcal mol}^{-1}$ (2)

 $O + N_2O \rightarrow 2NO$ $\Delta H = -37 \text{ kcal mol}^{-1}$ (3)

$$O + N_2 O \rightarrow N_2 + O_2$$
 $\Delta H = -79 \text{ kcal mol}^{-1}$ (4)

 $O + NO + M \rightarrow NO_2 + M$ $\Delta H = -72 \text{ kcal mol}^{-1}$ (5)

 $NO_2 + O \rightarrow NO + O_2$ $\Delta H = -46 \text{ kcal mol}^{-1}$ (6)

$$O + CO + M \rightarrow CO_2 + M$$
 $\Delta H = -127 \text{ kcal mol}^{-1}$
(7)

This system has received much attention mainly for its relevance in laser application as a possible source of vibrationally excited CO_2^4 and also for its kinetic interest. There are large discrepancies in the published rate constants of the exchange reaction k_1 , and nearly all the measurements were performed in shock tubes at high temperature.^{1-2,5} Obviously there is a lack of measurements at lower temperature which should provide information on the reliability of the activation energy values obtained at high temperature. In a previous publication⁶ we presented measurements of the critical ignition pressure of CO- N_2O mixtures in the temperature range 1060-1220 K. Using these results Zaslonko et al.⁵ obtained an evaluation of k_1 consistant with their high temperature results, but they did not explain the way they treated the data.

In this paper the rate constant k_1 has been derived from these measurements by using the thermal theory extended to the case of several parallel reactions.⁷ The results provide fairly good reliability of the activation energy value and are discussed in comparison with previous determinations.

Experimental Section

The critical ignition pressures were determined by a static method using a conventional gas-handling apparatus described in ref 6. The quartz cell (4.5 cm in diameter, 10 cm in length) was heated at a given temperature and the gas mixture was introduced at a pressure higher than the explosion limit. The operation was repeated by decreasing the pressure until no explosion occurred. Two different mixtures (I, 90% CO-10% N₂O; II, 50% CO-50% N_2O) were studied in the temperature range 1060-1220 K. The temperature dependence of the critical ignition pressure P_c is presented in Figure 1 for both cases I and II.

Analysis of Experimental Data

The classical thermal theory of explosion established for a system in which there is only one exothermic reaction predicts that, if a gas combustion is occurring in a particular vessel at the rate $v = ze^{-E/RT}$ with a heat of reaction Q, there will be an explosion for the values of P and T_0 which verify the critical condition of ignition⁸

$$\frac{Q}{\lambda} \frac{E}{RT_0^2} r^2 z e^{-E/RT_0} = \delta_{\rm cr}$$
(1)

 $(\delta_{cr}$ is a constant depending on the shape of the vessel, 2.17 in our case; λ is the heat conductivity of the gaseous mixture; r is the radius of the vessel; T_0 is the wall temperature.)

This theory can be extended to systems including several parallel reactions.⁷ In this case, the critical condition is written

$$\frac{1}{\lambda} \frac{E}{RT_0^2} r^2 \sum Q_i v_i e^{(E_i - E)/E} = \delta_{\rm cr}$$
(2)

with

$$E = \frac{\sum E_i Q_i \upsilon_i e^{E_i/E}}{\sum Q_i \upsilon_i e^{E_i/E}}$$
(3)

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TABLE I: Values of the Rate Constant k, of the Exchange Reaction for Different Starting Values of E_1^a

	•	-		-	-	
<i>T</i> , K	1227	1181	1129	1084	1063	
		I (90%	CO)			
k_{1}^{2} $k_{1}^{2}(E_{1} = 40)$ $k_{2}^{2}(E_{1} = 45)$	$1.1 imes 10^{5} \ 3.1 imes 10^{5} \ 2.8 imes 10^{5}$	$3.7 imes10^4\ 1.6 imes10^5\ 1.45 imes10^5$	$9.6 imes 10^3$ $7.2 imes 10^4$ $6.4 imes 10^4$	$2.4 imes 10^3\ 2.9 imes 10^4\ 2.6 imes 10^4$		
		II (50%	5 CO)			
$k_{1}^{2} (E_{1} = 20) \\ k_{1} (E_{1} = 40) \\ k_{1} (E_{1} = 45)$	$\begin{array}{c} 1.5 \times 10^{5} \\ 4 \times 10^{5} \\ 2.6 \times 10^{5} \\ 2.5 \times 10^{5} \end{array}$	5.1×10^{4} 2.1 × 10 ⁵ 1.25 × 10 ⁵ 1.2 × 10 ⁵	$\begin{array}{c} 1.35 \times 10^{4} \\ 1.1 \times 10^{5} \\ 6.4 \times 10^{4} \\ 5.7 \times 10^{4} \end{array}$	3.9×10^{3} 5.7×10^{4} 3.1×10^{4} 2.8×10^{4}	2.1×10^{3} 3.5×10^{4} 2×10^{4} 1.7×10^{4}	

^a k values in cm³ mol⁻¹ s⁻¹. E values in kcal mol⁻¹.



Figure 1. Temperature dependence of the critical ignition pressure P_{c} .

 $(Q_i \text{ is the heat of reaction of the } i \text{ reaction}; v_i = z_i e^{-E_i/RT}$ is the rate of the *i* reaction.)

Application to the Combustion of CO-N₂O Mixtures

Two exothermic parallel reactions are considered in the combustion of CO with N_2O ; (a) the exchange reaction 1 corresponding to a rate

$$v_{\rm a} = k_1 [N_2 O] [CO] = k_1 \gamma (1 - \gamma) [M]^{\frac{1}{2}}$$

with $Q_a = Q_1 = 87$ kcal mol⁻¹; (b) the N₂O decomposition that we reduce to the three first principal steps 2, 3, and 4. In the approximation of a stationary state of oxygen atoms, the rate of disappearance of N₂O can be written

$$v_{\rm b} = 2k_2[N_2O][M] = 2k_2(1-\gamma)[M]^2$$

The heat of reaction Q_b can be evaluated from the ΔH values of reactions 2, 3, and 4. When $k_3/k_4 \simeq 0.5$ is used,^{9,10} a value $Q_b \simeq 20$ kcal mol⁻¹ is obtained.

The values of the rate constant k_2 and activation energy E_2 of reaction 2 were determined in the temperature range 1070–1230 K in a separate work.¹¹

The values of k_1 and E_1 are calculated by the following iterative procedure:¹² Q_1 , k_2 , Q_2 , and E_2 are known and [M] corresponds to the critical pressure P_c determined experimentally at the initial temperature T_0 ; we choose an a priori value of E_1 , then (i) neglecting reaction 2, we calculated a value of k_1 higher than the final value from the critical conditions 1; (ii) from this value of k_1 , E is calcu-



Figure 2. Arrhenius plots of K_1 for several starting values of E_1 : A, 50% CO-50% N₂O; B, 90% CO-10% N₂O. Starting values of E_1 : \Box , 20 kcal mol⁻¹; X, 40 kcal mol⁻¹; O, 45 kcal mol⁻¹.

lated by using relation 3; (iii) a new value of k_1 is determined from relation 2. Constant values of k_1 are obtained after 2 or 3 iterations.

By performing these calculations at several temperatures, we obtain $k_1 = f(T_0)$. Different expressions $k_1 = f(T_0)$ correspond to different starting values of E_1 . We assume that the best starting value of E_1 is the one yielding the smallest difference between E_1 and the slope determined from the Arrhenius expression of k_1 .¹³

(13) Example of Calculation Mixture 50% CO-50% N_2O , $T_0 = 1227$ K; $P_c = 62 \text{ torr}$. $M = 0.8 \times 10^{-6} \text{ mol cm}^{-3}$. $k_2 = 7 \times 10^{14} \exp(-54.3/RT)$ cm³ mol⁻¹ s⁻¹ (obtained from ref 11). $\lambda = 1.95 \times 10^{-6} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$. λ , the heat conductivity of the gaseous mixture, is calculated for each temperature from the values of the heat conductivity and viscosity of the pure gases given in ref 15. We use the expression of Lindsay and Bromley¹⁶ as proposed by Gray and Wright.¹⁷ $v_a = 0.25k_1[M]^2$, $v_b = k_2[M]^2$. The starting value of $E_1 = 40$ kcal mol⁻¹. (1) Calculation of k_1 from relation

$$0.25k_1[\mathbf{M}]^2 = \frac{2.17\lambda RT_0^2}{Q_1 E_1 r^2} \rightarrow k_1 = 4.5 \text{ x } 10^5 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

(2) Calculation of E from the expression 3

$$E = \frac{0.25E_1Q_1k_1e^{E_1/E} + D_2Q_2k_2e^{E_2/E}}{0.25Q_1k_1e^{E_1/E} + Q_2k_2e^{E_2/E}}$$

 $E = 44.2 \text{ kcal mol}^{-1}$

(3) Calculation of k_1 from the critical condition 2

$$0.25Q_1k_1e^{(E_1-E)/E} + Q_2k_2e^{(E_2-E)/E} = \frac{2.17\lambda RT_0}{r^2[\mathbf{M}]^2E}$$

$$k_1 = 2.6 \text{ x } 10^5 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

From this value of k_1 we calculate again E then k_1 . The whole calculation can be done again with another starting value of E_1 .

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Letters



Figure 3. Arrhenius curves of k_1 : (1), ref 1; (2), ref 2; (3), ref 5; \bullet ref 18; □, this work; ▲, ref 3.

Results and Discussion

The values of k_1 were calculated for different values of E_1 . The results are shown in Table I for several starting values of E_1 and for different temperatures. The corresponding Arrhenius plots are shown in the Figure 2, A and Β.

For the mixture 50% CO–50% N_2O a calculation was made with the starting value $E_1 = 20$ kcal mol⁻¹ which was suggested by some results of other groups.^{1,2} The slope of the corresponding Arrhenius curve (Figure 2A) gives E_1 $\simeq 37$ kcal mol⁻¹. The difference between these two values is too large and 20 kcal mol⁻¹ is certainly not a good value for E_1 .

With the starting values of $E_1 = 45$ and 40 kcal mol⁻¹, in the case of the mixture 50% CO-50% N_2O , we obtain from the slopes of the Arrhenius curves the activation energies 42 and 40 kcal mol⁻¹, respectively. In the case of the mixure 90% CO-10% N_2O with these same starting values of E_1 , the two slopes lead to nearly the same value of the activation energy: 44 kcal mol^{-1} . In the CO-rich mixture the importance of the exchange reaction is enhanced as compared to the other mixture due to both the high CO concentration and the lower k_2 values resulting from higher pressure limits (the bimolecular rate constant for the decomposition of N₂O decreases when the total gas pressure increases as predicted by the theory of unimolecular decomposition).¹⁴ We consider therefore that the results are more reliable in this case giving $k_2 = 10^{13.2}$. $\exp(-44 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

The previous results of the literature are presented in Figure 3 showing the important scatter on the rate constants and activation energies. Milks and Matula² proposed $k_1 = 10^{11.32} \exp(-17 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Their very high values of k_1 are probably due to the presence of impurities in the gases used without purifi-cation. Lin and Bauer¹ found $k_1 = 10^{11.04} \exp(-23 \text{ kcal})$ mol^{-1}/RT) cm³ mol⁻¹ s⁻¹. According to the authors this expression is consistent with a negative activation energy of 23 kcal mol⁻¹ for the reaction O + CO + M which is not reasonable. The extrapolation to lower temperature of the more recent results of Zaslonko et al.,⁵ $k_1 = 10^{14.85\pm0.31}$. exp(-53 ± 4 kcal mol⁻¹/RT) cm³ mol⁻¹ s⁻¹, seems to be in better agreement with our results though they obtained a higher activation energy. A value of k_1 obtained by Borisov¹⁸ at 1100 K from measurements of ignition delays is in good agreement with the present determination.

In separate experiments, reaction 1 was studied in the slow reaction regime at lower pressure (15 torr). These experiments are still in progress but preliminary results³ yield an activation energy in good agreement with the results presented in this paper, the value of k_1 being, however, higher by a factor of about 3. In the present treatment of the pressure limits, the uncertainty in the absolute values of k_1 is obviously higher than in its variation with temperature. Therefore more confidence must be given to the activation energy deduced from this temperature dependence. Finally, the Arrhenius parameters obtained from this whole set of results for the exchange reaction of CO and N₂O are log $A = 13.7 \pm 0.4$ (A in cm³ $mol^{-1} s^{-1}$) and $E = 44 \pm 3 kcal mol^{-1}$.

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