RATE CONSTANT OF THE ELEMENTARY REACTION OF CARBON MONOXIDE WITH HYDROXYL RADICAL

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Using a supersonic molecular beam sampling technique coupled with a mass spectrometer, the concentrations of all stable and unstable species have been measured in the reaction zone of a lean carbon monoxide-hydrogen-oxygen flame (9.4%CO, 11.4%H₂, 79.2%O₂) burning at 40 Torr.

Reaction (1) $CO+OH \rightarrow CO_2+H$ is the main process for CO conversion to CO_2. From radical concentration profiles, it was determined that reaction (4) $CO+HO_2 \rightarrow CO_2+OH$ is negligible as compared to (1). The rate constant k_1 was determined from the CO_2 mole fluxes over a large temperature range (400°–1800°K).

The experimental data exhibit a marked and significant curvature in the plot of $\log k_1$ vs $1/T$. From 400° to 800°K, k_1 (8×10^{10} cm³ mole⁻¹ s⁻¹) increases only slightly, but above 1000°K the Arrhenius expression $k_1 = 2.32 \times 10^{12} \exp(-5700/RT)$ cm³ mole⁻¹ s⁻¹ up to 1800°K. The rate constant of reaction (9) $H_2+OH \rightarrow H_2O+H$ was determined similarly and found to be $7 \times 10^{12} \exp(-4400/RT)$ cm³ mole⁻¹ s⁻¹ in the temperature range of 600° to 1300°K. A curvature, less pronounced than for k_1, was observed.

Introduction

Whereas the combustion of hydrocarbons involves a complex mechanism with a large number of elementary processes, the reaction

$$CO+OH \rightarrow CO_2+H \qquad (1)$$
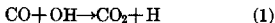
is fairly well accepted as the ultimate step for the conversion of carbon monoxide to carbon dioxide. Because of the importance of this elementary reaction, from a practical standpoint as well as more recently from a theoretical viewpoint, there have been numerous investigations to determine its rate constant and its temperature dependence.

Several groups have succeeded in using various methods to measure k_1 at different temperatures, but not over a very broad temperature range. Authors such as Dixon-Lewis,[1] Herron,[2] Greiner,[3] Smith,[4] and Stuhl[5] have determined k_1 around

room temperature (200–500°K) applying ESR mass spectrometry or absorption spectroscopy. Fenimore,[6] Dixon-Lewis,[7] Jost,[8] Porter,[9] Westenberg,[10] Hottel,[11] Eberius,[12] Peeters,[13] and Mahnen[14] have deduced the value of k_1 by various techniques in flame systems. Finally Stepanek,[15] Brabbs,[16] and Gardiner[17] measured k_1 at high temperature by shock tube methods.

From such a literature survey, a definite non-Arrhenius behavior of k_1 is apparent. This unexpected temperature dependence induced Dryer[18] to apply the transition state theory to compute the parameters of $k_1 = CQ(T) \exp(-E_0/RT)$, where E_0, the activation energy barrier between reactants and products in their zero point vibrational states, was assumed to be zero. The constant C was adjusted so that k_1 corresponds to the measured value of Greiner[3] at 300°K. In $Q(T)$, which contains the ratio of partition functions of the activated complex of the reactants (CO and OH), the vibration frequencies of the complex were assumed to be equal to those of the HONO molecule. The computed k exhibits curvature in the plot of $\log k_1$ vs $1/T$. Smith[4] reached similar conclusions about the tempera-
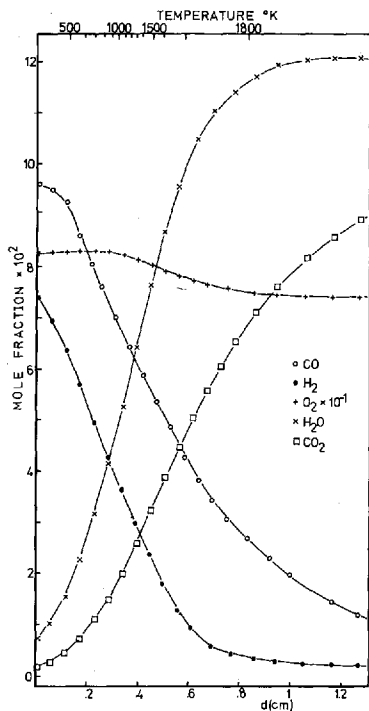

FIG. 1. Temperature and mole fractions of CO, O_2, H_2, H_2O, and CO_2 versus distance $(d=z)$ from burner in a lean carbon monoxide–hydrogen–oxygen flame (9.37%CO, 11.39%H_2, 79.24%O_2); $v_0 = 63.7$ cm/s; $p = 40$ Torr.

ture dependence of k_1 by assuming the formation of a nonlinear collision complex before passing through the activated state. Westenberg and de Haas[19] measured k_1 between 300°–915°K by means of a fast flow reactor coupled with a fixed ESR detector. They noticed slight upward curvature in the high temperature regime (~ 800°K).

In order to check experimentally the temperature dependence of k_1, we decided to measure it over a broad temperature range with the same technique. With this in mind, reaction (1) was studied in a lean $CO/H_2/O_2$ flame by means of temperature and composition profiles from 400° to 1800°K.

Experimental

A lean flame (9.4%CO, 11.4%H_2 and 79.2%O_2) burning at 40 Torr was stabilized on a removable cylindrical burner with a diameter of 5 cm. The sampling probe was a HF-deactivated quartz cone, 24 mm high, with an apex angle of 45°. At the top of the cone, an orifice of 0.1 mm in diameter opened into the first of three differentially pumped stages. The gas flow from the combustion chamber entered the first low-pressure stage (4×10^{-4} Torr) through the orifice of the sampling cone and underwent an isentropic expansion to give a supersonic jet. Then it entered the second chamber (pressure 10^{-5} Torr) through a skimmer located 2.2 cm from the quartz cone. The emerging beam was modulated to a controlled frequency before entering the ionization source of an Edwards E-60 mass spectrometer operating at a pressure of about 3×10^{-7} Torr. The ion current was amplified with an ion multiplier (16 dynodes Ag–MgO) and thereafter fed to a PAR 121 lock-in amplifier. The apparatus and the experimental technique have been described elsewhere.[13]

With such supersonic molecular beam sampling coupled with mass spectrometric detection, it was feasible to measure the ion current from stable species, radicals and atoms. Calibration for stable species, such as CO, CO_2, O_2, and H_2, in terms of relative mole fraction was done directly. Accurate calibration factors for O, H, and OH were obtained indirectly on the basis of the partial equilibrium of the H_2/O_2 system reactions; that partial equilibrium was, indeed, established in the burned gases to within a few percent was ascertained by using the method described by Peeters and Mahnen.[13] The ionizing electron energies were kept as low as possible, only two or three volts above the respective ionization potentials, to avoid fragment ion contributions.

The ion current at mass 33 was a combination of signals due to hydroperoxyl radicals and to $^{33}O_2$. Taking into account the mole fraction of oxygen from $m/e = 32$ data and the known isotopic abundance, it was possible to deduce $I_{HO_2}(33)$, i.e., the contribution of HO_2 to the total ion current at mass $m/e = 33$. The hydroperoxyl mole fraction X_{HO_2} was then determined indirectly as follows

$$X_{HO_2} = X_{O_2}[I_{HO_2}(33) \cdot Q_{O_2}]/[Q_{HO_2} \cdot I_{O_2}(32)]$$

where the Q_i's are the respective ionization cross sections. Q_{HO_2} was assumed to be the sum of the atomic cross sections and therefore equal to 3.25 Å² at 70 eV. We are aware of the fact that

such a calibration procedure gives only a lower limit for the HO_2-concentration. First, it does not take into account the fact that, upon electron impact, fragmentation to HO_2 in O_2^+ or to H^+ might occur in addition to simple ionization. Secondly, about 50% of the HO_2-radicals are destroyed by collision with the inner wall of the sampling probe. Therefore, the values in Fig. 2 could be low by a factor of two or three.

Temperature profiles were measured with a Pt–Pt/10%Rh thermocouple of 0.1 mm diameter, coated with several layers of Y_2O_3–BeO as suggested by Kent[20] to prevent recombination reactions. Radiation losses were corrected by the electric compensation method.[21] The area expansion ratio was measured using Peeters' technique[13] based on heat exchange between flowing fresh gases and the heated thermocouple at constant temperature.
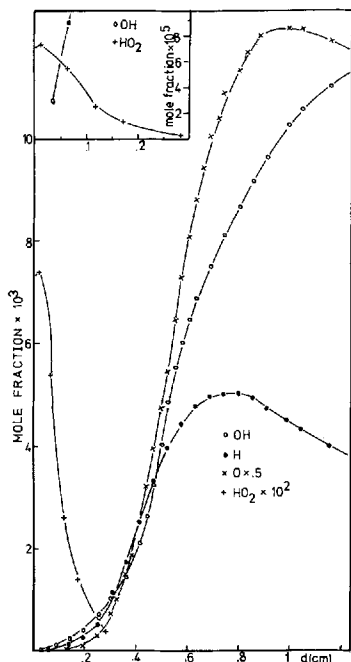

FIG. 2. Mole fractions of O, OH, H, and HO_2 versus distance $(d=z)$ from burner in the same flame as in Fig. 1.

Results

For a linear flow velocity of the fresh gases of 63.7 cm/s, the flame stabilizes sufficiently far away from the burner surface to allow sampling species and measuring temperatures in the preheating region without causing large disturbances of the flame by the sampling probe. The distance scale was corrected for the slight shift of the flame away from the burner when the quartz cone penetrated into the flame. The corrected concentration profiles are shown in Fig. 1 for stable species (CO, H_2, O_2, CO_2, H_2O) and in Fig. 2 for radicals (O, H, OH, HO_2). An enlargement of the OH and HO_2 profiles is inserted in Fig. 2. All concentration profiles were recorded out to $z = 4.0$ cm, but for the sake of clarity the profiles are drawn out only to the point where the maximum temperature is reached ($z = 1$ cm). The temperature scale is also given in Fig. 1. The area expansion ratio A varies as $(1 + 0.2z)$.

The mole fluxes per unit inlet area F_i can be expressed as

$$F_i = A N_i (v + V_i) \qquad [1]$$

where N_i is the local concentration of the ith species in mole cm^{-3}, V_i its local diffusion velocity, and v the local average mass velocity.

As a consequence of the large excess of oxygen, the mean molecular mass $\bar{M}$ was close to the mass of the oxygen molecule, and we assumed that the diffusion of the ith component occurred in oxygen (binary diffusion i-O_2). Therefore the diffusion velocity can be written as

$$V_i = -\frac{\mathfrak{D}_{i-O_2}}{X_i}\left[\frac{dX_i}{dz} - \frac{X_i d\bar{M}}{\bar{M} dz} + (k_T)_i \frac{d \ln T}{dz}\right] \qquad [2]$$

where z is the distance coordinate, $\mathfrak{D}_{i-O_2}$ the local binary diffusion coefficient of species i with a local mole fraction X_i, and k_{T_i} the binary thermal diffusion ratio at temperature T. The $\mathfrak{D}_{i-O_2}$ and $(k_T)_i$ have been calculated on the basis of equations and data taken from Hirschfelder, Curtiss and Bird.[34] The accuracy is estimated to be about 10%. The mole fluxes per unit inlet area of every species were calculated using Eqs. [1] and [2]. The mole flux profiles of H_2O, CO_2, OH, H, and O are shown in Fig. 3. For radicals the fluxes decrease, reach a minimum at around 1500°K and then increase again. The negative fluxes of the radicals in the preheating zone are due to the upstream diffusion of these species from the hotter region, where they are formed, to the cooler region where they are rapidly destroyed by
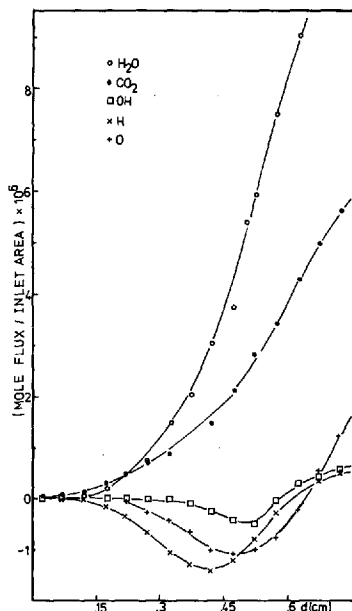
FIG. 3. Mole fluxes per unit inlet area (mole cm^{-2} s^{-1}) of H_2O, CO_2, OH, O, and H versus distance from burner, same flame as in Fig. 1.

fast reactions. The maximum deviations of total carbon-atom and hydrogen-atom fluxes from the initial values always remain smaller than 10%.

The net chemical reaction rate R_i is computed as

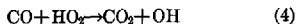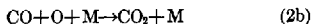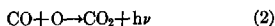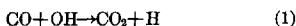$$R_i = dF_i / A \cdot dz \qquad [3]$$

The maximum carbon dioxide formation rate $(R_{CO_2})_{max}$ is 1.3×10^{-5} mole cm^{-3} s^{-1} at $z = 0.55$ cm and for water formation $(R_{H_2O})_{max}$ is 3.2×10^{-6} mole cm^{-3} s^{-1} at $z = 0.52$ cm.

Discussion and Conclusions

Since species such as H_2CO, HCO, CH_2 and so on do not occur at all in this flame, the CO-disappearance rate ought to be equivalent to the rate of CO_2 formation. However, because of the usual errors in determining fluxes, the CO_2-flux change is not everywhere the precise mirror image of the CO-flux change. In fact, the sum of experimental fluxes deviates between 5 and 10% from the original carbon flux (1.28×10^{-5} mole cm^{-2} s^{-1}). The most reasonable choice for evaluating the rate of CO to CO_2 conversions is, of course, the CO_2 flux gradient. In the first stage of the flame, the rate of CO conversion is so slight that the CO-flux changes less than 1% over 0.05 cm. On the other hand, the error of flux determinations is of the order of 10%. As to the CO_2-flux, its relative increase over the same distance is about 100% and thus much larger than the error in the flux itself. The same argument applies to the whole flame region considered; it can be noted that up to 1700°K ($z = 0.57$ cm) only about a fourth of the CO is consumed (see Figs. 1 and 3).
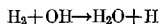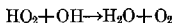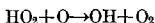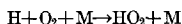
The following elementary reactions can be considered to explain the conversion from CO to CO_2

$$CO + OH \rightarrow CO_2 + H \qquad (1)$$

$$CO + O \rightarrow CO_2 + h\nu \qquad (2)$$

$$CO + O + M \rightarrow CO_2 + M \qquad (2b)$$

$$CO + O \rightarrow CO_2^* \qquad (3)$$

$$CO + HO_2 \rightarrow CO_2 + OH \qquad (4)$$

Neither process (2) nor (3) contributes significantly to CO conversion and both can be neglected in view of considering the low rate constants. Reaction (2) contributes at most 3–5% to the CO conversion, using Baulch's data.[22] Reaction (2b) will be discussed later. Reaction (4) has already raised some controversy in the literature.[23] According to Simonaitis,[24] $k_4 = 3 \times 10^6$ cm^3 mole^{-1} s^{-1} at 300°K, whereas according to Westenberg[25] the value is 6×10^{11}. Using Westenberg's value, the contribution of reaction (4) to the conversion rate would amount to 1×10^{-5} mole cm^{-3} s^{-1} at $z = 0.035$ cm ($T = 400$°K), where HO_2 is still larger than OH (see insert of Fig. 2). On the other hand, the observed total rate of CO consumption amounts to only 7×10^{-7} at this point. Hence, Westenberg's value is at least one order of magnitude too high and CO removal must be ascribed to reaction (1), even in the early stage of the flame, as follows from the mechanism
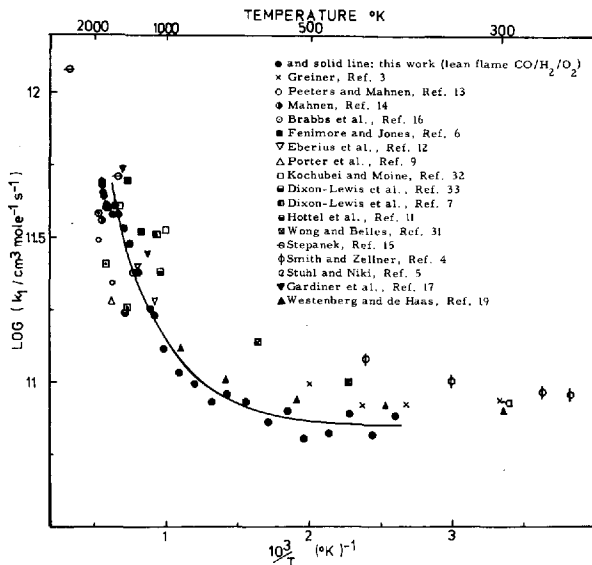
FIG. 4. Rate constants k_1 vs. reciprocal temperature.

given below:

$$H+O_2+M \rightarrow HO_2+M \qquad (5)$$

$$HO_2+H \rightarrow 2OH \text{ or } H_2+O_2 \qquad (6)$$

$$HO_2+O \rightarrow OH+O_2 \qquad (7)$$

$$HO_2+OH \rightarrow H_2O+O_2 \qquad (8)$$

$$H_2+OH \rightarrow H_2O+H \qquad (9)$$

The net rate of H atoms at $400°K$, where branching is definitely negligible, is given by

$$R_H = k_1[CO][OH] - k_5[H][O_2][M]$$
$$+ k_9[OH][H_2] - k_6[HO_2][H] \qquad [4]$$

Taking, at $400°K$, $k_5 = 10^{16}$ cm^6 mole^{-2} s^{-1},[27] $k_9 = 2 \times 10^{10}$ cm^3 mole^{-1} s^{-1},[19] and $k_6 = 3 \times 10^{13}$,[27] and the appropriate values of the concentrations of OH, H, O$_2$, H$_2$, and HO$_2$ at $z = 0.035$ cm, the

above equation reads numerically

$$-(1 \times 10^{-7}) = k_1[CO][OH] - (7 \times 10^{-7})$$
$$+ (1.1 \times 10^{-7}) - (1.1 \times 10^{-7}) \qquad [5]$$

It should be noted that the value of the last term of the above equation may be too low by a factor of two or three due to the uncertainty regarding the HO$_2$ concentration (see above). Thus it follows that the rate of reaction (1) must be equal to $(7 \pm 1) \times 10^{-7}$ which is very near to the observed value (7×10^{-7}) of the total CO disappearance rate, implying that reaction (4) as well as reaction (2b) are negligible even in the earliest part of the flame. The upper limit of k_4 is therefore about two orders of magnitude smaller than the value found by Westenberg.[25] Similar conclusions regarding k_4 can be arrived at based on the steady-state of HO$_2$ at the maximum of its flux, which occurs at about $z = 0.035$ cm. So, we are left with only reaction (1) as the main process for CO$_2$-formation.

The aforementioned mechanism is also in agreement with the fact that OH radicals appear
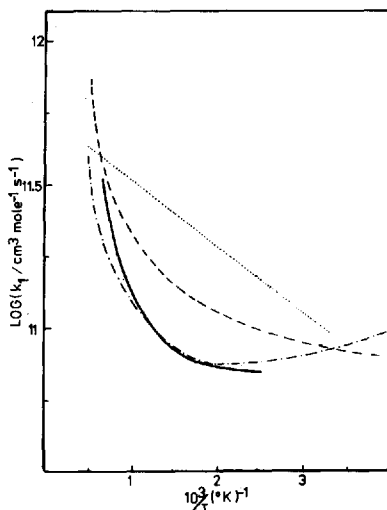
FIG. 5. Comparison of the temperature dependence of k_1. —·—· Dryer's analytical expression ($E_0 = 0$), Ref. 18; – – – – Smith's computed expression ($E_0 = 500$ cal/mole), Ref. 4; ···· Recommended equation from Baulch, et al.[22]; —— Interpolation through the experimental data of this work.

somewhat earlier in the flame than H-atoms and especially than O-atoms. The H-atoms diffusing upstream from the hotter part of the flame as well as those formed from OH via reactions (1) and (9) will react rapidly with O_2 in reaction (5) to produce HO_2. Some of the latter in turn give OH by reactions (6) and (7). In these processes, only O is consumed.

The net reaction rate of CO_2 can be written as

$$R_{CO_2} = k_1\{[CO][OH] - [CO_2][H]/K_1\}   [6]$$

where the equilibrium constant $K_1 = k_1/k_{-1}$ has been computed using thermodynamical data from JANAF Tables.[26] Values for k_1 obtained from Eq. [6] are shown in Fig. 4. The solid line fits the experimental data as measured for the lean $CO/H_2/O_2$ flame. The figure also compares our data with previous experimental values of k_1. The random error of the precision of our results is seen to be better than 15%. The accuracy of our data can best be assessed by comparing them with previous determinations. In the low temperature range, i.e., below 700°K, our results

are about 30% lower than the average values from Refs. 3–5, 19, and 31. Above 1000°K, our data are nearly equal to the averages of previous results.

In Fig. 5, beside the solid curve, Dryer's[18] and Smith's[4] analytical expressions are presented with Baulch's evaluation.[22] Above 1000°K, our results can be fitted to an Arrhenius-type expression with an "apparent" activation energy of 5.7 kcal/mole

$$k_{1app} = 2.3 \times 10^{12} \exp(-5700/RT) cm^3 mole^{-1} s^{-1}$$

$$(T > 1000°K)$$

Below 1000°K, k_1 decreases much more slowly and its value at around 400°K is 8×10^{10} cm^3 $mole^{-1}$ s^{-1}. The marked curvature in the Arrhenius plot of our data can definitely not be ascribed to experimental errors. Such a trend was also suggested recently by Westenberg and de Haas[19] and by Smith.[4] The discrepancies between the different sets of rate constants below 1000°K are so large that, in our opinion, it is not possible yet to discriminate between a very small (500 cal/mole or less) and a precisely zero activation energy (E_0). The rate constant k_{-1} of the reverse reaction can be estimated from k_1 and from the equilibrium constant[26]; it amounts to $k_{-1} = 4.8 \times 10^{14} \exp(-25\,000/RT)$ cm^3 $mole^{-1}$ s^{-1} in a temperature range from 650° to 1800°K.

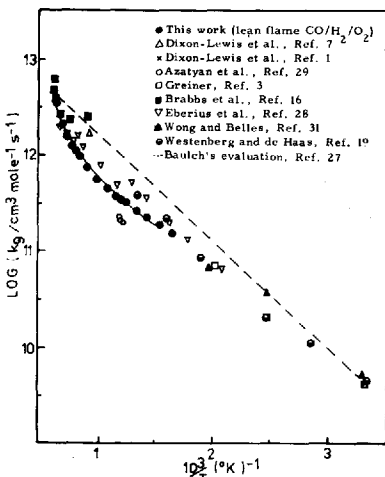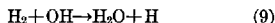FIG. 6. Temperature dependence or rate constant k_9.

The rate constant of the reaction

$$H_2 + OH \rightarrow H_2O + H \qquad (9)$$

has also been measured. The reason for evaluating the rate constant of this reaction is twofold. First, reaction (9) has often been investigated simultaneously with reaction (1) in the past; surprisingly, in many instances a straight line was found for the log k_9/k_1 vs $1/T$ plot[35,36] which would imply that k_9 does not obey an Arrhenius-type of relationship, either. Secondly, the rate constant of process (9) was measured as a control of the reliability of the kinetic method used here. It should be emphasized, however, that the determination of k_9 is much more complex than that of k_1. The rate of the reverse reaction (9) approaches the forward rate much sooner in the flame than is the case for reaction (1). Furthermore since k_9 was derived from the mole flux of H_2O, the contribution of reaction (10) in both directions

$$OH + OH \rightarrow H_2O + O \qquad (10)$$
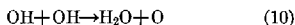
had also to be taken into account. This was done by computing the net rate of reaction (10) and (−10) from the respective observed concentration profiles and using the value of $k_{10} = 6.3 \times 10^{12}$ $\exp(-1100/RT)$ cm^3 mole^{-1} s^{-1} recommended by Baulch, et al.,[27] and in very good agreement with most of the recent determinations except Ref. 17. The rate of process (10) is of the same order of magnitude as the rate of reaction (9).

The rate constant was derived from

$$R_{H_2O} = k_9 \left[(H_2)(OH) - \frac{(H_2O)(H)}{K_9} \right]$$

$$+ k_{10} \left[(OH)^2 - \frac{(H_2O)(O)}{K_{10}} \right] \quad [7]$$

The values of k_9 are shown in Fig. 6; a slight curvature is noticeable. Our experiments in the low temperature range (600°–1000°K) yield data somewhat smaller than those reported by Eberius, et al.,[28] and by Westenberg and de Haas,[19] but larger than those proposed by Azatyan et al.[29] At higher temperatures, our results agree fairly well with those of Brabbs, et al.,[16] and of Eberius, et al.[28] If our data are to be represented by an Arrhenius-type expression, the best fit is obtained for $k_9 = 7 \times 10^{12} \exp(-4400/RT)$ cm^3 mole^{-1} s^{-1} between 600°–1300°K.

REFERENCES

1. DIXON-LEWIS, G., WILSON, W. E., AND WESTENBERG, A. A.: J. Chem. Phys. *44*, 2877 (1966).
2. HERRON, J. T.: J. Chem. Phys. *45*, 1854 (1966).
3. GREINER, N. R.: J. Chem. Phys. *46*, 2795 (1967). GREINER, N. R.: J. Chem. Phys. *51*, 5049 (1969).
4. SMITH, I. W. M. AND ZELLNER, R.: J. Chem. Soc. Faraday Trans. II, *69*, 1617 (1973).
5. STUHL, F. AND NIKI, H.: J. Chem. Phys. *57*, 3671 (1972).
6. FENIMORE, C. P. AND JONES, G. W.: J. Phys. Chem. *62*, 1578 (1958). FENIMORE, C. P. AND JONES, G. W.: J. Chem. Phys. *39*, 1514 (1963).
7. DIXON-LEWIS, G., SUTTON, M. M., AND WILLIAMS, A.: Trans. Faraday Soc. *61*, 255 (1965).
8. JOST, W., SCHECKER, H. G., AND WAGNER, H. G.: Z. Phys. Chem. Neue Folge *45*, 47 (1965).
9. PORTER, R. P., CLARK, A. M., KASKAN, W. E., AND BROWNE, W. E.: *Eleventh Symposium (International) on Combustion*, p. 907, The Combustion Institute, 1967.
10. WESTENBERG, A. A. AND FRISTROM, R. M.: *Tenth Symposium (International) on Combustion*, p. 473, The Combustion Institute, 1965.
11. HOTTEL, H. C., WILLIAMS, G. C., NERHEIM, N. H., AND SCHNEIDER, G. R.: *Tenth Symposium (International) on Combustion*, p. 111, The Combustion Institute, 1965.
12. EBERIUS, K. H., HOYERMANN, K., AND WAGNER, H. G.: *Fourteenth Symposium (International) on Combustion*, p. 147, The Combustion Institute, 1973.
13. PEETERS, J. AND MAHNEN, G.: *Fourteenth Symposium (International) on Combustion*, p. 133, The Combustion Institute, 1973.
14. MAHNEN, G.: Contribution à l'étude du mécanisme de déflagration. Flammes éthylène-oxygène. Dr. Sc. thesis, Université Catholique de Louvain, 1973.
15. STEPANEK, S.: Messung der Geschwindigkeitskonstanten der Elementarreaktion $CO_2 + H \rightarrow CO + OH$ hinter Stosswellen mittels Infrarotspektroskopie. Deutsche Luft-und Raumfahrt, Report 69–79, November 1969.

16. BRABBS, T. A., BELLES, F. E., AND BROKAW, R. S. *Thirteenth Symposium (International) on Combustion*, p. 129, The Combustion Institute, 1971.

17. GARDINER, W. C. JR., MALLARD, M. C., Mc-FARLAND, M., MORINAGA, K., OWEN, J. H., RAWLINS, W. T., TAKEYAMA, T., AND WALKER, B. F.: Fourteenth Symposium (International) on Combustion, p. 61, The Combustion Institute, 1973.

18. DRYER, F., NAEGELI, D. W., AND GLASSMAN, I.: Combust. Flame *17*, 270 (1971).

19. WESTENBERG, A. A. AND DE HAAS, N.: J. Chem. Phys. *58*, 4061 (1973).

20. KENT, J. H.: Combust. Flame *14*, 279 (1970).

21. BONNE, U., GREWER, T., AND WAGNER, H. G.: Z. Phys. Chem. *26*, 93 (1960).

22. BAULCH, D. L., DRYSDALE, D. D., AND LLOYD, A. C.: High Temperature Reaction Data, Report 1, Leeds University 1968; BAULCH, D. L., DRYSDALE, D. D., AND HORNE, D. G.: *Fourteenth Symposium (International) on Combustion*, p. 107. The Combustion Institute, 1973.

23. WESTENBERG, A. A.: Annu. Rev. Phys. Chem. *24*, 77 (1973).

24. SIMONAITIS, R. AND HEICKLEN, J.: J. Phys. Chem. *77*, 1096 (1973).

25. WESTENBERG, A. A. AND DE HAAS, N.: J. Chem. Phys. *76*, 1586 (1972).

26. JANAF Thermochemical Tables, 2nd Edition NSRDS-NBS 37, Washington (1970).

27. BAULCH, D. L., DRYSDALE, D. D., HORNE, D. C., AND LLOYD, A. C.: *Evaluated Kinetic Data for High Temperature Reactions*, Vol. I, p. 119, 1972.

28. EBERIUS, K. H., HOYERMANN, K., AND WAGNER, H. G.: *Thirteenth Symposium (International) on Combustion*, p. 713, The Combustion Institute, 1971.

29. AZATYAN, V. V., ROMANOVICH, L. B., AND SYSOEVA, S. G.: Fiz. Goren. Vzryva *3*, 77 (1967).

30. DIXON-LEWIS, G., SUTTON, M. M., AND WILLIAMS, A.: *Tenth Symposium (International) on Combustion*, p. 495, The Combustion Institute, 1965.

31. WONG, E. L. AND BELLES, F. E.: National Aeronautics and Space Administration Rept. T.N. D-5707, N-70-20629, 1970.

32. KOCHUBEI, V. F. AND MOINE, F. B.: Kinet. Katal. *10*, 1203 (1969). English Trans., p. 992.

33. DIXON-LEWIS, G.: Proc. R. Soc. Lond. *A330*, 219 (1972).

34. HIRSCHFELDER, J. O., CURTISS, C. F., AND BIRD, R. B.: *Molecular Theory of Gases and Liquids*, 2nd Printing, J. Wiley, 1964.

35. FENIMORE, C. P. AND JONES, G. W.: J. Chem. Phys. *39*, 1514 (1963).

36. WILSON, W. E.: J. Phys. Chem. Ref. Data *1*, 535 (1972).

COMMENTS

Frederick Kaufman, University of Pittsburgh, USA. It should be emphasized that "non-Arrhenius" behavior of rate constants must be the rule rather than the exception for all processes which have a small energy barrier. The pre-exponential factor contains ratios of partition functions (or activation entropy terms) which are weak functions of temperature corresponding roughly to T^n dependences with n in the ± 1–2 range. In going from 300°–2000°K, this corresponds to a change of up to 6–8 kcal/mole in the Arrhenius activation energy and points up the danger of reading too much physical reality into a simple two-parameter expression. We are thus presented with the dilemma that experimental uncertainties do not warrant the use of more than two parameters to fit k vs T data over more limited temperature ranges whereas physical reality does require more complexity.

Authors' Reply. Perhaps the only surprising fact is that the expression "non-Arrhenius reaction" was introduced in the language of chemical kinetics only quite recently. Actually, including a T^n type function in the rate constant expression is in many cases not sufficient to represent the temperature dependence of the "pre-exponential factor" over an extended temperature range.

Assuming a completely linear HO–CO activated complex and zero activation energy barrier, it follows from transition state theory that k_1 should vary with temperature as

$$k_1 = C \cdot T^{-3/2} \prod_6 \left[1 - \exp\left(-h\nu_i/kT\right)\right]^{-1} / \prod_2 \left[1 - \exp\left(-h\nu_j/kT\right)\right]^{-1}$$

where the six ν_i are the vibration frequencies of the complex (minus one), and the two ν_j are those of the reactants. In this case, k_1 should show a negative temperature dependence at the lower temperatures (i.e., $T^{-3/2}$).

The fact that k_1 appears to be essentially con-

stant from about 300° to 600°K could indicate that a few of the transition state vibration frequencies are only a few hundred cm⁻¹. An alternative explanation for the near constancy of k_1 at low temperatures is that the activation energy barrier is not strictly zero but rather about 1 kcal/mole.

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W. S. Nip, University of Toronto, Canada. During a recent investigation[1] of the reaction of H atoms with NH_3, we had occasion to measure also the rate of the reaction between H and CO_2. k_{-1} for the reaction $CO + OH \rightarrow CO_2 + H$ was determined over the temperature range 1600–2100°K by monitoring the pseudo-first order decay of CO_2 in the partial equilibrium region of a shock-heated 0.2% CO_2/9% H_2/1% O_2 mixture in inert diluent. We obtained

$$k_{CO_2+H} = 10^{14.47 \pm 0.35} \exp(-29400 \pm 3100/RT)$$

and hence

$$k_{CO+OH} = 10^{12.51} \exp(-8200/RT) \, cm^3 \, mole^{-1} \, sec^{-1}$$

with the activation energies in cal mole⁻¹. This value of k_1 agrees well with that reported in the present paper.

REFERENCE

1. Dove, J. E. and Nip, W. S.: Canad. J. Chem. *52*, 1171 (1974).

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H. Eberius, DFVLR, Institut für Reaktionskinetik, W. Germany. The accuracy of data derived from flame measurements is influenced by several parameters and may be considerably different for different points in the flame. For example there is a finite concentration of CO_2 just above the burner whereas the rate of CO_2 formation is rather small. This shows the importance of diffusion in this region. On the other hand the diffusion is disturbed by the sampling probe. Can you give a figure of the absolute accuracy of the rate constant derived for the reaction $CO + OH \rightarrow CO_2 + H$ and how the accuracy changes in the temperature range from 400°K up to the final temperature?

Authors' Reply. In order to assess the accuracy of rate constants derived as in the paper, one could consider the (somewhat simplified) equation by which the net reaction rate R_i of a species is computed

$$R_i \simeq N_0 T_0 \left[\left(\frac{v_0}{T_0} - \frac{d(D_i/T)}{dz} \right) \frac{dX_i}{dz} - \frac{D_i}{T} \frac{d^2 X_i}{dz^2} \right].$$

Where v_0 is the initial stream velocity at temperature T_0 and N_0 the corresponding total molar concentration, D_i is the local (binary) diffusion coefficient at temperature T, X_i is the mole fraction and z the distance coordinate.

For CO_2 in the considered flame, the coefficient of dX/dz is always positive and never very different from v_0/T_0. Clearly, relative errors are largest here where dX/dz and d^2X/dz^2 have the same sign, i.e. at the low temperature side of the flame. The absolute value of the second term (diffusional contribution) is about 65% of the first term at 400°K, and about 25% at 1775°K.

Assuming possible errors of 10% in the derivatives of X and in the ratio D/T, one can estimate the maximum cumulative error in R_i (all individual errors influencing the result in the same direction). For our data, the maximum possible error would then be 70% at 410°K, about 35% between 600 and 1200°K, and less than 20% above 1500°K. Of course, the average probable errors will be a good deal less. As far as the values of the rate constant are concerned, an additional error of some 10% has to be taken into account in view of the uncertainty of the OH-calibration factor.

That the effect of the sampling probe on diffusion processes is not too important is in our opinion demonstrated by the following: in a CH_4/O_2 flame—where diffusion is more important than in the $CO/H_2/O_2$ flame—the mole fluxes of the reaction CH_4 and the product H_2O, as computed using Eqs. (1) and (2) of the paper, remain very nearly equal to their initial values (zero for H_2O) up to about 1100°K, although the respective mole fractions deviate greatly from the fresh-gas values.[1] The fluxes must indeed be constant in that region since chemical reaction does not occur yet to a significant extent.

REFERENCE

1. Peeters, J. and Mahnen, G.: *Fourteenth Symposium (International) on Combustion,* p. 133, The Combustion Institute, 1973.