Performance of Cylindrical Flow Reactors in a Kinetic Study of the Isomerization of Cyclopropane

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The interaction of mass and heat transfer with chemical reaction has been investigated for thermally induced reactions in cylindrical flow reactors. Theoretical expressions indicated that measured rate constants would be less than true rate constants under certain circumstances. These expressions were tested by experiments on the isomerization of cyclopropane near 900 K. The effect of axial mass transfer on the measured rate constant was well represented by two expressions from the literature. According to one of these, the measured rate constant would be reduced by a fraction approximately equal to $kr^2/(48D) + kDt^2/l^2$, where k is the true rate constant, D, the diffusion coefficient, t, the average residence time, and l, the reactor length. According to the other expression, an upper limit to the fractional reduction would be $kr^2/(48D) + kDt^2/l^2$ or $0.5\ kt$, whichever is smaller. For incomplete radial heat transfer, a new expression has been derived; it was found to adequately represent the experimental data. According to this expression, the fractional reduction in the measured rate constant is approximately $r^2/\kappa t$, where κ is the thermal diffusivity. These expressions may be used to assist in selecting suitable conditions for kinetic experiments.

Introduction

In the use of a laminar flow reactor, it is customary to assume that all the entering gas molecules spend the same time in the reactor and warm to reaction temperature instantaneously at the inlet, and that the pressure is constant throughout the tube. In many cases, these assumptions are necessary due to the complexity of the reactions being studied, which often involve free-radical intermediates. For simple, first-order reactions, these assumptions allow one to obtain the rate constant by the following simple expression:

$$-\ln (C/C_0) = k_{\text{app}}t \qquad (1)$$

where C_0 and C are the reagent concentrations entering and leaving the reactor, respectively, k_{app} is the apparent first-order rate constant, and t is the residence time.

In order to use eq 1 reliably, it is important for one to understand the limitations of these assumptions. As an example of the errors possible, it has been reported that a change in reactor size can cause a twofold change in measured rate constants.[1] It is a simple matter to measure the pressures at the inlet and outlet to confirm that the pressure is constant. It is more difficult to test the assumptions of plug flow (perfect radial mass transfer, negligible axial diffusion) and constant temperature (perfect radial heat transfer, negligible axial heat transfer at the reactor entrance and exit). Various theoretical expressions are available in the literature, but there have been relatively few experimental tests.

In the present article, the latter two assumptions have been experimentally tested by using the thermal isomerization of cyclopropane as a model first-order reaction.

Mass Transfer. The occurrence of reaction causes the concentration of reactant to decrease as it proceeds through the reactor. This concentration gradient in turn causes the reactant to diffuse toward the exit. Because of diffusion, the residence time of reactant molecules is less than t, the value calculated from the average linear velocity and the reactor length. The rate constant calculated from eq 1 would be less than the correct value.

The usual theoretical approach to this problem is to neglect radial concentration gradients and solve the one-dimensional, axial continuity equation with appropriate boundary conditions. Supposing that $C = C_0$ at the reactor entrance and that reaction continues to extinction downstream from the sampling point, one obtains[2-4]

$$k_{\text{app}} = \frac{l^2}{2Dt^2}[(1 + 4kDt^2/l^2)^{1/2} - 1] \qquad (2)$$

where l is the reactor length, D the diffusion coefficient, t the residence time, defined in the preceding paragraph, and k the true rate constant.

According to eq 2 the fractional error in k_{app} is kDt^2/l^2 to a first approximation. This may be used as a "rule of thumb" to determine suitable limits for experimental conditions.[2]

When the parabolic velocity profile is taken into account, it has been shown that D may be replaced by an effective diffusion coefficient, G, equal to $D + r^2l^2/(48Dt^2)$, where r is the reactor radius.[5,6] Equation 2 then becomes[7]

$$k_{\text{app}} = \frac{l^2}{2Gt^2}[(1 + 4kGt^2/l^2)^{1/2} - 1] \qquad (3)$$

If eq 3 is expanded as a Taylor series in t^2, one finds the fractional error in k_{app} is approximately $kr^2/(48D) + kDt^2/l^2$.

For a thermally induced reaction, as in the present case, more realistic boundary conditions would allow for back-diffusion of products at the inlet and for quenching of the reaction at the reactor outlet.[8] Mulcahy and Pethard[9] have derived an expression which leads to

$$k_{\text{app}} = -t^{-1} \ln [2/([1 + \phi] \exp([(1 + 2\mu s)^{1/2} - 1]/\mu) + [1 - \phi] \exp(-[(1 + 2\mu s)^{1/2} + 1]/\mu))] \qquad (4)$$

where $\phi = (1 + \mu s)/(1 + 2\mu s)^{1/2}$, $\mu = 2Gt/l^2$, and $s = kt$. Values of k_{app} have been calculated by computer with eq 4. Contours of constant k_{app}/k are shown in Figure 1 as a function of s and μs. Detailed examination of these numerical results indicates that the fractional error in k_{app} is approximately $0.5s/(1 + \mu^{-1})$. When μ^{-1} is much greater than unity, the fractional error reduces to $0.5\mu s$, which is the same as the limiting error from eq 3 ($kr^2/(48D) + kDt^2/l^2$). When μ^{-1} is much less than unity, the fractional error becomes $0.5s$ or $0.5kt$. The product, $0.5kt$, is approximately half the fractional conversion, so errors should be small at small conversion. For intermediate values of μ^{-1}, the fractional error is less than $0.5\mu s$ or $0.5s$, whichever is smaller.

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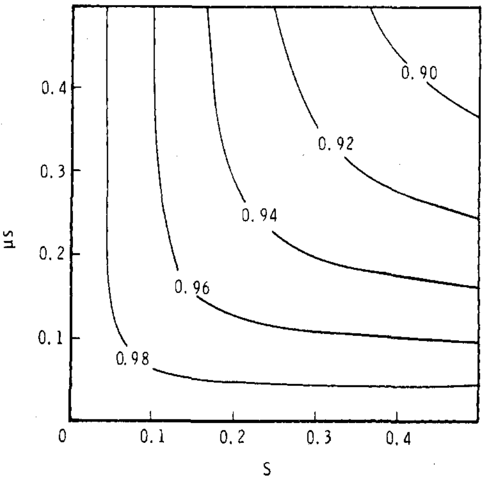

Figure 1. A graphical representation of eq 4 as a function of s and μs. The curves represent contours on which k_{app}/k has the fixed value (e.g., 0.98) shown.

Incomplete Radial Heat Transfer. The assumption that molecules warm to the reactor temperature in a negligible time is no longer valid as the residence time itself decreases. This effect, considered by Mulcahy and Pethard[9] for a first-order reaction, is expressed by

$$\frac{k_{app}}{k} = 1 - \frac{r^2}{3.658\kappa t}\left[0.577 + \ln\left\{\frac{E_A}{R}(0.82)\left(\frac{T_w - T_i}{T_w^2}\right)\right\}\right] \qquad (5)$$

where κ is the coefficient of thermal diffusivity, E_A, the activation energy, T_w, the reactor temperature, T_i, the temperature of entering reactant, and R the gas constant. This expression indicates that, for a given reactor, the apparent rate constant decreases hyperbolically as the reaction time decreases.

In a conventional flow system, similar to the one adopted here, measurable first-order rate constants range from about 10^{-5} to 10 s^{-1}. For first-order reactions, preexponential factors usually lie between 10^{12} and 10^{17} s^{-1}. To have a measureable value of k, then, it may be shown that E_A/RT_w must be between 30 and 60. If $(T_w - T_i)/T_w$ is between 0.1 and 0.7, the factor in square brackets in eq 5 must be close to 3. As an approximate guide, this examination of the equation indicates that the fractional experimental error caused by incomplete heat transfer must be about $r^2/\kappa t$. (See also ref 9.)

The treatment of Mulcahy and Pethard made use of the "cup-mixing" temperature, which gives more weight to the temperature near the axis where the flow velocity is greater. This approach neglects radial diffusion, which would permit a molecule to experience temperatures near the wall and near the axis before exitting or reacting. An alternative treatment by Gilbert[10] takes simple averages rather than cup-mixing averages, in effect assuming perfect radial diffusion or plug flow. In the present article we are concerned with relatively small perturbations caused by incomplete heat transfer. For gases, the thermal diffusivity and molecular diffusion coefficient are similar in magnitude; deviations from perfect radial mixing should be minor and simple averages are to be preferred.

Mulcahy and Pethard have shown, however, that Gilbert's expression does not have the correct limiting behavior for slow flows. We have carried out a derivation analogous to that of Mulcahy and Pethard, starting with the average temperature in a cross section of the reactant gas:

$$T_{av} = T_w - (T_w - T_i)0.58\exp(-m_0 x) \qquad (6)$$

where $m_0 = 3.658\kappa t/(lr^2)$, x is the distance along the reactor, and the factor, 0.58, has been calculated by numerical integration of the radial temperature function in ref 11.

T_w in the above expression should be the temperature of the inside of the reactor wall. In practice, one measures either the temperature of the outside of the reactor wall or the temperature in an air space around the reactor. The case of an internal thermocouple well will not be considered here, as this would distort the velocity profile assumed in deriving eq 6.

The temperature of the outside of the reactor may be calculated by considering the heat flux at the inside of the wall. According to ref 11, the heat flux per unit area into the gas is given by

$$q = 1.499\lambda(T_w - T_i)r^{-1}\exp(-m_0 x) \qquad (7)$$

where λ is the thermal conductivity of the gas. Furthermore, the heat flux from the reactor wall is[11]

$$q = \frac{\lambda_1(T_1 - T_w)}{r \ln r_1/r} \qquad (8)$$

where λ_1 is the thermal conductivity of the wall and T_1 and r_1 are the external temperature and radius of the wall. Equating these two fluxes, one finds

$$T_w = T_1 - 1.499(T_w - T_i)\lambda\lambda_1^{-1}\ln(r_1/r)\exp(-m_0 x) \qquad (9)$$

Similarly, one may calculate the temperature, T_2, in the air space around the reactor, at a distance, r_2, from the axis. If λ_2 is the thermal conductivity of air, the result is

$$T_2 = T_1 + 1.499(T_w - T_i)\lambda\lambda_2^{-1}\ln(r_2/r_1)\exp(-m_0 x) \qquad (10)$$

Combining eq 6, 9, and 10, one obtains

$$T_{av} = T_2 - F(T_w - T_i)\exp(-m_0 x) \qquad (11)$$

where

$$F = 0.58 + 1.499\lambda[\lambda_1^{-1}\ln(r_1/r) + \lambda_2^{-1}\ln(r_2/r_1)] \qquad (12)$$

Following the integration procedure of Mulcahy and Pethard,[9] we obtain the result:

$$\frac{k_{app}}{k} = 1 - \frac{r^2}{3.658\kappa t}\{0.577 + \ln[E_A F(T_w - T_i)/(RT_w^2)]\} \qquad (13)$$

In using this equation, one can assume that T_w is the measured wall temperature, T_1 or T_2. Usually the factor, F, lies between 0.6 and 1.0 and the fractional error caused by incomplete heat transfer remains close to $r^2/\kappa t$.

Cyclopropane Isomerization. The isomerization of cyclopropane is believed to be a simple, first-order homogeneous reaction,[12] which makes it a suitable choice to test the above theoretical models.

The equilibrium constant for the isomerization may be calculated from thermochemistry[13] to be 2.8 × 10^3 at 900 K. Even at 98% conversion the rate of the forward reaction should be 50 times as fast as the reverse reaction. The reverse reaction may be neglected in calculations.

The product, propylene, may also decompose, producing methane, ethylene, and smaller amounts of other products. From experimental data in the literature,[13] one can calculate an apparent first-order rate constant of 2.3 × 10^{-3} s^{-1} for propylene decomposition at 50 torr and 897 K. This is two orders of magnitude slower than the rate constant for cyclopropane isomerization and should not interfere with observed propylene yields.

The rest of this article describes experimental measurements of k_{app} for cyclopropane isomerization at various

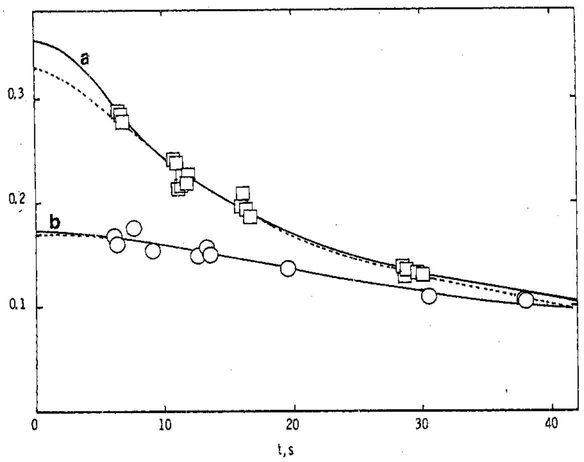

Figure 2. Apparent rate constants for the isomerization of cyclopropane at 100 torr and 916 K (□) and 50 torr and 898 K (○), using 18- and 45-cm long furnaces, respectively, and a 17-mm diameter reactor. Curves are least-squares fits to eq 3 (---) and eq 4 (—).

residence times in reactors of different sizes. The results are compared with the theoretical models described earlier.

Experimental Section

A general description of the apparatus has been given elsewhere.[14]

Quartz flow reactor tubes of 2, 3, 4, 6, and 17 mm i.d. were heated by 18- or 45-cm long, nichrome-wound resistive furnaces. In the case of the 6- or 17-mm reactors, a thermocouple was placed in a 4-mm o.d. tube, which was placed along the outside of the reactor. In certain specified experiments, the thermocouple tube was placed along the reactor axis. For the 2-, 3-, and 4-mm reactors, external thermocouples were placed inside coaxial quartz tubes of 8, 11, and 11 mm i.d., respectively. The thermocouple was moved along the reactor to take a temperature profile, but during an experiment it was positioned at the midpoint to enable correction of any drift of temperature. The temperature profile was used in a computer program[14] to calculate the length of the reaction zone.

Reactant and product concentrations were analyzed in a gas chromatograph with a 2-m, 10% silicone oil on Chromosorb W column at 0 °C. Cyclopropane (Matheson) was degassed at nitrogen-boiling and isopentane-melting temperatures. It contained about 0.3% propylene as an impurity.

Results

Apparent rate constants were calculated from eq 1. Where the conversion was less than one-half, cyclopropane concentrations, C, were calculated from C_0 and the measured concentration of propylene.

Mass Transfer. According to the interpretation of eq 4 and Figure 1, the effect of mass transfer on k_{app} becomes significant when *both* $0.5kt$ and $kr^2/(48D) + kDt^2/l^2$ increase to values close to unity. This occurs when the conversion and reactor radius are large and when the reactor length is short. Conversion becomes large when the temperature is high, when the flow rate is slow, and when the radius and length are large. In these experiments, the temperature was limited to about 900 K or less by the furnace construction and the flow rate had to be 2×10^{-6} mol s^{-1} or greater to be accurately measured. With these constraints, the effect of mass transfer could only be observed in the reactor of largest radius.

In Figure 2 are shown plots of the apparent rate constants as a function of residence time for experiments with the 17-mm diameter reactor. The reaction was performed at 916 K and 100 torr with an 18-cm long furnace and external thermocouple for Figure 2a, and at 898 K and 50 torr with a 45-cm long furnace and internal thermocouple well for Figure 2b. In both cases, as the reaction time increased, the apparent rate constant decreased.

TABLE I: Diffusion Coefficients and Rate Constants from Least-Squares Fits to Figure 2

conditions	theor model	D, cm^2 s^{-1}	k, s^{-1}
916 K, 100 torr,	eq 3	4.5 ± 0.4	0.33 ± 0.01
Figure 2a	eq 4	7.5 ± 1.2	0.35 ± 0.03
898 K, 50 torr,	eq 3	10.5 ± 1.4	0.171 ± 0.004
Figure 2b	eq 4	13 ± 2	0.172 ± 0.007

The dashed and solid curves were obtained by nonlinear least squares with eq 3 and 4, respectively, as models and D and k as parameters. Values of D and k found are listed in Table I. Here and elsewhere, quoted uncertainties are standard deviations.

Incomplete Radial Heat Transfer. According to eq 5 or 13, incomplete radial heat transfer becomes significant as $r^2/(\kappa t)$ increases. The thermal diffusivity is inversely proportional to pressure. The residence time is proportional to pressure and reactor volume ($\pi r^2 l$) and inversely proportional to flow rate. One would expect to observe the effect of incomplete heat transfer in short reactors at fast flow rates.

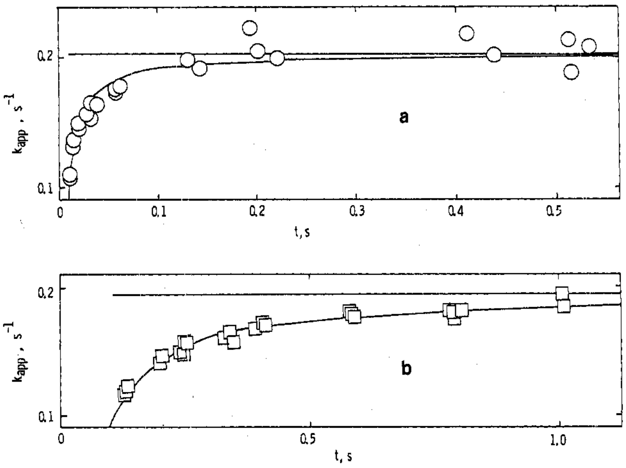

Figure 3. Apparent rate constants at 50 torr and 897 K obtained by using 4- (○) and 17-mm (□) diameter reactors and an 18-cm long furnace. Curves are least-squares fits to eq 13. The horizontal lines show the values of the parameter, k.

Plots of apparent rate constants as a function of time are shown in Figure 3 for the reaction carried out at 50 torr and 897 K with the 18-cm long furnace. Figure 3a was obtained by using a 4-mm diameter reactor and Figure 3b, a 17-mm reactor. These plots clearly illustrate the lowering of apparent rate constants at short times.

The curved lines were obtained by nonlinear least squares with eq 13 as the model and κ and k as parameters. Because of the high thermal conductivity of quartz, the term, $\lambda_1^{-1} \ln r_1/r$, in eq 13 was neglected. The thermal conductivity of air was taken[15] as 1.5×10^{-4} cal cm^{-1} K^{-1} s^{-1}. The position, r_2, of the thermocouple was assumed to be half way between the containing walls. An initial estimate of κ was found by using $F = 0.58$. The thermal conductivity of cyclopropane, λ, required in eq 12, was then found from the relation $\lambda = \kappa C_0 C_p$, where C_p is the heat capacity of cyclopropane.[16] Successive values of κ and λ were found from fits to eq 13 and from $\lambda = \kappa C_0 C_p$, respectively. For experiments at 50 torr and 897 K, final values of κ were calculated to be 8.3 ± 0.5, 12.6 ± 0.3, 9.4 ± 0.6, and 12.2 ± 0.4 cm^2 s^{-1} for reactors of 3-, 4-, 6-, and

TABLE II: Rate Constants at 50 torr in Different Reactors

furnace length[a]	reactor diam, mm	thermocouple placement[b]	k,[f] s^{-1}
L	2	O	0.176[c]
L	17	I	0.176[c]
L	17	I	0.172[d]
S	3	O	0.210[e]
S	4	O	0.201[e]
S	6	O	0.202[e]
S	17	O	0.188[e]
S	17	I	0.207[c]

[a] L = long (45 cm), S = short (18 cm). [b] O = outside and I = internal thermocouple. [c] From experiments where the effects of axial mass transfer and incomplete heat transfer were minimal. [d] From a least-squares fit to eq 4. [e] From least-squares fits to eq 13. [f] Adjusted to 897 K.

17-mm diameter, respectively. The average was 11 ± 2 cm^2 s^{-1}. Values of k are listed in Table II. The appropriate values of k are also shown as the horizontal lines in Figure 3, a and b.

Reactors of Different Sizes. Table II shows rate constants obtained at 50 torr and about 897 K by using different reactor sizes. Rate constants either were obtained in conditions wherein the effect of axial mass transfer and incomplete radial heat transfer were minimal or else were calculated by least-squares fits to eq 4 or 13. Because of the impossibility of exactly reproducing reactor temperatures from day to day, observed rate constants were adjusted to 897 K, using a reported Arrhenius activation energy[12] of 65 500 cal mol^{-1}.

Discussion

Comparison of Rate Constants. On the average, rate constants in Table II, determined with the short furnace, were 14% larger than those determined with the long furnace. Temperature measurements were usually made at 2.5-cm intervals along the reactor. The size of these intervals, 15% of the length of the short furnace, would lead to imprecision in the calculated length of the reaction zone and, hence, in the residence times. We believe the data obtained with the long furnace to be more reliable. For a fixed furnace length, the rate constants are in satisfactory agreement.

Mass Transfer. The results in Figure 2 clearly demonstrate the effect of mass transfer on the apparent rate constant.

The diffusion coefficient is proportional to $T^{3/2}$ and inversely proportional to pressure.[17] Adjustment of the values of D in the upper two lines of Table I to 50 torr and 898 K yields $D = 8.7 \pm 0.8$ cm^2 s^{-1} (eq 3) and 15 ± 2 cm^2 s^{-1} (eq 4), in agreement with the values in the lower two lines of Table I. When the reported Lennard-Jones parameters for cyclopropane were used,[18] a theoretical value of the diffusion coefficient was calculated by the method of ref 17 to be 8 cm^2 s^{-1} at 50 torr and 898 K.

Comparing the two models, eq 3 provides values of D in better agreement with the theoretical value and values of k and D with smaller standard deviations. However, eq 4 is based on more realistic boundary conditions and would be preferred on theoretical grounds. In Figure 2a the difference in the estimated values of k, using the two models, is 8%. Clearly, unless one is certain that a particular model is accurate, or unless the extrapolation is short, there is considerable risk in extrapolating apparent rate constants to find a "true" rate constant.

Fortunately, axial mass transfer is unlikely to have a significant effect in most experiments. To reduce the apparent rate constant by 10% in Figure 2b, the conversion had to be increased to 83%, which is outside the range of most experiments. As noted earlier, at the temperature and flow rates of these experiments, a mass transfer effect could not be observed with reactor diameters smaller than 17 mm.

Incomplete Radial Heat Transfer. The early stage of the reaction is of great importance in kinetic study of more complicated reactions. With flow reactors, this stage of reaction can be approached by increasing the flow rate. With fast flows, incomplete heat transfer could be serious, unless considered properly.

From the kinetic theory of gases,[17] the predicted value of κ at 897 K and 50 torr is 6 cm^2 s^{-1}. By extrapolation of low temperature measurements,[16] κ has been estimated to be 7 cm^2 s^{-1}. Least-squares fits to the experimental data lead to a larger value, 11 ± 2 cm^2 s^{-1}.

The observed diffusion coefficients were also larger than the predicted values. The similarity between the observed values of κ and D is encouraging. However, the objective of these experiments was to explore the limitations of flow reactors, not to measure precise transport coefficients. The experimental system differs from the model assumed in deriving eq 3, 4, and 13 in at least two important respects:

(i) The theory assumed that the variation of temperature along the reactor wall was a step function, rising abruptly from room temperature to the reaction temperature. In reality, the temperature rise must be gradual. Therefore, the reagent would be warmed somewhat before entering the furnace. Complete heat transfer would then require less time inside the furnace and a least-squares fit would lead to a larger apparent value of κ.

(ii) Because of the interaction of heat transfer and flow, the radial velocity function would be more sharply peaked[11] than the simple parabola assumed in deriving eq 3–13. Just as inclusion of a parabolic profile led to an effective diffusion coefficient, G, which was greater than D, a more sharply peaked profile could lead to an even greater apparent value of D.

Conclusion

Equation 13 appears to correctly represent the dependence of observed rate constants on heat transfer. Under the present experimental conditions, the effect of axial mass transfer on k_{app} could only be observed with one reactor and it was not possible to determine whether of eq 3 or 4 better represented the data. Until an experimental distinction between these equations is possible, the authors recommend the use of eq 4, which is based on more realistic boundary conditions. Equation 4 should only be used to extrapolate to find true rate constants when the extrapolation is short.

As indicated in the Introduction, the fractional error in k_{app} according to eq 4 may be estimated as $0.5s/(1 + \mu^{-1})$. An upper limit to the error is $0.5kt$ or $kr^2/(48D) + kDt^2/l^2$, whichever is smaller. The fractional error caused by incomplete heat transfer is approximately $r^2/\kappa t$. These expressions may be used as "rules of thumb" to guide the choice of experimental conditions for kinetic experiments with flow reactors.

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COMMUNICATIONS TO THE EDITOR

EPR Study on Spatial Distribution of Reaction Intermediates in a Free-Burning Methane–Air Flame

Sir: In the course of a study to exploit a wider application of the electron paramagnetic resonance (EPR) technique to the study of chemical combustion,[1] we recently succeeded in detecting H atoms, O atoms, and OH radicals, together with molecular O_2, and in determining their distribution in a methane–air flame burning freely in open air (a Bunsen-type flame) by means of the ordinary EPR technique combined with a low-pressure sampling of burning gases. It is essential to know the spatial distribution of not only stable but also unstable chemical species in combusting systems for the fundamental elucidation of combustion chemistry. The unstable species of primary importance are mostly paramagnetic atoms and free radicals. Their EPR detection has been suggested to be useful for combustion study,[2] but its application has been almost limited to combustion at low pressure[3-6] in focussing the elucidation of reactions in a primary reaction zone.

In the present study, a flame was obtained from a methane–air mixture (0.8 of the stoichiometric composition of air) flowing at a rate of 1000 cm^3/min through a burner lip of 0.8 cm diameter. The brilliant inner flame was almost flat at ca. 1 mm from the burner lip, and the faint outer cone flame was 10 mm high. The combusting gases were sampled through a pinhole of an uncooled quartz probe and led to a cylindrical TE_{01n} EPR cavity (Varian, E-235). The quartz pillbox was set in the cavity to facilitate the detection of the OH radicals through their electric dipole transition.[7] The sample gas took about 0.8 ms to reach the cavity and was measured at 0.2 torr.

Figure 1A shows a typical example of EPR spectra of the sample gases. The spectral lines are assigned in the order of the increasing magnetic field to H ($^2S_{1/2}$), OH ($^2\pi_{3/2}$, $J = 5/2$, $m_j^+ \leftrightarrow (m_j - 1)^-$), O ($^3P_2$ and $^3P_1$), OH ($^2\pi_{3/2}$, $J = 3/2$, $m_j^+ \leftrightarrow (m_j - 1)^-$), and OH ($^2\pi_{3/2}$, $J = 3/2$, $m_j^- \leftrightarrow (m_j - 1)^+$). The rotational temperature of the OH radicals was estimated to be 400 K in the cavity from the relative spectral intensities. The spectrum consisting of many lines due to O_2 was recorded upon turning off the flame (see Figure 1B). Clearly, the O_2 molecules were consumed in the flame.

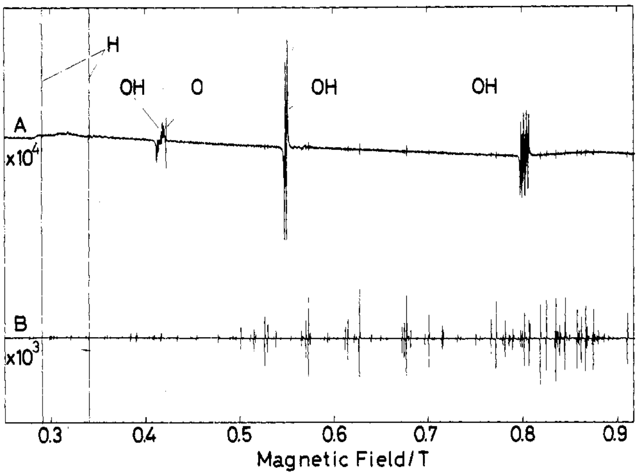

Figure 1. EPR spectra of sampled gases from a methane–air Bunsen flame (A) and from unburned methane–air premixed gas (B). The pressure of the sampled gas in the EPR cavity is about 0.2 torr.

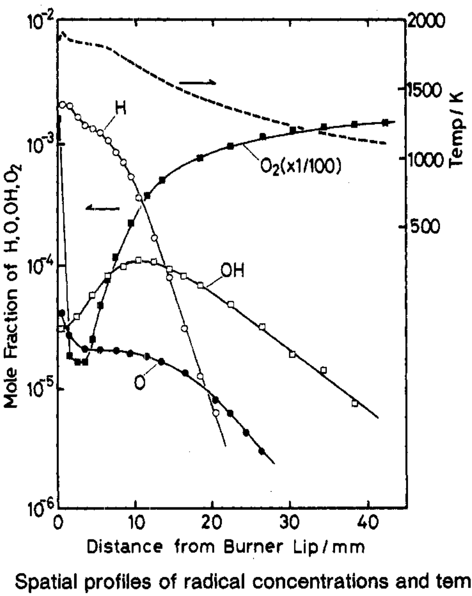

Figure 2. Spatial profiles of radical concentrations and temperature in the methane–air Bunsen flame with an air excess ratio of 0.8.

By moving the sampling pinhole along the center axis of the flame, the spatial distribution of the paramagnetic species was determined as shown in Figure 2. The concentrations of the H and O atoms were calibrated with O_2 and that of the OH radicals with NO. Temperature in the flame was assumed to be unchanged at 1800 K, though it decreased from 1950 K near the burner lip to 1200 K at

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