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High Temperature Photochemistry (HTP): Kinetics and Mechanism Studies of Elementary Combustion Reactions over 300-1700 K

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High Temperature Photochemistry (HTP): Kinetics and Mechanism Studies of Elementary Combustion Reactions over 300-1700 K

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Abstract—The HTP technique makes it possible to study the kinetics and mechanisms of elementary reactions of important combustion-related free radicals over wide temperature ranges. It utilizes standard flash photolysis methods to generate the radicals and resonance fluorescence diagnostics to follow their time-dependent concentrations, from which kinetic and mechanistic information is derived. The use of a single technique to explore the kinetics of reactions over wide temperature ranges gives high confidence in the experimentally determined temperature dependences and provides a precise data base for both theoretical and empirical extrapolation of kinetic parameters to other temperatures of interest. Results obtained in HTP studies of the reactions $O + CH_4$, $H + H_2O$, $OH + CH_4$, and $OH + C_6H_6$ are discussed.

INTRODUCTION

The development of combustion devices which can burn fossil fuels more effectively and emit less pollution than is currently possible requires, among other inputs, reliable kinetic data on important elementary reactions occurring during the combustion process. The more reliable kinetic information that is becoming available is due to significant advances in both experimental and predictive techniques. This paper describes one experimental technique, High Temperature Photochemistry (HTP), which was developed to measure the rate coefficients of elementary hydrocarbon combustion reactions over a wide temperature range, *e.g.*, from 300 to 1800 K. Reliable rate coefficient values over this large temperature range provide a data base for design calculations and for comparison with theoretical studies, and serve as benchmarks for developing other new experimental methods.

The technology for producing controlled high temperature environments in which to carry out kinetic studies was developed and used in the High Temperature Fast Flow Reactor (HTFFR) by Fontijn and coworkers (1979). In HTP this technology was merged with the flash photolysis/resonance fluorescence (FP/RF) technique to produce a method suitable for determining the rate coefficients of reaction of labile free radicals. HTFFR technology makes it possible to measure rates at high temperature; photochemical methods avoid practically all of the gas-surface interactions which may present kinetic problems at high temperature.

This paper summarizes the results of HTP studies on four reactions of importance in hydrocarbon combustion. Some limitations on the use of the HTP technique are also discussed.

APPARATUS AND EXPERIMENTAL METHODS

The HTP apparatus has been described previously in detail (Felder *et al.*, 1980). The major changes made in the apparatus since that publication have been described in subsequent work discussed below. Briefly, the apparatus consists of an

alumina reaction tube, resistively heated and thermally insulated. Reaction zone temperature, pressure, and the concentrations of the individual gases can be varied independently. Metered flows of gases are admitted near the upstream end of the reactor and/or through a movable cooled inlet at any axial position within the reactor. The cooled inlet is used to vary the residence time of the reagents in the hot reactor tube. In the studies reported here, no dependence of the kinetic data on residence time was observed when one or more of the reagents was added through the cooled inlet. At high temperatures, the use of the cooled inlet minimizes reagent thermal dissociation.

Experiments are carried out in N_2 (for O-atom measurements) or Ar (for OH measurements to avoid N_2 quenching of the OH resonance fluorescence diagnostic radiation) diluent obtained as boil-off from the liquids. High purity reactant gases are metered directly from cylinders using inverted buret or sonic orifice flow meters. For reagents which are liquids at room temperature, vapors are produced by bubbling some atmospheric pressure diluent through a thermostatted reservoir of the thoroughly degassed high purity liquid.

The optical plane (reaction zone) of the reactor is shown schematically in Figure 1. The O atoms or OH radicals are generated from the vacuum ultraviolet photolysis of an appropriate photolyte (O_2 or CO_2 for O atoms, H_2O for OH) using either a flashlamp or a pulsed low pressure microwave powered rare gas discharge lamp. The concentrations of the radicals are monitored using resonance fluorescence (for O and OH) or chemiluminescence (for O atoms). The sources of diagnostic radiation for resonance fluorescence are microwave excited low pressure (≈ 0.2 kPa) discharge flow lamps containing O_2 (<1 percent in Ar or He for O atoms) or H_2O (3 percent in He for OH). The resonance fluorescence radiation is viewed at right angles to the flow and photolysis lamps using appropriate windows (e.g., LiF or CaF_2 windows for the 130 nm O-atom radiation; Suprasil windows and optics for the 310 nm OH radiation) and detectors (a bare magnetically focused electron multiplier for O-atom fluorescence; a cooled photomultiplier tube with 310 nm interference filter for OH). For chemiluminescence measurements of O-atom concentrations, NO is added to the diluent flow ($\leqslant 1$ percent) into the HTP reactor and the $O + NO \rightarrow NO_2{}^* \rightarrow NO_2 + h\upsilon$ chemiluminescence is observed in the 500–600 nm region using a photomultiplier and cutoff glass filtered detector. For both resonance fluorescence and chemiluminescence, the signal light intensities are directly proportional to the atom or radical concentration. The time-dependent fluorescence or chemiluminescence intensity is measured by accumulating signal over many (500–5000) photolysis flashes using a multichannel scaler (10–100 μs/ channel); the accumulated signal is then transferred to a microcomputer for analysis.

The conditions of the experiment (see Table I for a summary) are arranged so that pseudo-first order kinetics applies to the reactions (chemical removal rates) of the photolytically generated species, i.e., the concentrations of the reactant gases (CH_4, C_6H_6) are always at least a factor of 100 greater than those of the radical species. Thus, only relative concentrations of the free radical species need to be measured and there is no need for an absolute intensity calibration of the fluorescence or chemiluminescence signal. Other processes such as flow and diffusion contribute to removal. These physical removal processes are not strictly first order, but conditions are arranged so that their contributions are small and can be treated as first order.

Secondary reactions which affect the concentration of the measured free radical must be accounted for in the analysis when such reactions have large rates, i.e., when the reactions involve a major species such as the photolyte with a minor species.
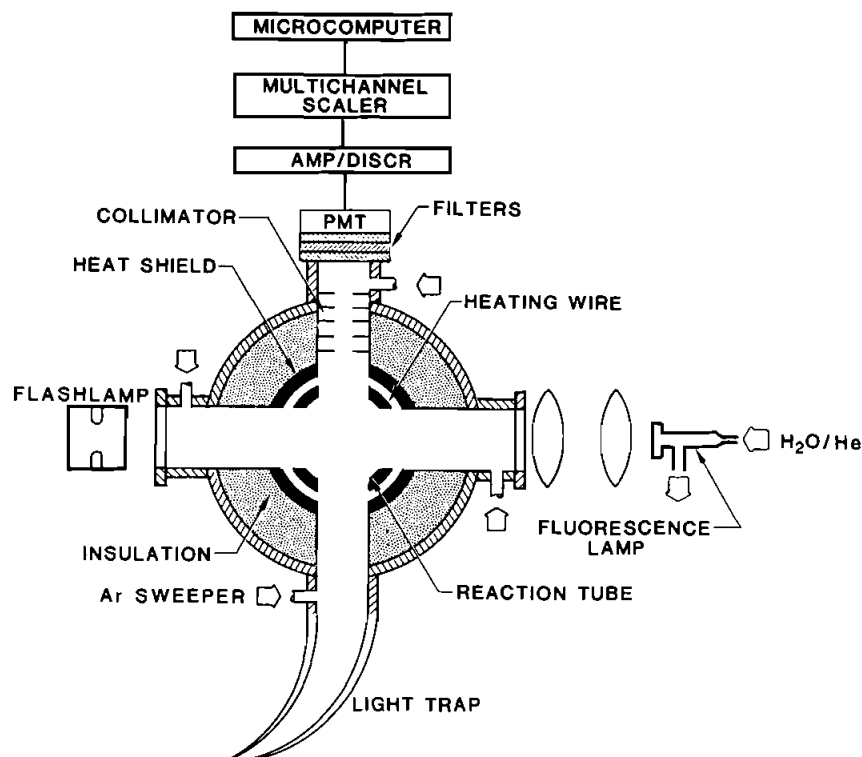
FIGURE 1   Optical plane of HTP reactor configured for OH kinetics experiments. From Madronich and Felder (1985).

TABLE 1
Ranges of experimental conditions covered in HTP kinetic measurements

	O-atom kinetics	OH kinetics
Temperature, K	420–1670	300–1500
Flow velocity, cm s^{-1}	5–120	20–150
Diluent gas number density, cm^{-3} (pressure, kPa)	[N$_2$]: 0.2–90 × 10^{17} (p: 0.7–53)	[Ar]: 3–35 × 10^{17} (p: 5–30)
Reagent number density, cm^{-3}	[CH$_4$]: 0.4–850 × 10^{13}	[CH$_4$]: 1–20 × 10^{13} [C$_6$H$_6$]: 1–40 × 10^{13}
Photolyte number density, cm^{-3}	[O$_2$]: 2–8 × 10^{15} [CO$_2$]: 3–7 × 10^{15}	[H$_2$O]: 0.5–60 × 10^{14}
Radical number density, cm^{-3}	[O]: ≈ 1 × 10^{10}	[OH]: ≈ 1–5 × 10^{10}

RESULTS

$$O + CH_4 \rightarrow OH + CH_3 \tag{1}$$

This reaction is one of the most extensively studied (see Felder and Fontijn, 1979 and 1980 and references therein) of all hydrocarbon oxidation reactions and good

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"agreement" between low and high temperature data exists. The existing
experimental data on $k_1(T)$ ranged from 250-2250 K and originated from a variety
of techniques. The HTP studies span 420-1670 K, the largest range covered by a
single technique.

Figure 2, an Arrhenius plot, shows the HTP measurements of $k_1(T)$ over
420-1670 K; the measured values span nearly five orders of magnitude
($\approx 4 \times 10^{-16}$ to $\approx 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). The two photolytes, O_2 and CO_2
were used over the following ranges: (i) pulsed 147 nm photolysis of O_2 over
400-1250 K and (ii) vuv flash photolysis of CO_2 over 700-1670 K. These were
combined with the two [O] measurement methods: (i) resonance fluorescence for
550-1670 K and (ii) O/NO chemiluminescence for 400-800 K. All measurements
agree in their regions of overlap and connect smoothly. Experimental conditions
were varied to show that the $k_1(T)$ values are independent of pressure, reaction zone
residence time, and reactant mixing method over the entire measurement range.

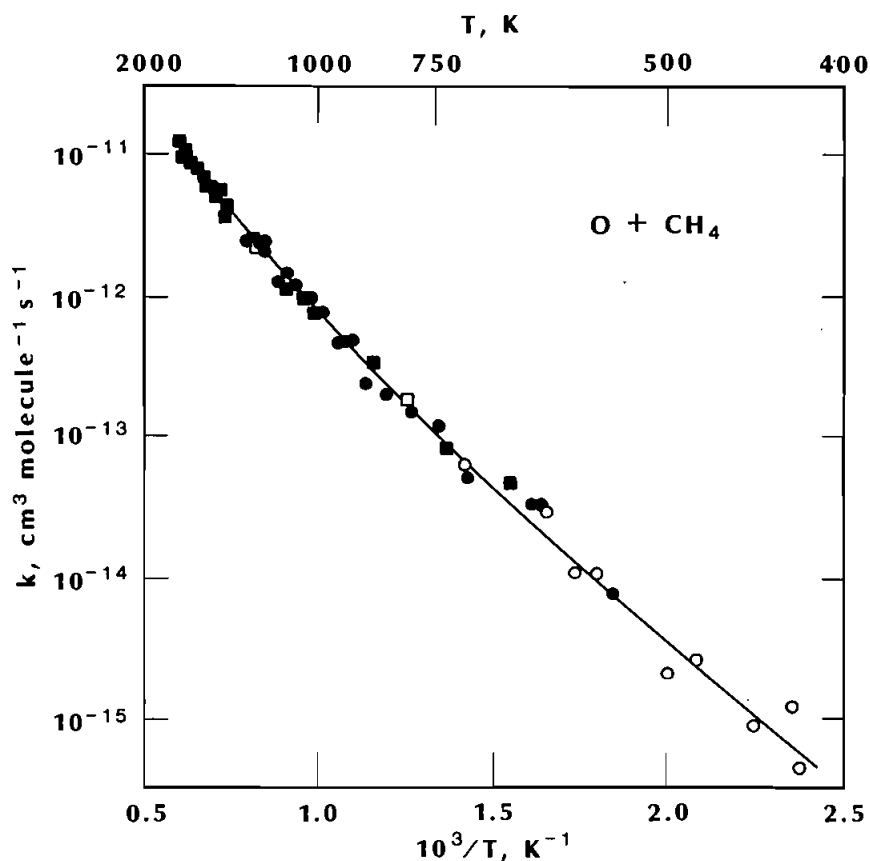FIGURE 2   Arrhenius plot of HTP measurements of $O + CH_4$ rate coefficient. Error bars omitted for
clarity. Solid line is fit to data. ■—CO_2 flash photolysis, O-atom resonance fluorescence detection; ●—
O_2 pulsed photolysis (147 nm), O-atom resonance fluorescence detection; ○—O_2 pulsed photolysis
(147 nm) chemiluminescence detection; □—O_2 flash photolysis, O-atom resonance fluorescence
detection.

The HTP results are empirically described by the nonlinear least-squares fit (Bevington, 1969) to a three-parameter expression of the form $A\,T^{n}\exp(-B/T)$ (in cm^3 molecule^{-1} s^{-1} units):

$$k_1(T) = (8.7 \pm 1.9) \times 10^{-19}\ T^{2.5 \pm 0.1}\ \exp[-(3570 \pm 60)/T],$$

where the uncertainties given are one standard deviation. A weighted fitting method is used where the weights for the individual rate coefficient values are obtained by propagation of errors from the raw data and used according to the methods described by Cvetanovic and coworkers (1975, 1977, 1977a, 1979).

$$H + H_2O \rightarrow H_2 + OH \tag{2}$$

In extending the range of temperature which can be explored by the FP/RF method beyond 1000 K, it was found (Madronich and Felder, 1984) that the use of H_2O as a photolyte to produce OH is complicated by reaction (2) which regenerates OH from the photolytically produced H atom. Reaction (2) is also of importance in combustion systems. Its reverse is a critical step in H_2/O_2 combustion chemistry which is a fundamental building block of hydrocarbon combustion mechanisms, and reaction (-2) has been extensively studied (cf. Ravishankara et al., 1981; Dixon-Lewis and Williams, 1977, and references therein). No direct experimental data were available from reaction (2); the only data available were inferred from flame kinetic studies (Fenimore and Jones, 1958; Dixon-Lewis et al., 1965). Elucidation of the kinetics of reaction (2) is the basis for interpreting the quantitative behavior of any high temperature kinetics study in which H_2O is used as a source of OH. We therefore examined the effects of reaction (2) on OH temporal profiles above 1000 K and determined k_2 at 1158, 1274, and 1387 K based on resonance fluorescence measurements of such temporal profiles.

A typical fluorescence intensity ($\propto$ [OH]) profile, obtained from H_2O photolysis at 1274 K, is shown in Figure 3. The reduction in [OH] at late times is due to its removal from the observation zone by diffusion and flow, while at early times reaction (2) produces OH on a time scale comparable to that of the flow and diffusive losses. The shape of this early time profile could be altered by varying the [H_2O] at a fixed total pressure, temperature, and total gas flow. At low [H_2O] (e.g., $\leq 1 \times 10^{14}$ cm^{-3} at 1274 K) the profiles are simple exponentials because the rate of reaction (2) is small; at high [H_2O] (e.g., $> 1 \times 10^{16}$ cm^{-3} at 1274 K), qualitatively similar behavior is observed, but the fluorescence intensity decreases with increasing [H_2O], presumably due to quenching. At the high [H_2O], reaction (2) goes to completion on a time scale shorter than can be resolved by our apparatus. At intermediate concentrations, nonexponential behavior like that illustrated in Figure 3 is observed, with the early time [OH] being either constant (neither rising nor falling) or exhibiting maxima whose temporal positions could be shifted by changing [H_2O]. The range of [H_2O] over which the maxima could be observed was proportional to total pressure, consistent with decreasing the contribution of diffusion while holding other factors constant. The shapes of the decay profiles were independent of flashlamp energy over at least a factor of 4.

The temporal profiles were analyzed according to a kinetic model described elsewhere (Madronich and Felder, 1984), and the resulting value of the rate coefficient fit by the simple Arrhenius expression (in cm^3 molecule^{-1} s^{-1}):

$$k_2 = (5.2 \pm 4.5) \times 10^{-10}\ \exp[-(11.1 \pm 1.1) \times 10^3/T].$$
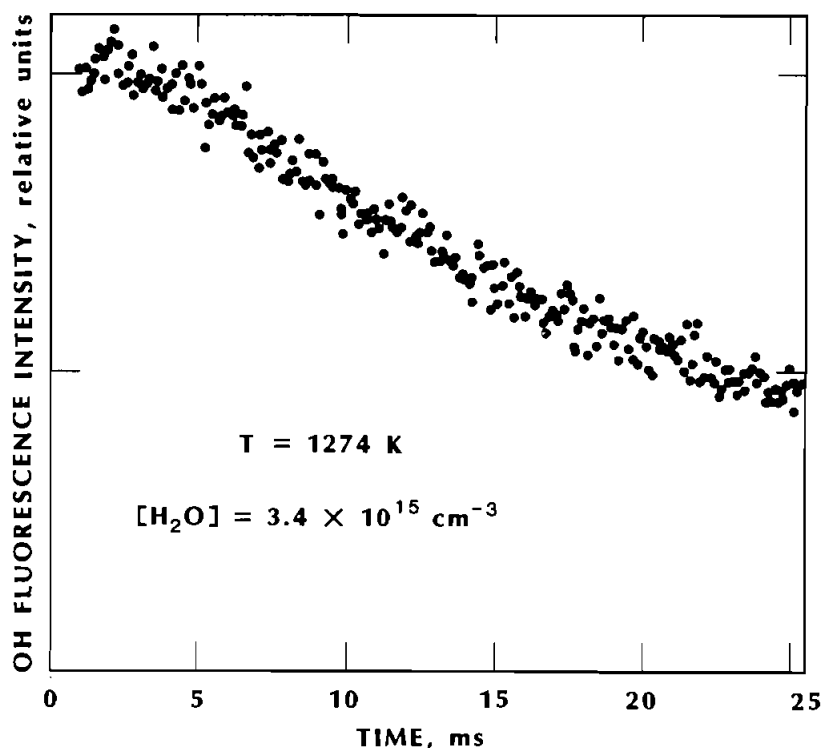
FIGURE 3   Typical OH fluorescence intensity profile with second reactant absent. From Madronich and Felder (1984).

The data and fit are shown in Figure 4 along with other measurements of k_2 from flame data. Values of k_2 calculated from measurements of k_{-2} and the equilibrium constant (*JANNAF Tables*, continously updated) for reaction (2) are also shown for comparison. With this information on k_2, it is possible to account for contributions of reaction (2) to the OH temporal profiles in the presence of added reagent; OH kinetics can be treated quantitatively when H_2O is used as the photolyte at temperatures above 1000–1100 K.

$$OH + CH_4 \rightarrow CH_3 + H_2O \tag{3}$$

The HTP study of reaction (3) spanned 300–1500 K (Madronich and Felder, 1985), the widest temperature range which had been studied by a single technique. Methane concentrations ranged from 1 to 5×10^{13} molecule cm^{-3} at 1500 K and from 0.6 to 5×10^{16} at 298 K and were at least a factor of 100 greater than $[OH]_0$ at all temperatures. A typical experimental OH fluorescence intensity profile is shown in Figure 5. The decay is accurately described by a single exponential function of the form

$$I(t) = a \exp(-t/\tau) + b,$$

as were all such profiles obtained in the presence of significant amounts of CH_4, where the constant, b, has been added to account for the presence of background

(non-varying) intensity. The rate information is contained in the characteristic decay time τ which is given by

$$\tau^{-1} = p + k_3[CH_4],$$

where p is taken to be the approximately first order rate coefficient for removal of OH from the reaction zone by flow and diffusion.

For small or zero $[CH_4]$, deviations from simple exponential behavior were observed, particularly for temperatures above 1000 K. Some such deviations result from the only approximate validity of the first order flow and diffusion loss assumption, but the major effect above 1000 K results from reaction (2). It should be noted that H atoms diffuse out of the reaction zone much more rapidly than OH radicals so that the amount of OH produced by reaction (2) is much smaller than $[OH]_0$, the photolytically produced OH, which accounts for most of the observed fluorescence signal. Furthermore, in the presence of CH_4, the H atoms produced in the photolysis are rapidly scavenged in the reaction
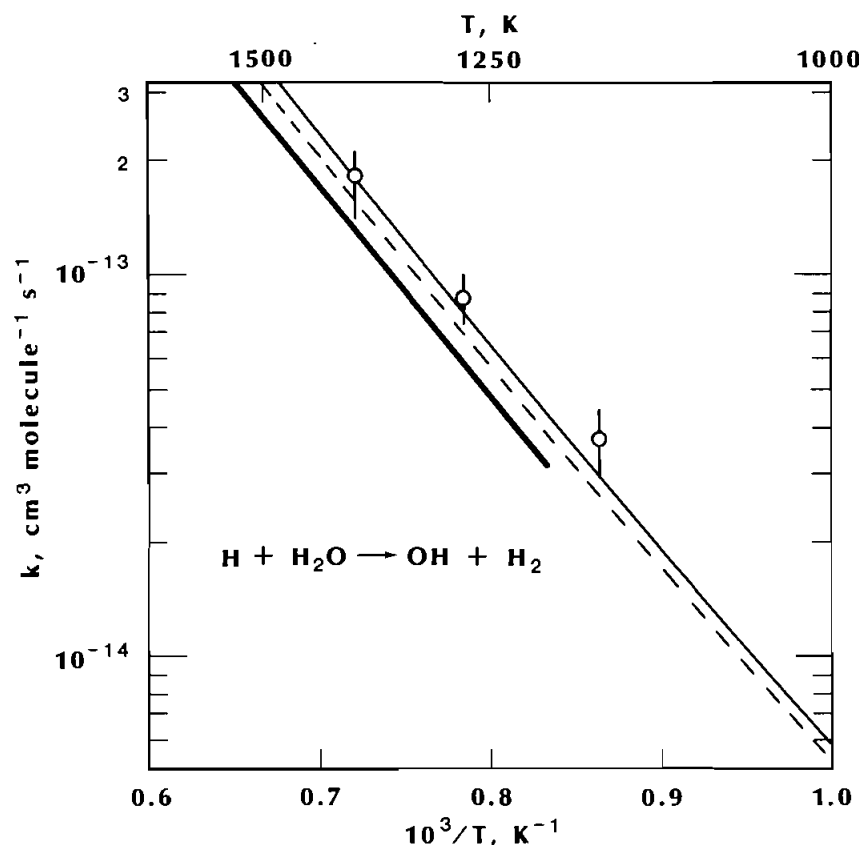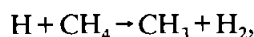
$$H + CH_4 \rightarrow CH_3 + H_2,$$

FIGURE 4 Arrhenius plot of $H + H_2O$ rate coefficient. From Madronich and Felder (1984). (o Madronich and Felder (1984); From reverse reaction: (—) shock tube data, Gardiner et al. (1973), as revised in Dixon-Lewis (1977); (- -) fit to FP/RF data, Ravishankara et al. (1981) and Tully and Ravishankara (1980). (——) fit to combined data of this work and from reverse reaction data of Ravishankara et al. (1981) and Tully and Ravishankara (1980).

producing relatively unreactive methyl radicals, so that interference from reaction (2) is minimized. Figure 5 shows the simple exponential decay of [OH] when CH_4 is present for kinetic measurements. The measured rate coefficient values for reaction (3) are displayed in Figure 6 in Arrhenius form. The data were fit over 298-1512 K to the modified Arrhenius expression (in cm^3 molecule^{-1} s^{-1}):

$$k_3(T) = 10^{-16.59 \pm 0.68} T^{1.83 \pm 0.17} \exp\{-(1396 \pm 134)/T\}.$$

Combining the HTP data with other high quality data of Jeong and Kaufman (1982) (268-473 K) and Tully and Ravishankara (1980) (298-1020 K) yields the recommended rate coefficient (in cm^3 molecule^{-1} s^{-1}):

$$k_3(T) = 9.50 \times 10^{-18} \, T^{1.96} \exp(-1328/T).$$
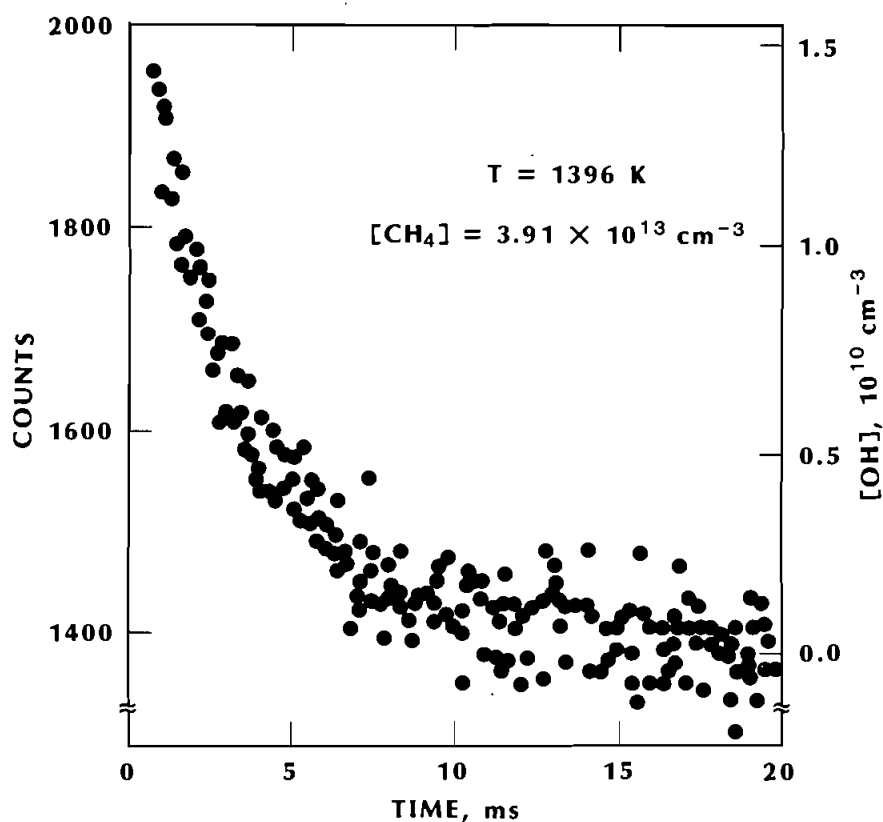

FIGURE 5   Typical OH fluorescence intensity profile with second reactant (CH_4) present. From Madronich and Felder (1985). See also Figure 3. Estimated absolute [OH] (not required for rate coefficient determinations) indicated.

This expression deviates at most 6 percent from the fitting expressions of the three individual experimental studies over the temperature ranges covered in those studies. Even allowing for some small systematic errors in each study, it appears fairly certain that the recommended $k_3(T)$ is now known to an accuracy of 10 percent or better over 268-1512 K.
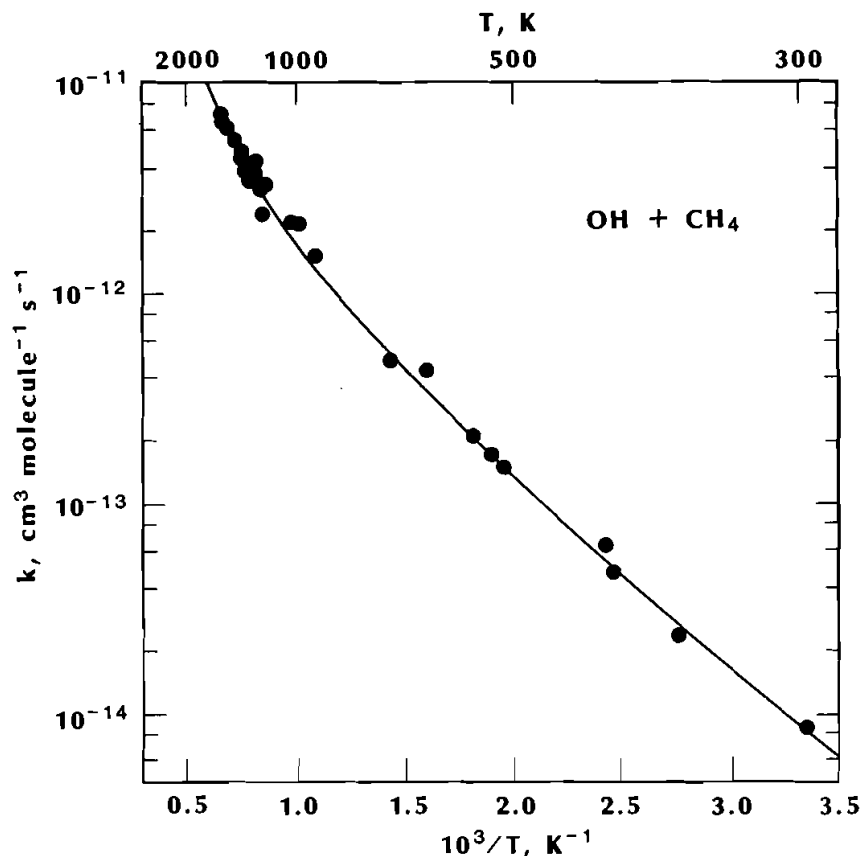
FIGURE 6   Arrhenius plot of HTP measurements of OH + CH$_4$ rate coefficient. From Madronich and Felder (1985). Error bars omitted for clarity. Solid line is fit to data.

$$OH + C_6H_6 \rightarrow Products \tag{4}$$

The destruction of aromatic hydrocarbons, and particularly of unsubstituted rings such as C$_6$H$_6$, is an area of intense interest in combustion because of the role such processes play in the combustion of high aromatic content fuels, in the formation of carcinogenic aromatic pollutants, and in the production of aromatics in fuel-rich flames, possibly affecting the rate of soot generation in such flames. For these reasons, the reactions of the ubiquitous flame radical, OH, with C$_6$H$_6$ is of special interest. Reaction (4) has received considerable attention, but no direct measurements of its rate coefficient had been reported above. $\approx$ 1000 K. HTP kinetic measurements have now extended this range to 1410 K (Madronich and Felder, 1985a).

Below about 600 K, the reaction proceeds via an electrophilic OH addition, with the formation of a long-lived complex that can be collisionally stabilized (Hansen et al., 1975; Perry et al., 1977). Above about 600 K to 1020 K, the FP/RF studies of Tully et al., (1981) produced an overall rate coefficient for OH disappearance which

showed Arrhenius behavior characteristic of a single process, different from the addition reaction. Isotopic substitution studies (Tully *et al.*, 1981) indicate that the reaction proceeds by abstraction in the temperature range they covered

$$OH + C_6H_6 \rightarrow C_6H_5 + H_2O. \tag{4a}$$

Howard (1983) suggested, based on the data of Bittner and Howard (1981), that a second, high temperature, nonabstraction channel was neeeded to explain their molecular beam sampling mass spectrometry results on C_6H_6 oxidation in low pressure flames. Their data indicate that $OH + C_6H_6$ is the primary loss channel for C_6H_6, but the low $[C_6H_5]$ observed implies that abstraction is unimportant compared to the channel(s) that lead to $C_6H_5OH + H$. This conclusion is supported by the calculations of Lin and coworkers (Hsu *et al.*, 1985; Lin and Lin, 1984) who conclude that above ≈ 600 K, the reaction of OH with C_6H_6 proceeds exclusively by

$$OH + C_6H_6 \rightleftharpoons C_6H_6OH \,\# \rightarrow C_6H_5OH + H. \tag{4b}$$
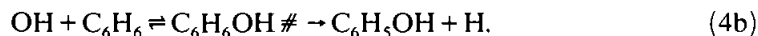
Their calculated rate coefficient for OH loss is in excellent agreement with the measured rate coefficient of Tully *et al.*, (1981); in disagreement with the isotopic substitution experiments, the abstraction channel was calculated to have a negligible contribution at all temperatures.

For both possible channels (reactions 4a and 4b), one of the products (C_6H_5 or H) can react with H_2O, which is present in HTP experiments as the photolytic parent of OH. Reactions ($-4a$) and (2) regenerate OH, but they were expected to do so at different rates. Since k_2 was known, it seemed possible that the channel producing C_6H_5 (reaction 4a) might be distinguished from that producing H (reaction 4b) measuring the extent to which secondary OH was produced in the HTP reactor when $[H_2O]$ was suitably high. Such measurements were carried out at ≈ 1300 K.

1. *Rate coefficient of the OH + C_6H_6 reaction over 800–1400 K* At each temperature investigated in the range covered, rate coefficients were determined by analyzing OH decay traces at different $[C_6H_6]$. The range of $[C_6H_6]$ covered was $(1.3–34) \times 10^{13}$ cm^{-3} compared to initial $[OH]$ in the range $(1–10) \times 10^{10}$ cm^{-3}, so that $[C_6H_6] \geqslant 100$ $[OH]$. Thus, psuedo-first-order kinetics is expected to prevail, and radical–radical reactions occur at negligible rates. Above 1000 K, the effects of reaction (2) were considered. Unlike the kinetic situation prevailing in the HTP study of reaction (3), C_6H_6 apparently does not react rapidly with the H atom fragment of the water photolysis (Nicovich and Ravishankara, 1984). H atoms diffuse out of the reaction zone much more rapidly than does OH so that $[OH]$ produced by reaction (2) is significantly smaller than the photolytically generated concentration, $[OH]_0$. The effect of correcting for reaction (2) is to increase the k_4 by 10–30 percent over that which would be estimated from the data if reaction (2) were ignored (*i.e.*, if the observed decay curves were fit to a single exponential decay). At temperatures < 1000 K, the effect of the correction is negligible, and a single exponential fit describes the data well.

The OH/C_6H_6 rate coefficients measured using HTP over 790–1410 K are displayed in Arrhenius form in Figure 7. No systematic differences appear between
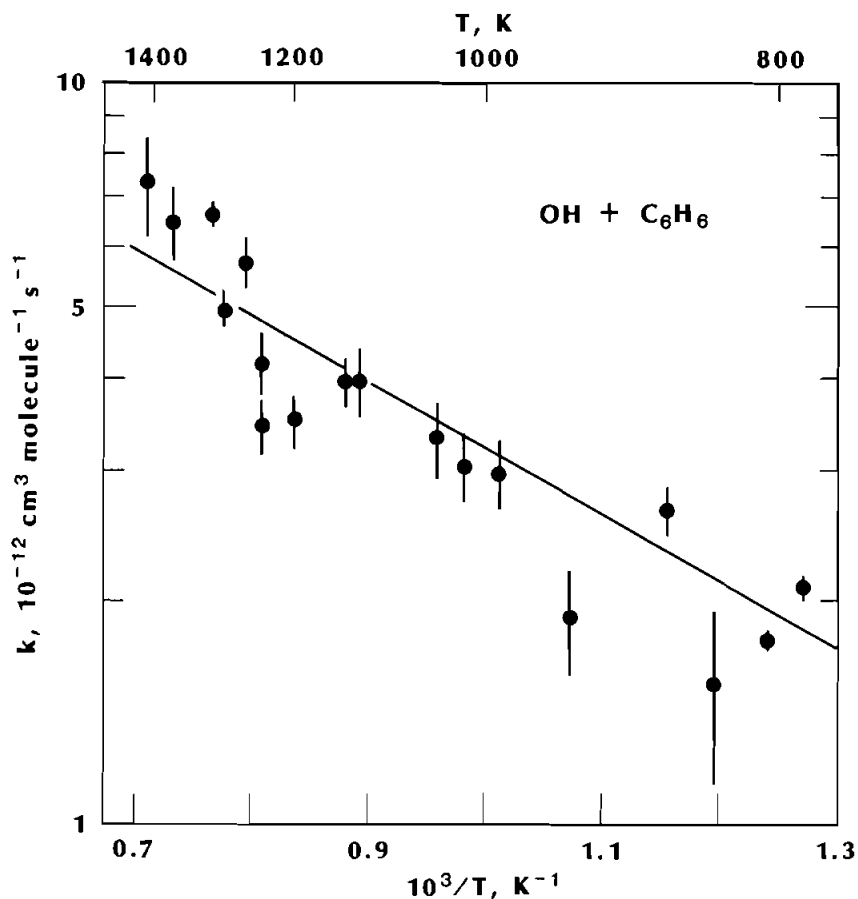
FIGURE 7   Arrhenius plot of HTP measurements of $C_6H_6 + OH$ rate coefficient. From Madronich and Felder (1985a). Some previously unpublished data added; solid line is fit to data.

data obtained with LiF and Suprasil flashlamp windows. The data were fit with the simple Arrhenius expression (in cm^3 $molecule^{-1}$ s^{-1}):

$$k_4(T) = (2.5 \pm 0.3) \times 10^{-11} \exp[-(2050 \pm 125)/T].$$

The previous work by Tully *et al.* (1981) at lower temperatures agrees well with these measurements.

2. *Mechanism of reaction at 1300 K*   The mechanism of reaction (4) was investigated near 1300 K (Madronich and Felder, 1985a) by exploiting the information present in OH temporal profiles as a function of $[H_2O]$. A typical profile is shown in Figure 8. Qualitatively similar traces were obtained over the entire range of $[C_6H_6]$ in these measurements. The strong curvature seen in Figure 8 was present only at high $[H_2O]$; at low $[H_2O]$, it was unequivocally absent.
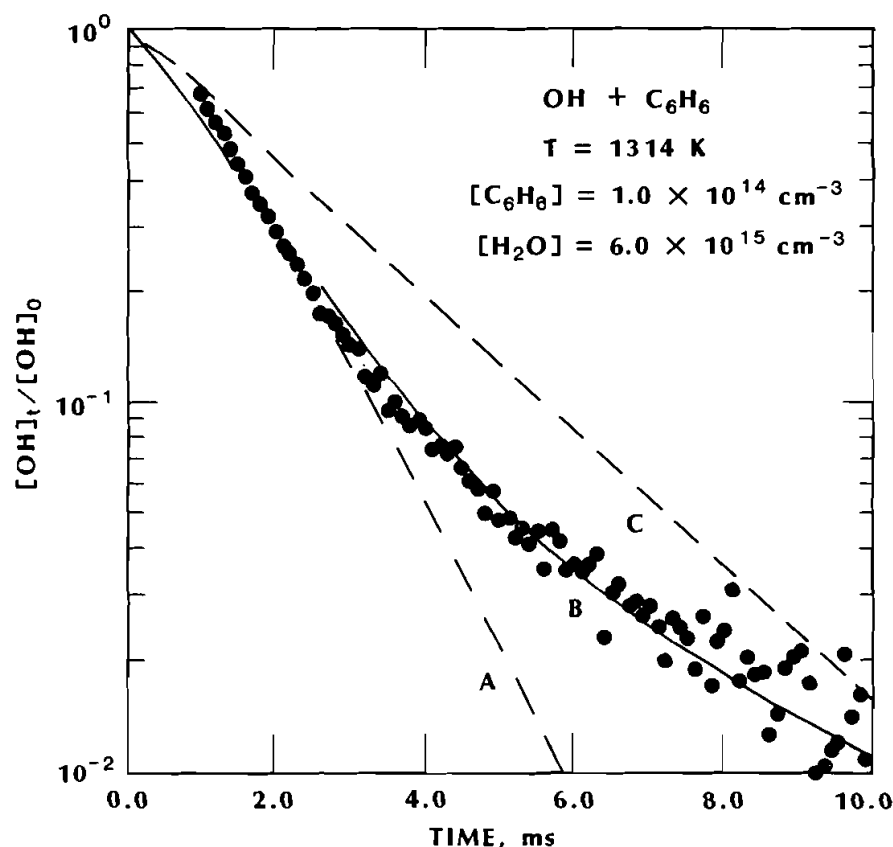
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FIGURE 8   OH fluorescence intensity profile with second reactant (C_6H_6) present and with "high" H_2O. From Madronich and Felder (1985a). See also Figures 3 and 5. Lines are calculated from models described in text.

Calculations from three different model reaction schemes predicting [OH] temporal profiles were compared to the observed data in Figure 8 (and others like it at differing $[C_6H_6]$). All three models included: equal initial photolytically produced concentrations of H and OH, $[H]_0 \equiv [OH]_0$; flow and diffusion losses for H, OH, and C_6H_5; and secondary OH production from reaction (2). The input data were obtained from separate measurements. The reaction models differed in the assumed identity and fate of the products of the OH + C_6H_6 reaction.

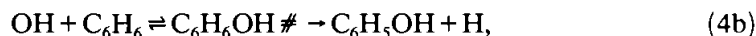In model A, only the abstraction reaction was considered

$$OH + C_6H_6 \rightarrow C_6H_5 + H_2O,$$ (4a)
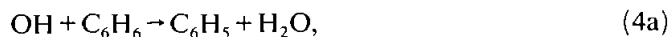
and k_{4a} was taken to be $= k_4$ measured.

In model B, both abstraction and the reverse reaction were considered

$$OH + C_6H_6 \rightleftharpoons C_6H_5 + H_2O,$$ (4a, $-$4a)

with $k_{4a} \equiv k_4$ (measured above) and k_{-4a} calculated from k_4 and thermochemical data.

In model C, only H atom elimination was considered

$$OH + C_6H_6 \rightleftharpoons C_6H_6OH \# \rightarrow C_6H_5OH + H, \tag{4b}$$

with $k_{4b} \equiv k_4$ (measured) and $k_{4a} = k_{-4a} = 0$.

The experimental observations are compared with the calculations in Figure 8. Qualitatively similar results were obtained over a factor of ≈ 4 variation in $[C_6H_6]$. In all cases, the best agreement with the data was obtained with model B. Based on these results, it seems clear that reaction (4a) is the dominant channel for the $OH + C_6H_6$ reaction near 1300 K and, in accord with previous work, can be said to be the dominant reaction channel in the 600–1300 K range. Additional numerical simulations using all three reactions (4a, $-4a$, and 4b), in which the value of the branching ratio k_{4b}/k_4 (where $k_4 = k_{4a} + k_{4b}$) was varied from 0 to 1 using the HTP data indicated that, quite conservatively $k_{4a}/k_{4b} > 4$. Finally, the value of k_{-4a} was varied in model B calculations by ± 30 percent from the thermochemically calculated value. These variations produced clear deviations of the calculated curves from the observed OH decay profiles, leading to an estimated experimental value (in cm^3 molecule^{-1} s^{-1})

$$k_{-4a}(1300 \text{ K}) \approx (1.0 \pm 0.3) \times 10^{-14}.$$

DISCUSSION

The examples given above demonstrate the utility of extending the range over which the FP/RF method is used for obtaining kinetic data to temperatures above 1000 K. The results of HTP investigations provide direct and accurate measurements of rate coefficients useful to quantitative understanding of combustion chemistry and the method can be utilized to extract detailed mechanistic information under special conditions. It is worth emphasizing that HTP, like its low temperature FP/RF analogs, retains the capability to control pressure, temperature, residence time and individual species concentrations independently. This provides a valuable cross check on experimental accuracy as well as allowing classical investigations of reaction mechanism through pressure and concentration effects on the observed radical concentration profiles.

The large range of temperature over which the HTP technique provides reliable kinetic data includes ranges available to traditional lower temperature methods and ranges accessible with shock tubes and flames. To obtain maximum benefit from such a capability, care must be taken in analyzing and evaluating kinetic data to insure that valid statistical techniques are used. We and others have emphasized this need on several occasions (e.g., Fontijn and Felder, 1979, 1979a; Cvetanovic et al., 1975, 1979), and we take this opportunity to reiterate the necessity for following detailed and accurate experimental error assessment, propagation, and weighting techniques in presenting results for others to use. It is unfortunately still common practice to ignore such procedures; even worse, improper fitting programs or weighting procedures are sometimes applied, resulting in misleading estimates of fit quality and parameters.

Even if these procedures are strictly followed and the complete data analysis is carried out properly, many applications require values for rate coefficients lying outside the experimentally accessible temperature range. The questions that must then be addressed are how to extrapolate the experimental observations reliably to

the desired temperature range and how to assess the uncertainty inherent in that extrapolation. To this end, it must be recognized that the mathematical forms and fitting parameters computed to describe the temperature dependence of the experimental data are essentially empirical and valid only over the experimental temperature range. Great progress is still being made in the quantitative theoretical evaluation of these parameters for complex systems. Until such time as they can be specified with certainty for a given reaction, we have argued (Madronich and Felder, 1985) that the extrapolation of experimental data is a useful means for estimating needed data outside the range of measurement.

The $H + H_2O$ reaction is an interesting example of a reaction channel which opens at the high temperatures accessible with HTP (Madronich and Felder, 1984). It also points up the necessity to examine even the simplest systems for possible kinetic interferences (and opportunities to explore previously unmeasured kinetics, Madronich and Felder, 1985a). The design and construction of the HTP apparatus are suitable for attaining temperatures above 1800 K, but the utility of the apparatus for kinetic measurements may be limited by factors other than materials of construction. In the case of OH kinetic studies, independent of the choice of reactant molecule, the thermal decomposition of the photolyte, H_2O, is one such limitation. The presence of thermally generated OH which is comparable at 1500 K to the $|OH|_0$ produced in the photolytic flash results in a deterioration of the signal-to-noise ratio because of the background fluorescence from the thermally generated OH. In order to maintain a constant signal to noise ratio, i.e., to continue to observe the time-dependent fluorescence signal from photolytically produced OH amid the growing scatter generated by the time-independent fluorescence from thermally produced OH, the detection sensitivity must be at least doubled for each 30 K increase in reactor temperature based on the temperature dependence of the equilibrium constant. Since the detection sensitivity is already high (Madronich and Felder, 1985) (comparable to that obtained in low temperature FP/RF analogs to the HTP), and since even a large increase in detection sensitivity extends the temperature range by only a small amount, this does not appear to be a reasonable approach. Reducing the residence time in the reactor adversely affects the mixing and heating of the gases and also becomes less useful at higher temperatures where the homogeneous reactions approach equilibrium more rapidly and where the equilibrium concentration of OH is much higher. For kinetic studies, it is also important to recognize that thermally generated OH will react with the reagent gas and may reduce its concentration by an amount which will affect the results, or that the reaction may produce secondary species which can affect the observed kinetics. For all of the HTP results reported, flow conditions were varied widely to assure that such effects were absent, negligible, or accounted for. Work up to now has permitted reliable OH kinetic measurements up to 1500 K, and indications are that measurements on OH kinetics up to 1600 K are feasible using the present apparatus.

The thermal stability of reactant molecules can also be a problem, which can be minimized if a cooled inlet is used. Even then, the reactant molecule must be thermally stable-for at least 5 ms to mix completely with the other gases. Other kinetic methods such as shock tubes and pulsed laser heating in which high reaction temperatures are achieved "instantaneously" avoid these thermal stability problems (possibly in exchange for some others, one suspects). In HTP studies, CH_4 was found to be stable up to at least 1670 K (Felder and Fontijn, 1979a) and C_6H_6 up to 1500 K (Madronich and Felder, 1985).

Reaction between photolyte and reactant may require the use of an alternative

photolyte. For example, we found it necessary to substitute CO_2 for O_2 as a source of O atoms in our high temperature studies of the O/CH_4 reaction because CH_4/O_2 mixtures were found to react spontaneously at temperatures above ≈ 1200 K (Felder and Fontijn, 1979, 1980).

With these possible problems addressed, the extension of the FP/RF method to high temperatures, as embodied in the HTP technique, provides a useful tool with which to determine accurate rate coefficient values over wide temperature ranges. The measurements made demonstrate the high degree of reliability which can be expected from such determinations, and the data bases provided are among the most complete for any chemical reactions. Such measurements should be especially useful for comparison with predictions from the significantly advanced capabilities in both theoretical understanding of individual reactions and in the ability to model complex reacting systems.

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