Rates of Processes Initiated by Pulsed Laser Production of F Atoms in the Presence of HCl, CH₄, and CF₃H

CHRISTOPHER M. MOORE, IAN W. M. SMITH, and DAVID W. A. STEWART School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

Abstract

Time-resolved vibrational chemiluminescence from HF has been recorded following the production of F atoms by the pulsed laser photolysis ($\lambda = 266 \text{ nm}$) of F₂ in the presence of HCl, CH₄, and CF₃H. In the first two cases, experiments have been conducted by observing emission from HF($\nu = 3$) at four temperatures from 295 to 139 K. Rate constants have been determined over this range of temperature for the reactions of F atoms with HCl and CH₄ and of CH₃ radicals with F₂, and for the relaxation of HF($\nu = 3$) by HCl and CH₄. The reaction of F atoms with CF₃H is slower than those with HCl and CH₄ and measurements on the emission from HF($\nu = 2$) have been used to infer rate constants for reaction and relaxation only at 295 K. © 1994 John Wiley & Sons, Inc.

Introduction

The characterization of nascent vibrational, and in some cases rovibrational, product state distributions from spectroscopic observations of infrared chemiluminescence has played an important role in the development of the field of molecular reaction dynamics [1]. In a variant of this method, time-resolved observations of chemiluminescence from the vibrationally excited products of reactions initiated by pulsed laser photolysis can be used to measure the thermal rate constants for some elementary reactions [2-7] and, in favorable cases, for the relaxation of molecules in specific vibrational states [6]. This technique has proved especially useful for reactions of F and Cl atoms producing vibrationally excited HF and HCl. For these reactions, kinetic methods like resonance fluorescence [8,9] and laser-induced fluorescence [10], based on electronic spectroscopy of the radical atom, are difficult to apply, since the relevant atomic transitions lie at vacuum ultraviolet wavelengths. On the other hand, the vibrational bands of HF and HCl are at quite short wavelengths in the near infrared, where detectors are at their most sensitive, and the large vibrational anharmonicity of hydride molecules means that bands from different excited levels are comparatively well-separated and easy to resolve. Reactions of F and Cl atoms are important in a number of environments, ranging from the media of chemical lasers [11] to the earth's atmosphere, especially the stratosphere [12]. In addition, these reactions are frequently employed in laboratory experiments to generate other free radicals for investigations of the kinetics and mechanisms of their reactions.

In general, the exothermicity of the reaction producing a vibrationally excited product will be such that the product is produced in several excited vibrational levels. Under these circumstances, one of two conditions must be satisfied, if analysis of the trace of infrared emission with time is to yield an accurate value for the rate constant of the reaction producing the vibrationally excited species. Possible complications are entirely avoided if one discriminates against emission from all vibrational levels except the highest (ν_{max}) significantly populated in the reaction. Then, in the case where the reaction produces HF, it can easily be shown [6] that the intensity (I) of emission from $\text{HF}(\nu = \nu_{\text{max}})$ obeys the equation:

(i)
$$I\alpha [HF(\nu = \nu_{max})] = A\{\exp(-k_{1st}''t) - \exp(-k_{1st}'t)\}$$

where $A = [F]_0 k'_{1st}/(k'_{1st} - k''_{1st})$, with $[F]_0$ the initial concentration of F atoms formed by laser photolysis of the precursor, and k'_{1st} and k''_{1st} are pseudo-first-order rate constants associated with the total removal of F atoms, exclusively or predominantly by the reaction under investigation:

(1)
$$F + HR \longrightarrow HF(\nu \le \nu_{max}) + R$$

and the relaxation of $HF(\nu = \nu_{max})$:

(2)
$$HF(\nu = \nu_{max}) + M \longrightarrow HF(\nu < \nu_{max}) + M$$

It should be noted that fitting the emission traces to a double exponential form yields two first-order constants λ_{fast} and λ_{slow} either of which may, in principle, be $k'_{1\text{st}}$ (or $k''_{1\text{st}}$).

In cases where the pseudo-first-order rate constant for reaction is very much larger than those for relaxation of HF from vibrationally excited levels, then eq. (i) can be approximated to

(ii)
$$I \alpha [HF(0 < \nu \le \nu_{max})] = [F]_0 \{1 - \exp(-k'_{1st}t)\}$$

In this case, the measurements yield rate constants only for the reaction, not for relaxation.

The time-resolved vibrational chemiluminescence technique was first used for kinetic purposes by Moore and his co-workers [2] to obtain rate constants for the reactions of Cl atoms with HBr and HI over a temperature range from 220 K to 400 K, the Cl atoms being generated by ultraviolet laser photolysis of Cl₂. Heidner et al. [3] and Wurzberg and Houston [4] both investigated the kinetics of the important reactions between F atoms and H₂, D₂ using multiphoton infrared dissociation of SF_6 to obtain F atoms. In all these studies, the total fundamental emission from the vibrationally excited hydrogen halide was observed but the requirement for the reaction to be much faster than relaxation seems to have been satisfied. On the other hand, the measurements of Houston and co-workers on the reactions of F atoms with HCl, HBr, and HI [5] less obviously satisfied this condition, as pointed out by Wrigley and Smith [6]. Wrigley and Smith created F atoms by pulsed laser photolysis of F_2 using a frequency-quadrupled Nd: YAG laser ($\lambda = 266$ nm) and observed high overtone emissions from specific excited vibrational levels, corresponding to the highest which could be populated by the reaction under investigation. This method has been adopted in the present work.

An important extension of the time-resolved vibrational chemiluminescence technique was made by Leone and co-workers [7]. They realized that the method could be used to study the kinetics of chain reactions, in which the reaction of halogen atoms with a molecular species is one of the chain propagation steps. The kinetic equations describing the variation of emission intensity with time become more complicated (see below) but, for favorable cases, it is possible to extract the rate constants for both of the chain propagation steps, as well as for the relaxation of molecules from the level from which emission is being observed. Again, the analysis is made simpler and more certain if emission is observed only from the highest populated level of the emitting species.

In the present article, we report the results of experiments in which the timeresolved vibrational chemiluminscence method has been used to examine the kinetics of processes which follow the creation of F atoms by pulsed laser photolysis of F_2 in the presence of HCl, CH_4 , and CF_3H . Part of the motivation of this work has been our continuing interest in chemical kinetics at low [13] and ultra-low temperatures [14], and the systems containing HCl and CH_4 have been studied down to 139 K. Low temperature measurements proved impossible on the system containing CF_3H . A number of factors contribute to this difficulty, including the slowness of the primary reaction involving F atoms, even at room temperature.

Experimental

The methods and procedures used in the present series of experiments are similar to those employed by Smith and Wrigley [6]. Gas mixtures of known composition were prepared by conventional flow methods in a reaction vessel constructed from Pyrex. This vessel was equipped with a double jacket; refrigerant could be flowed through the inner jacket, while the outer jacket was permanently evacuated [13]. Temperatures in the region from which vibrational chemiluminescence was observed were measured in a separate series of experiments using a calibrated thermocouple [13]. In contrast to the experiments of Smith and Wrigley, the molecular reactant used in the present experiments (HCl, CH₄, or CF₃H) was admitted through an injector which terminated a few centimetres upstream from the observation zone, in order to minimize any 'dark' prereaction and any reaction initiated by previous laser shots. The partial pressure of F_2 in the gas mixtures was usually in the range of 0.05–0.5 torr. The total pressure in any single series of experiments was kept constant by the addition of carrier gas (in most experiments Ar, but in some N₂, see below) at values of 15 torr in experiments on F + HCl, 3 torr for F + CH₄, and 25 torr for F + CHF₃.

Reaction, and formation of vibrationally excited HF, was initiated by photolyzing a fraction of the F₂ in the gas mixture using pulses of radiation at $\lambda = 266$ nm from a frequency-quadrupled Nd: YAG laser (Spectron Lasers, model 800) operating at 10 Hz and yielding ca. 25 mJ per pulse. The laser beam entered through the central injector and passed axially along the remainder of the reaction cell.

In experiments on the reactions of F atoms with HCl and CH₄, the HF (3, 0) emission was observed through the Pyrex walls of the reaction cell and its jackets using a red-sensitive photomultiplier tube (RCA C31034-02). The photomultiplier tube was mounted in a light-tight housing, which also contained a lens to gather the vibrational chemiluminescence and a filter (Hoya IR-85) to reduce background light, mainly fluorescence from the windows of the reaction cell. In experiments on $F + CF_3H$, the photomultiplier tube was replaced by a liquid-N₂ cooled InSb photovoltaic detector and HF(2,0) emission was observed. Emission in the fundamental vibrational bands was eliminated by a piece of plastic which transmitted radiation at wavenumbers \geq ca. 4600 cm⁻¹ but absorbed > 99% of radiation in the region of the HF fundamental bands.

Signals from the photomultiplier tube or the infrared detector were sent through a transient recorder (Data Laboratories, DL910) and accumulated in a microcomputer (BBC Acorn, model B). Although the optical filtering reduced the size of the signals resulting from window fluorescence, they were still comparable in magnitude to the chemiluminscence signals. Consequently, it was necessary to subtract the 'background' signals (i.e., from window fluorescence only) from the signals recorded in a 'real' experiment (i.e., chemiluminescence plus window fluorescence) to obtain a chemiluminescence trace for subsequent analysis. These traces were fitted by a nonlinear least-squares fitting program to appropriate mathematical functions (see below).

The reagent gases (HCl, CH₄, and CF₃H) were admitted to the reaction cell as a 4-8% mixture in Ar or N₂. The primary gases were taken from cylinders without further purification. Their sources were as follows: HCl (Air Products, 99.6% pure); CH₄ (SIP Analytical, CP Grade); CF₃H (Air Products, 99.25%); Ar (BOC Ltd., zero grade, 99.998%); and N₂ (BOC Ltd., 'O₂ free'). F₂ was introduced as a preprepared mixture of 4.77% in He (Distillers M G).

Results and Discussion

Kinetics of HF(v = 3) Formed in the Reaction of F atoms with HCl

Time-resolved vibrational emission in the HF(3,0) band following the photolysis of F_2 in the presence of HCl was observed at four different temperatures: 294, 218, 179, and 139 K. A typical trace of this chemiluminescence is shown in the inset to Figure 1. In each series of experiments performed at a particular temperature, time-resolved emission traces were recorded at different concentrations of HCl, the F_2 partial pressure and the total pressure of the gas mixture being kept constant.



Figure 1. Plot of the first-order rate constants λ_{slow} measured in experiments on F_2/HCl mixtures at 138 K against the concentration of HCl. The inset shows a trace of the HF (3,0) emission from a mixture at 294 K which contains 1.44×10^{15} molecule cm⁻³ of F_2 and 2.28×10^{15} molecule cm⁻³ of HCl diluted to a total pressure 14.0 torr.

All these traces could be fitted accurately to a double exponential function of the form:

(iii) Signal =
$$A' \{ \exp(-\lambda_{slow} t) - \exp(-\lambda_{fast} t) \}$$

using a nonlinear least-squares fitting program. The fact that the signal traces take this form confirms that the kinetics of HF(v = 3) in this reaction system are determined entirely by the reaction of F atoms with HCl [15],

(1a)
$$\mathbf{F} + \mathrm{HCl} \longrightarrow \mathrm{HF}(\nu \leq 3) + \mathrm{Cl}; \quad \Delta_r H^o = -139.6 \text{ kJ mol}^{-1}$$

and the relaxation of $HF(\nu = 3)$ predominantly by collision with HCl,

(2a)
$$\operatorname{HF}(\nu = 3) + M \longrightarrow \operatorname{HF}(\nu < 3) + M$$

The reaction of the Cl atoms produced in reaction (1a) with F_2

(3a)
$$\operatorname{Cl} + \operatorname{F}_2 \longrightarrow \operatorname{ClF} + \operatorname{F}; \quad \Delta_r H^\circ = -92 \text{ kJ mol}^{-1}$$

is too slow to propagate the chain reaction involving HCl and F_2 to any significant degree.

The values of λ_{fast} and λ_{slow} were both found to vary linearly with the concentration of HCl yielding second-order rate constants. In Ar carrier gas, the plots of λ_{fast} against [HCl] have slightly steeper gradients than those of the corresponding plots of λ_{slow} against [HCl] and have larger intercepts on the [HCl] = 0 axis. The latter observation indicates that λ_{fast} should probably be equated to $k_{1\text{st}}'' = \sum k_{2\text{a}}[M]$, the sum of the psuedo-first-order rate constants for relaxation of HF(v = 3) by each species present in the gas mixture, and $\lambda_{\rm slow}$ to $k'_{\rm 1st}$, the psuedo-first-order rate constant for the reaction of F atoms with HCl. In order to confirm this assignment, some experiments were carried out using N_2 as carrier gas. N_2 is known [16] to relax vibrationally excited HF much more rapidly than argon. Consequently, in these experiments with N_2 present, λ_{fast} was observed to increase significantly compared with otherwise similar experiments in argon, whereas λ_{slow} was unaffected by the change in carrier gas. Our finding that the relaxation of $HF(\nu = 3)$ by HCl is faster than the reaction of F atoms with HCl is in agreement with the conclusion of Smith and Wrigley [6(a)]. Figure 1 shows a plot of values of λ_{slow} versus [HCl] and Table I summarizes the rate constants for the reaction of F atoms with HCl (k_{1a}) and for the relaxation of HF($\nu = 3$) by HCl (k_{2a}) . Our data at room temperature are compared with those determined by Wrigley and Smith [6(a)].

Our room temperature values of k_{1a} and k_{2a} (HCl) are in good agreement with those determined by Smith and Wrigley [6(a)], using a very similar method. The

TABLE I. Rate constants $(k/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for the reaction of F atoms with HCl and for the relaxation of HF($\nu = 3$) by HCl at different temperatures.

T/K	k_{1a} reaction	No. of runs	k _{1b} (relaxation)	No. of runs	Ref.
296	$7.0 \pm 0.3^{\mathrm{a}}$	_	11.4 ± 0.7		[6(a)]
294	7.2 ± 0.5	7	9.6 ± 1.2	4	this work
218	6.1 ± 0.5	4	11.2 ± 1.3	3	this work
179	6.7 ± 0.8	4	8.6 ± 1.3	4	this work
139	6.7 ± 0.3	2	$8.8~\pm~1.0$	2	this work

^a Quoted errors correspond to one standard deviation.



Figure 2. Arrhenius plot of the rate constants for reaction (1a) of F atoms with HCl. The squares represent our data, with \pm one standard deviation shown; the circles are the results of Wurzburg and Houston [5(b)]; and the triangle shows the rate constant determined at room temperature by Smith and Wrigley [6(a)].

only previous study of the temperature-dependence of the rate constant for reaction between F atoms and HCl is that of Wurzberg and Houston [5(b)]. We compare our results to theirs in Figure 2. It is seen that there is good agreement on the lack of temperature-dependence of this rate constant at temperatures below room temperature, despite the fact that there is some doubt about the accuracy of Wurzberg and Houston's data since unresolved emission in the HF fundamental vibrational bands was observed in their experiments.

There have been no previous studies of the temperature dependence of the rate of relaxation of $HF(\nu = 3)$ by HCl. Experiments by Bott and Cohen [17] on the relaxation of $HF(\nu = 1)$ by HCl demonstrate the insensitivity of the rate of that process over the temperature range from 295 to 1100 K. Our values of k_{2a} (HCl) are plotted against temperature in Figure 3. It seems that the process of energy transfer in collisions between vibrationally excited HF and HCl may be dominated by the strong attractive forces between the two molecules resulting from the formation of a hydrogen bond.

Kinetics of HF(v = 3) Formed in the Reaction of F Atoms with CH_4

Experiments on the emission from $HF(\nu = 3)$ when F_2 was photolyzed in the presence of CH_4 were carried out at the same four temperatures (294, 218, 179, and 139 K) as the experiments on F + HCl. However, the F + CH_4 system is more complex, since now the chain reaction, carried by the reaction between CH_3 radicals and F_2 , proceeds at a significant rate. Consequently, and as shown in the typical emission trace displayed in the insert to Figure 4, the traces of time-resolved chemiluminescence do not comprise an exponential rise and exponential fall returning to zero intensity at long times. Rather the intensity of emission approaches an approximately constant finite value at long times, resulting from the reaction between CH_4 and a steady-state concentration of F atoms, $[F]_{ss}$.



Figure 3. Rate constants for relaxation of HF(v = 3) by HCl (\bigcirc) and CH₄ (\blacksquare) at temperatures from 294 to 139 K.

The analysis of time-resolved infrared chemiluminescence traces in the situation where a reaction chain propagates has been considered by Leone and co-workers [7]. When, as in our experiments, one observes emission from only the highest vibrational level of the emitter, it is necessary to consider the kinetics of three processes [15]:

(1b)
$$\mathbf{F} + \mathbf{CH}_4 \longrightarrow \mathbf{HF}(\nu \leq 3) + \mathbf{CH}_3; \quad \Delta_r H^o = -131.5 \text{ kJ mol}^{-1}$$

(2b)
$$\operatorname{HF}(\nu = 3) + M \longrightarrow \operatorname{HF}(\nu < 3) + M$$

(3b) $CH_3 + F_2 \longrightarrow CH_3F + F; \quad \Delta_r H^o = -301 \text{ kJ mol}^{-1}$

It is possible to obtain an analytical expression for how the concentration of the emitting species, $[HF(\nu = 3)]$, varies with time if one assumes: (a) that there is no significant depletion of the reagents CH_4 and F_2 over the period of observation, and (b) that chain termination by radical-radical combination is negligibly slow, so that the sum of the concentrations [F] and $[CH_3]$ is equal to the concentration of F atoms, $[F]_0$, initially produced by the pulsed photolysis of F_2 . Under these circumstances, the concentration of $HF(\nu = 3)$ is given by:

(iv)
$$[HF(\nu = 3)] = A\{1 - \exp(-\lambda_{slow}t)\} + B\{\exp(-\lambda_{slow}t) - \exp(-\lambda_{fast}t)\}$$

where $\lambda_{slow} = \sum k_{2b}$ [M], the sum of the pseudo-first-order rate constants for relaxation from HF($\nu = 3$) by each species M present in the gas mixture, and $\lambda_{fast} = k_{1b}[CH_4] + k_{3b}[F_2]$, the sum of pseudo-first-order rate constants for the chain propagating steps (1b) and (3b). The values of A and B are most usefully expressed in terms of [F]₀ and [F]_{ss}, where [F]_{ss} is given by:

(v)
$$[\mathbf{F}]_{ss} = [\mathbf{F}]_0 k_{3b} [\mathbf{F}_2] / (k_{1b} [\mathbf{CH}_4] + k_{3b} [\mathbf{F}_2])$$

In terms of these concentrations,

(vi)
$$A = [F]_{ss}k_{1b,\nu=3}[CH_4]/\lambda_{slow}$$

(vii) and
$$B = ([F]_0 - [F]_{ss})k_{1b,\nu=3}[CH_4]/(\lambda_{fast} - \lambda_{slow})$$

where $k_{1b,\nu=3}$ is the rate constant for the reaction between F and CH₄ producing $HF(\nu = 3)$.

In principle, the three rate constants k_{1b} , k_{2b} , and k_{3b} could all be determined by fitting traces of time-resolved infrared chemiluminescence from $HF(\nu = 3)$ to a function of the form given in eq. (iv) and then observing how λ_{fast} , λ_{slow} , and A/Bdepend on the concentrations of CH_4 and F_2 . In practice, following Leone and coworkers [7], we adopted a rather different procedure in which particular series of experiments were designed to yield particular rate constants.

The first such series of experiments were carried out with a relatively low concentration of F_2 and various concentrations of CH_4 . Under these conditions, i.e., with $k_{3b}[F_2] \ll k_{1b}$ [CH₄], the effects of chain propagation are small, eq. (iv) reduces to eq. (iii), and the values of k_{1b} and k_{2b} could be deduced from an analysis similar to that carried out for the experiments on F_2/HCl mixtures. In this case, previous work [12,16] has established unequivocally that λ_{fast} can be equated to the sum of the psuedo-first-order rate constants for reactions (1b) and (3b), and λ_{slow} to the pseudo-first-order rate constant for relaxation of HF molecules from $\nu = 3$. Experiments in which the concentration of F_2 was kept constant and that of CH₄ varied were performed in order to determine k_{1b} and k_{2b} (CH₄). An example of a plot of λ_{fast} versus [CH₄] is displayed in Figure 4, and the values of the second-order rate constants for reaction between F atoms and CH₄ and for relaxation of HF($\nu = 3$) by CH₄ are listed in Table II.

Since the first-order rate constant $\lambda_{\text{fast}} = k_{1b}[\text{CH}_4] + k_{3b}[\text{F}_2]$, it should, in principle, be possible to determine k_{3b} from the values of the $[\text{CH}_4] = 0$ intercepts of plots, like that in Figure 4, of λ_{fast} versus $[\text{CH}_4]$. This method was applied but yielded rather imprecise values of k_{3b} .

In a second series of experiments, the concentration of F_2 was varied at low, fixed, concentrations of CH_4 . Now the effect of chain propagation was apparent as in the



Figure 4. Plot of the first-order rate constants $\lambda_{\rm fast}$ measured in experiments on F_2/CH_4 mixtures at 294 K against the concentration of CH₄. The inset shows a trace of the HF (3,0) emission from a mixture at 294 K which contains 1.54×10^{15} molecule cm⁻³ of F₂ and 1.4×10^{14} molecule cm⁻³ of CH₄ diluted to a total pressure of 3.01 torr.

T/K	k_{1b} (F + CH ₄)	k_{2b} (relaxation)	k_{3b} (CH ₃ + F ₂)	No. of Runs	Ref.
room	57 ± 3	_	_	_	[18]
250 - 450	$300 \exp(-400/T)$	_	-	_	[12]
295	-	18 ± 4	-		[21]
300-400	-	_	$6.6 \exp(-550/T)$	-	[20]
294	53. \pm 3.0 ^a	$18. \pm 2.6$	1.17 ± 0.07	3	this work
218	$53. \pm 3.$	21. \pm 2.	$0.70~\pm~0.07$	1	this work
179	$74. \pm 6.5$	$20. \pm 1.3$	0.60 ± 0.06	3	this work
139	$80. \pm 9.$	$22. \pm 2.$	$0.17~\pm~0.05$	1	this work

TABLE II. Rate constants $(k/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for the reaction of F atoms with CH₄, for the relaxation of HF(v = 3) by CH₄, and for the reaction of CH₃ radicals with F₂ at different temperatures.

^a Quoted errors correspond to one standard deviation.

trace of vibrational chemiluminescence shown in the inset to Figure 4. However, the signals at long time decayed slowly due to consumption of the relatively low concentration of CH_4 . To circumvent this difficulty, the following procedure was adopted.

First, the traces were analyzed by fitting them to a function of the form given in eq. (iv) but truncating the fit at delays where the signal reached approximately constant values. These fits were carried out using values for λ_{slow} based on the relaxation rate constant $k_{2b}(CH_4)$ obtained from the first series of experiments. The values of λ_{fast} varied linearly with [F₂] but gave only an approximate value for k_{3b} since, even at the highest [F₂] used, k_{1b} [CH₄] was still appreciably larger than $k_{3b}[F_2]$.

The third, and preferred, way of finding k_{3b} was based on the magnitude of the asymptotic signal from $HF(\nu = 3)$. To use this method, it is necessary to reference the size of this signal at long times to that the signal would have at zero time if λ_{fast} was infinitely large. Inspection of eq. (iv) shows that, in this limit, the concentration of $HF(\nu = 3)$ at zero time, i.e. $[HF(\nu = 3)]_0$, would simply be A. Similarly, the concentration of $HF(\nu = 3)$ at long times, i.e., $[HF(\nu = 3)]_{ss}$, is equal to B. Consequently, one can write:

(viii)

$$A/B = [\mathrm{HF}(\nu = 3)]_{\mathrm{ss}}/[\mathrm{HF}(\nu = 3)]_0 = I_{\mathrm{ss}}/I_0$$
$$= (k_{3\mathrm{b}}[\mathrm{F}_2]/k_{1\mathrm{b}}[\mathrm{CH}_4])\{(\lambda_{\mathrm{fast}} - \lambda_{\mathrm{slow}})/\lambda_{\mathrm{slow}}\}$$

where I_{ss} and I_0 are the intensities of the vibrational chemiluminescence at long times (in the absence of CH₄ depletion), and that estimated by back-extrapolation of the signals on the decaying portion of the signal traces. This analysis is essentially that given by Dolson and Leone [7(b)] without the approximation, which would not always be appropriate in our experiments, that $k_{3b}[F_2] << k_{1b}[CH_4]$.

In practice, the value of $I_{\rm ss}$ was obtained by fitting a trace of vibrational chemiluminescence from the second series of experiments with high $[F_2]$ in the way that has been described. I_0 was estimated from signals on the rapidly decaying portion of the trace and the value of $\lambda_{\rm slow}$ from the previously determined rate constant for relaxation of $\rm HF(v=3)$. Then, from the gradient of a plot of $(I_{\rm ss}/I_0)$ vs. $[F_2] (\lambda_{\rm fast} - \lambda_{\rm slow})/(\lambda_{\rm slow} k_{\rm 1b}[\rm CH_4])$ the value of $k_{\rm 3b}$ could be determined. An example of such a plot is given in Figure 5 and this method was employed to give the values



Figure 5. Plot of $(I_{\rm ss}/I_0)$ from F_2/CH_4 mixtures at 294 K versus $[F_2] (\lambda_{\rm fast} - \lambda_{\rm slow})/(\lambda_{\rm slow} k_{\rm 1b} [CH_4])$. The gradient of this line corresponds (see text) to $k_{\rm 3b}$, the rate constant for reaction (3b) between CH₃ radicals and F₂.

of k_{3b} for different temperatures that are listed in Table II. Application of the two methods which rely on the dependence of λ_{fast} on [F₂] gave values of k_{3b} consistent with those listed in Table II.

There have been surprisingly few attempts to measure rate constants for the elementary reaction between F atoms and CH_4 . It serves as the main sink for any fluorine atoms which are released into the stratosphere as fluorine-containing compounds such as the CFCs are broken down. Atkinson et al. [12] recommend k_{1b} $(298 \text{ K}) = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and the Arrhenius expression: } k_{1b}(T) = 3.0 \times 10^{-10} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for use between } 250 \text{ and } 450 \text{ K}.$ The kinetic measurements most closely resembling our own are those of Fasano and Nogar [18]. They essentially used the method employed by Houston and co-workers [4,5] in which F atoms are produced by infrared multiphoton dissociation of SF_6 and total infrared chemiluminescence is observed from the vibrationally excited HF molecules which are produced. Fasano and Nogar's experiments were performed only at room temperature at which they found k_{1b} (298 K) = (5.7 ± 0.3) × 10⁻¹¹ cm³ molecule⁻¹ s^{-1} , in excellent agreement with our value at 294 K. Our results, which show that k_{1b} increases as the temperature falls below ca. 200 K, are not in good agreement with an extrapolation of the Arrhenius expression recommended by Atkinson et al. [12]. The reaction between F atoms and CH₄ is appreciably faster at low temperatures than had previously been thought. This kind of variation of rate constant with temperature is unusual for a presumably direct reaction between a radical and a saturated molecule, but it is not unprecedented. Recent measurements [14(b)] on the reaction of CN radicals with C_2H_6 show that its rate constant reaches its maximum value at 26 K.

Coupled with the results of Fasano and Nogar [18], our measurements suggest that the rate constant k_{1b} for the reaction of F atoms with CH₄ at 298 K is slightly lower than had previously been thought [12]. This reaction and its rate constant have frequently been used as the reference in measurements of relative rates, in which the intensities of infrared chemiluminescence from HF product molecules are compared under fast flow conditions [19]. If our value of k_{1b} is confirmed, then it will

be necessary to rescale the values of the rate constants for other reactions derived by comparison with that for $F + CH_4$.

Our values of the rate constant k_{3b} for reaction between CH₃ radicals and F₂ at temperatures from 294 to 139 K are listed in Table II and displayed on an Arrhenius plot in Figure 6. They fit the Arrhenius expression: $k_{3b}(T) = 7.0 \times 10^{-12} \exp(-490/T)$ cm³ molecule⁻¹ s⁻¹. As far as we are aware, the only previous determination of the rate constants for this reaction is by Seeger et al. [20]. Their rather indirect measurements yielded an Arrhenius expression for k_{3b} between 300 and 400 K: $k_{3b}(T) = 6.6 \times 10^{-12} \exp(-500/T) \text{ cm}^3$ molecule⁻¹ s⁻¹, with error limits of about a factor of two in both the A-factor and the activation energy. Within these wide error limits, the results of Seeger et al. are clearly consistent with our findings.

The rate constant k_{2b} for the relaxation of $HF(\nu = 3)$ by CH_4 which we find at room temperature is in excellent agreement with that determined by Lampert et al. [21]. As for the relaxation of $HF(\nu = 3)$ by HCl, the rate constants show no significant dependence on temperature. The values of k_{2b} are compared with those of k_{2a} in Figure 3.

Kinetics of $HF(\nu = 3)$ Formed in the Reaction of F Atoms with CF_3H

The processes which are initiated when F atoms are generated in the presence of CF_3H are formally similar to those in the F + CH_4 system [15]:

(1c) $\mathbf{F} + \mathbf{CF}_3\mathbf{H} \longrightarrow \mathbf{HF}(\nu \leq 2) + \mathbf{CF}_3; \quad \Delta_r \mathbf{H}^\circ = -123_{.5} \text{ kJ mol}^{-1}$

(2c)
$$\operatorname{HF}(\nu = 2) + M \longrightarrow \operatorname{HF}(\nu < 2) + M$$

(3c)
$$CF_3 + F_2 \longrightarrow CF_4 + F;$$
 $\Delta_r H^\circ = -385 \text{ kJ mol}^{-1}$

However, they do differ in some important respects. First, the exothermicity of reaction (1c) is insufficient for HF to be formed in the $\nu = 3$ vibrational level, in other than a very low yield. Smith [19(a)] estimated that ca. 1% of the HF formed in



Figure 6. Arrhenius plot of the rate constants for reaction (3b) of CH_3 radicals with F_2 .

this reaction is produced in $\nu = 3$, whereas 40% is generated in $\nu = 2$. Consequently in this case $\nu_{max} = 2$ and, as stated earlier, in these experiments the (2,0) vibrational chemiluminescence was observed. The other differences concern the absolute and relative values of the rate constants for processes (1c)-(3c). In the case of CF₃H, the rate constant for relaxation of $HF(\nu = \nu_{max})$ is much larger than that for the primary reaction of F atoms. As a result, the concentrations of $HF(\nu = \nu_{max})$ are much lower than those in experiments on the systems containing HCl and CH₄. Although the spontaneous emission coefficient for the (2,0) band is about an orderof-magnitude larger than that for the (3,0) emission, this advantage is largely lost because of the longer wavelength and intrinsically less sensitive detector needed to observe the longer wavelength emission. Finally, the absolute value of the rate constant for the $F + CF_3H$ reaction at room temperature is more than 100 times less than the corresponding rate constant for $F + CH_4$. These factors mean that the quality of the vibrational chemiluminescence traces from experiments on $F + CF_3H$ is much poorer than that from $F + CH_4$ even at room temperature. Reaction (1c) must clearly have an activation energy so that the situation becomes even worse as the temperature is lowered.

For these reasons, we only report, in Table III, rate constants at 294 K. The rate constant for reaction (1c) is in good agreement with that determined by Clyne and Hodgson [8(b)] in discharge-flow experiments coupled to detection of F atoms by resonance absorption. Our results confirm that the highly exothermic reaction between $CF_3 + F_2$ is rather slow, although our estimate of its rate constant is not in very good agreement with the value determined by Plumb and Ryan [22]. There has been no previous determination of the rate at which CF_3H relaxes any vibrational level of HF.

Summary

The experiments reported in this article demonstrate that time-resolved observations of vibrational chemiluminescence can, in favorable cases, be used to determine rate constants for reactive and inelastic processes at low temperatures. The rates of the F + HCl and F + CH₄ reactions, as well as those of the relaxation of $HF(\nu = 3)$ by HCl and CH₄, remain rapid as the temperature is lowered as far as 139 K, and our results suggest that the kinetics of these reactions could be studied at ultra-low temperatures [14]. The present work also constitutes the first direct kinetic study of the chain reaction between F₂ and CH₄. It provides new kinetic data for the F + CH₄ reaction and provides the first accurate rate constants for the CH₃ + F₂ reaction. Finally, our results confirm that the rate constants for the reactions of general form, F + CF_xH_y \rightarrow HF + CF_xH_{y-1}, decrease as x increases [19].

TABLE III. Rate constants $(k/10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ for the reaction of F atoms with CF₃H, for the relaxation of HF(v = 2) by CF₃H, and for the reaction of CF₃ radicals with F₂ at 294 K.

T/K	k_{1c} (F + CF ₃ H)	k_{2c} (relaxation)	$k_{3c} (CF_3 + F_2)$	No. of runs	Ref.
298	1.5 ± 0.1	-	-	_	[8(b)]
295	-	-	0.70	-	[22]
294	1.2 ± 0.4^{a}	$16. \pm 3.$	$0.15~\pm~0.04$	3	this work

^a Quoted errors correspond to one standard deviation.

Acknowledgment

We thank SERC and the CEC, under its Science Plan program, for support of our work on gas-phase kinetics at low temperatures. CMM and DWAS are also grateful to SERC for the award of research studentships.

Bibliography

- R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity, Oxford University Press, New York, 1987.
- [2] (a) F.J. Wodarczyk and C.B. Moore, Chem. Phys. Lett., 26, 484 (1974); (b) K. Bergmann and C.B. Moore, J. Chem. Phys., 63, 643 (1975); (c) C.-C. Mei and C.B. Moore, J. Chem. Phys., 67, 3936 (1977); (d) C.-C. Mei and C.B. Moore, J. Chem. Phys., 70, 1759 (1979).
- [3] R.F. Heidner III, J.F. Bott, C.E. Gardner and J.E. Melzer, J. Chem. Phys., 72, 4815 (1980).
- [4] E. Wurzburg and P. L. Houston, J. Chem. Phys., 72, 4811 (1980).
- [5] (a) E. Wurzburg, A.J. Grimley, and P.L. Houston, Chem. Phys. Lett., 57, 373 (1978); (b) E. Wurzburg and P.L. Houston, J. Chem. Phys., 72, 5915 (1980).
- [6] (a) I. W. M. Smith and D. J. Wrigley, Chem. Phys. Lett., 70, 481 (1980); (b) I. W. M. Smith and D. J. Wrigley, Chem. Phys., 63, 321 (1981).
- [7] (a) D.J. Nesbitt and S.R. Leone, J. Phys. Chem., 86, 4962 (1982); (b) D.A. Dolson and S.R. Leone, J. Chem. Phys., 77, 4009 (1982); (c) L.J. Kovalenko and S.R. Leone, J. Chem. Phys., 80, 3656 (1984); (d) D.A. Dolson and S.R. Leone, J. Phys. Chem., 91, 3543 (1987); (e) D.J. Donaldson and S.R. Leone, J. Phys. Chem., 90, 936 (1986).
- [8] (a) M.A.A. Clyne and W.S. Nip, Int. J. Chem. Kinet., 10, 367 (1978); (b) M.A.A. Clyne and A. Hodgson, Chem. Phys., 79, 351 (1983).
- [9] For example: (a) A. R. Ravishankara and P. H. Wine, J. Chem. Phys., 72, 25 (1980); (b) R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem., 84, 2009 (1980).
- [10] (a) M Heaven, T. A. Miller, R. R. Freeman, J. C. White, and J. Bokor, *Chem. Phys. Lett.*, **86**, 458 (1982); (b) G. S. Selwyn, L. D. Baston, and H. H. Sawin, *Appl. Phys. Lett.*, **51**, 898 (1987).
- [11] R.W.F. Gross and J.F. Bott, Eds., Handbook of Chemical Lasers, Wiley, New York, 1976.
- [12] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data, 18, 881 (1989).
- [13] (a) P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans., 89, 631 (1993); (b) M. J. Frost,
 P. Sharkey, and I. W. M. Smith, J. Phys. Chem., 97, 12254 (1993).
- [14] (a) I. R. Sims, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, B. R. Rowe, and I. W. M. Smith, J. Chem. Phys., 97, 8798 (1992); (b) I. R. Sims, J. L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthauser, and I. W. M. Smith, Chem. Phys. Lett., 211, 461 (1993); (c) I. R. Sims, P. Bocherel, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, B. R. Rowe, and I. W. M. Smith, J. Chem. Phys., 100, 4229 (1994).
- [15] Reaction enthalpies are calculated from the enthalpies of formation listed in W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina in *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 10, JPL publication 92–20, 1992.
- [16] S.R. Leone, J. Phys. Chem. Ref. Data, 11, 953 (1982).
- [17] J.F. Bott and N. Cohen, J. Chem. Phys., 58, 4539 (1973).
- [18] D.M. Fasano and N.S. Nogar, Chem. Phys. Lett., 92, 411 (1982).
- [19] (a) D.J. Smith, D.W. Setser, K.C. Kim, and D.J. Bogan, J. Phys. Chem., 81, 898 (1977); (b)
 A.S. Manocha, D.W. Setser, and M.A. Wickramaaratchi, Chem. Phys., 76, 129 (1983); (c) B.S.
 Agrawalla and D.W. Setser in Gas-Phase Chemiluminescence and Chemi-Ionization, A. Fontijn, Ed., North-Holland, Amsterdam, 1985.
- [20] C. Seeger, G. Rotzoll, A. Lübber, and K. Schügerl, Int. J. Chem. Kinet., 13, 39 (1981).
- [21] J.K. Lampert, G.M. Jurisch, and F.F. Crim, Chem. Phys. Lett., 71, 258 (1980).
- [22] I.C. Plumb and K.R. Ryan, Plasma Chem. Plasma Process., 6, 11 (1986).

Received December 23, 1993 Accepted March 1, 1994