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Infrared Emission Spectra of HCl in CCl₄-Inhibited C₂H₄-O₂ Explosion by a Rapid Scan Infrared Spectrometer

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Abstract

The infrared emission spectra of HCl were observed in the explosion of CCl₄ added to a mixture of C₂H₄ and O₂ by a rapid scan spectrometer. From the detection of the *R* branch heads due to the (1-0), (2-1), and (3-2) transition and the survey of *P* branch lines, it was concluded that the vibrational excited states of HCl were distributed below $v=3$ during emission growth.

T_{rot} and T_{vib} at peak intensity were estimated from the intensities of the *P* branch lines to be 1750K and 2800K, respectively, which indicated that thermal equilibrium was not reached in the combustion wave. These results led to the conclusion that the predominant reaction for HCl formation is $\text{H} + \text{CCl}_4$ or $\text{CCl}_3 \rightarrow \text{CCl}_3$ or $\text{CCl}_2 + \text{HCl}$. The inhibition mechanism was discussed on the basis of the knowledge of the previously reported rate constants.

1. Introduction

It is well known that the addition of halogen compounds to flames slows down flame propagation and it is generally accepted that inhibition by these compounds are surely the results of chemical processes¹⁾.

Most of the previous studies of the inhibition mechanism have been made by comparing the observed flame properties with the predicted ones, which were derived by using an assumed inhibition mechanism and known rate constants^{2,3)}.

There have been limited direct observations related to elementary reactions or intermediates. We considered that the study of the infrared emission spectra in inhibited flames would be valuable from the standpoint of the reaction mechanism because it is known that much of the energy which is released by the chemical reaction initially takes the form of vibrational energy in the newly formed chemical bond, and is observed as infrared chemiluminescence. Thus if information on the vibrationally excited state of the product at the initial stage of the reaction can be obtained from the infrared emission spectra, it might be possible to estimate the most important elementary reaction.

Recently we have built a rapid scan infrared spectrometer and have showed that it was

a useful tool for the study of infrared emission in combustion waves^{4,5}. In this paper, we have applied this instrument to the investigation of the infrared emission spectra of the inhibited flame, especially, of HCl produced in the explosion reaction CCl₄-added stoichiometric mixture of C₂H₄ and O₂.

The infrared emission spectra of hydrogen halides in flames have been reported on HCl^{6,7}, HBr⁸) and HF⁹) in halogen-hydrogen flames. Among these, the emission band of HCl has been most extensively studied, being because it was the first example which gave direct proof that the association reaction produced vibrationally excited molecules¹⁰.

2. Experimental

The rapid scan infrared spectrometer and the related electronic circuits for this experiment were described previously in detail⁴. However, improvements thereafter were made in the data recording system by using a waveform recorder instead of a photographing device. Therefore, the important points will be briefly mentioned here. The instrument was a modified conventional grating infrared spectrometer which was equipped with a rapidly oscillating mirror and a PbSe detector (Hamamatsu TV, p791).

The frequency of the oscillation was 50cps; and therefore, the spectra could be obtained every 20ms. The wavenumber range in one scanning period was several hundreds cm⁻¹ at around a fixed central wavenumber. Signals from the detector were passed through a voltage follower and amplified 100 times by an amplifier (FET operational amplifiers, LF 356, were used). The amplified signals were followed on a 1K words, 8 bit, waveform recorder (NF Design Circuit Block, wave memory, WM 811A). The combustion was provoked by a spark discharge. The wave memory and the spark discharge were triggered simultaneously by the pulse train from the synchronization circuit.

The role of this circuit is not only to synchronize the period of the trigger pulse train with the oscillation of the mirror, but also to adjust the phase shift between the oscillation period and the center of the wavenumber region to be scanned.

All data stored in the wave memory were displayed and recorded on an X-Y recorder. The rise time of the whole detection circuit was 3μs, which corresponded to the optical resolution of 0.2cm⁻¹ at 3000cm⁻¹, whereas the optical resolving power determined by the slit width was 4cm⁻¹ at 300μm and at 3000cm⁻¹.

The reaction cell was a 7cm diam. by 40cm long pyrex vessel with stainless steel electrodes for spark discharge at one end. The emission was observed at right angles to the direction of the flame propagation from an optical window 12cm away from the electrodes.

The geometry of the optical path and the reaction vessel is shown in Fig. 1. The absorption spectrum of HCl at the fundamental region, which was measured with the same optical resolution, is shown in Fig. 2.

C₂H₄ and O₂ were obtained from commercial cylinders without further purification. CCl₄ vapor was obtained by distilling in vacuum from liquid CCl₄. The pressure range studied was 10mmHg for C₂H₄ and CCl₄, and 30mmHg for O₂.

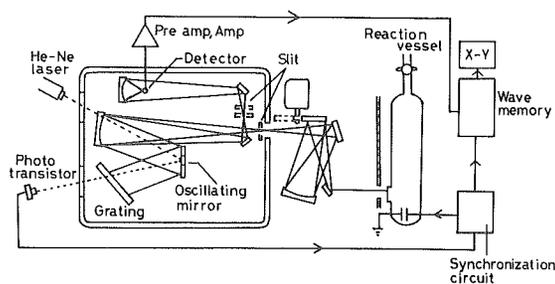


Fig. 1 Geometry of optical path in this experiment.

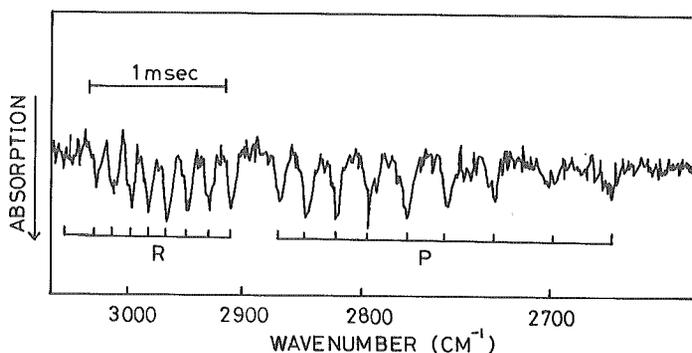


Fig. 2 Absorption spectrum of HCl gas. Pressure; 400mmHg, slit width; $300\mu\text{m}$.

3. Results

3.1 Flame propagation

When the mixture of 10mmHg of C_2H_4 and 30mmHg of O_2 was ignited, strong infrared emission bands due to H_2O and CO_2 were observed.

On the other hand, when 10mmHg of CCl_4 was added to the above mixture, the emission of H_2O disappeared and an emission band due to HCl appeared. Fig. 3 shows the effect of CCl_4 on the flame velocity, which was represented by the emission of CO_2 at 2300cm^{-1} .

In the reaction mixture without CCl_4 , the emission began to rise in less than 1ms after the spark, whereas in the inhibited flame the emission began to rise at 3ms, reaching a peak intensity in 6ms. The emission growth pattern was reproducible in the samples of the same composition. For comparison, the behavior of the emission of HCl, which was represented by the band head emission of $\nu(1-0)$ sequence at 3170cm^{-1} , was indicated in Fig. 3(c).

The emission fluctuations, which seemed to have been induced by an audible vibration in the pressure, were observed in the emission of CO_2 in the uninhibited flame and in the emission of HCl, as shown in Fig. 3(a) and (c).

It is interesting that the rise time for the HCl was longer than that for the CO_2 in the same flame.

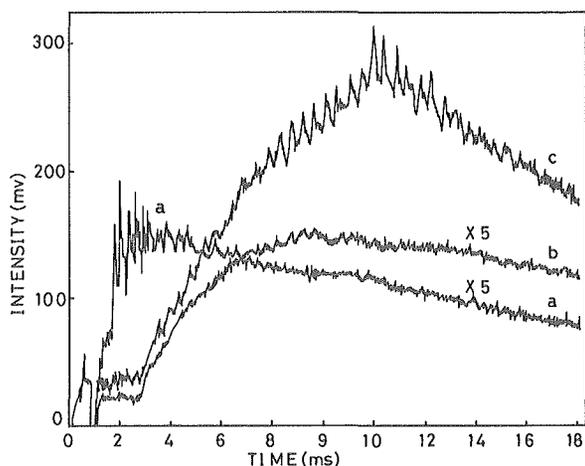


Fig. 3 Infrared emission growth pattern after ignition.

- a ; CO₂ emission in C₂H₄+O₂ flame measured at 2300cm⁻¹.
 b ; CO₂ emission in C₂H₄+O₂+CCl₄ measured at 2300cm⁻¹.
 c ; HCl emission in C₂H₄+O₂+CCl₄ measured at 3170cm⁻¹. Slit width was 300μm for all spectra.

3.2 Emission spectra of HCl

The emission bands of HCl in the fundamental region around 2900cm⁻¹ were measured at different times after the spark; Fig. 4 shows the results. The emission spectra were recorded by setting 3000cm⁻¹ to 4ms, 5ms, and 8ms from the spark trigger time, respectively. The band heads of $\nu(1-0)$, $\nu(2-1)$, and $\nu(3-2)$ were identified. The existence of the $\nu(2-1)$ lines was also confirmed by detecting the $R(6)$ line at 2891cm⁻¹ and the $R(10)$ line at 2955cm⁻¹.

In order to confirm the existence of $\nu(3-2)$ sequence and to investigate vibrational states higher than $\nu=3$, the wavenumber from 2900cm⁻¹ to 2400cm⁻¹ was scanned during emission rising.

Fig. 5(a) illustrates the spectrum of the emission lines from 2900cm⁻¹ to 2700cm⁻¹. Most of the stronger lines are the P branch of $\nu(1-0)$ emission. Although the P and R branch lines due to $\nu(2-1)$ and the R branch line due to $\nu(3-2)$ were overlapped by the $\nu(1-0)$ sequence, the $P(1)$ and $P(2)$ of $\nu(2-1)$ and the $R(5)$ and $R(6)$ of $\nu(3-2)$ could be identified at 2741, 2719, 2768, and 2784cm⁻¹, respectively, as depicted in Fig. 5(a).

Fig. 5(b) is the spectrum from 2800 to 2400cm⁻¹ measured during emission rising. No lines due to higher sequences than $\nu(4-3)$ were detected definitely. Therefore, it was concluded that in the flame inhibited by CCl₄, the vibrationally excited HCl was distributed at states below $\nu=3$.

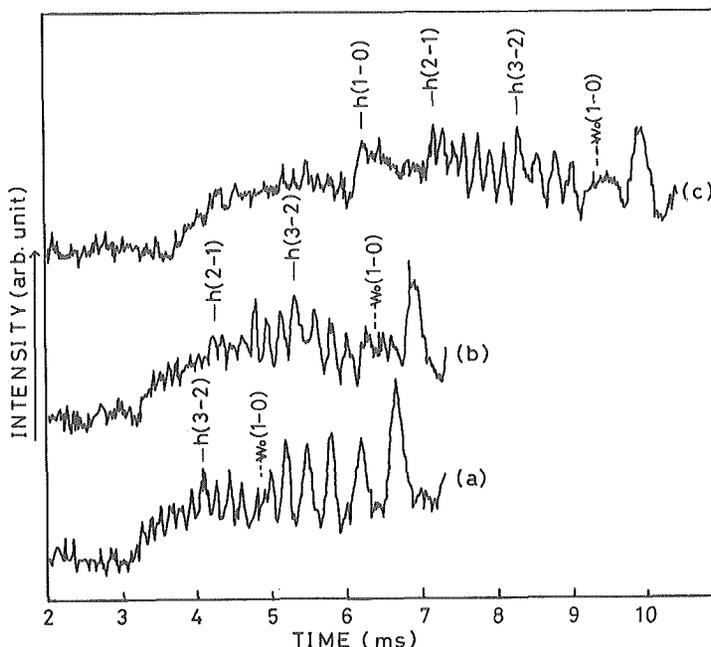


Fig. 4 *R* branch emission spectra of the fundamental band of HCl in the inhibited flame at early stage of emission growth. The spectra were obtained by setting 3000cm⁻¹ at the time
 a ; 4ms, b ; 5ms, and c ; 8ms from the trigger pulse for ignition. The wavenumber is 3180cm⁻¹ for *h* (1-0), 3070cm⁻¹ for *h* (2-1), and 2960cm⁻¹ for *h* (3-2). ω₀(1-0) indicates the position of the band origin of *v* (1-0), 2886cm⁻¹.

3.3 Estimation of the rotational temperature

Rough estimation of the rotational temperature of the inhibited flame at maximum intensity was made by using the relative intensity of each line of *P* branch from the *v*(1-0) band and the following Boltzmann distribution equation for the rotational states¹¹.

$$\log \frac{I_J}{(\omega_J)^4 S_J F_J} \propto -J'(J'+1)Bhc/kT \quad (1)$$

Where I_J is the emission intensity at J , ω_J is the wavenumber of the emission line at J , $S_J = J+1$ for *P* branch, J and J' are the rotational quantum number of the lower and upper *v* state, and F_J is the vibrational-rotational interaction factor, which is close to unity in the case of HCl¹⁰.

The emission spectrum of the whole *P* branch used for the calculation is shown in Fig. 6. The intensity of each line was normalized to the value at maximum intensity, 12ms after the spark, based on the emission rising curve in Fig. 3(c), the result of which is shown in Fig. 7.

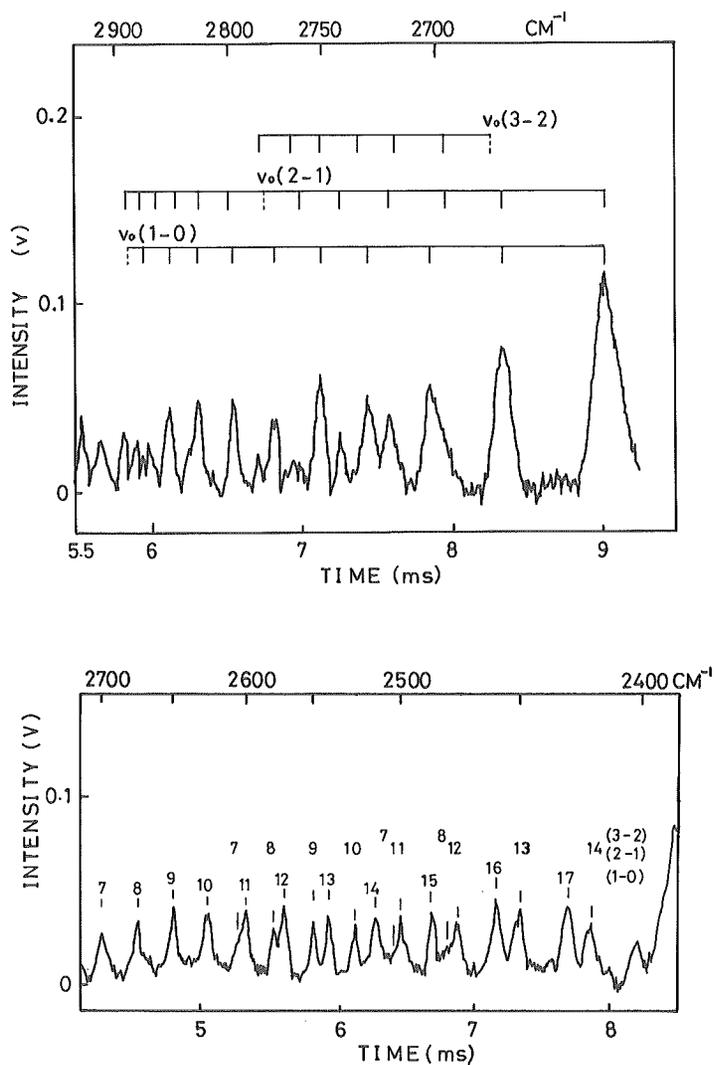


Fig. 5 P branch emission spectra of the fundamental band of HCl in the inhibited flame at early stage of emission growth.

a; 2900-2700 cm^{-1} , b; 2700-2400 cm^{-1} .

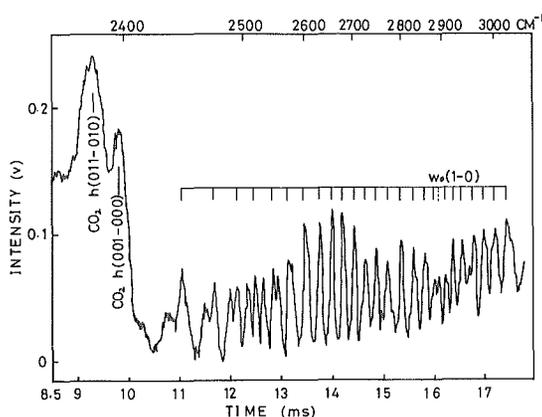


Fig. 6 P branch emission spectrum of HCl at around peak intensity. The assignment of the only ν (1-0) band are described.

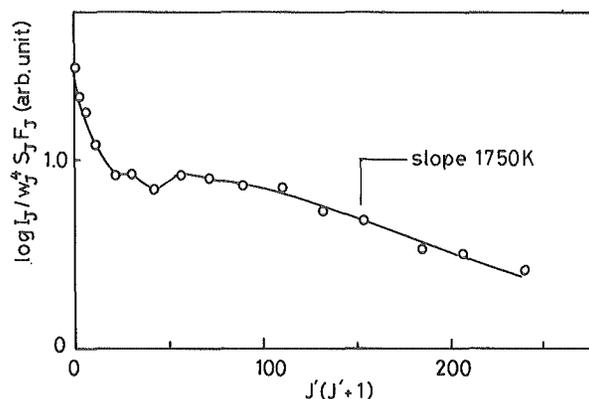


Fig. 7 The plots of the Boltzmann equation (1) by using the data of Fig. 6.

The intensity distribution was not fitted to the single temperature parameter. The strong self absorption was recognized on the lines between $J'=0$ to $J'=9$. The straight line, which obeyed equation (1), was obtained for the lines $J'=9$ and $J'=15$, the slope of which indicated $T_{\text{rot}}=1750\text{K}$.

3.4 Estimation of the vibrational temperature

The vibrational temperature was calculated by using the intensities at lines $J=9$ and $J=14$ of P branch due to $\nu(1-0)$ and the corresponding lines of $\nu(2-1)$ in the spectra which were measured at 12ms after the ignition. These lines were selected because they were free from overlapping by any other lines. Average intensity of the lines due to $\nu(2-1)$ relative to $\nu(1-0)$ lines was 0.45. Relative population was obtained by equation (2).

$$N_{v'} = \frac{I_{J^{v'v}}}{(\omega_0)_{v'v}^4 |R^{v'v}|^2} \quad (2)$$

Where $I_{J^{v'v}}$ is the emission intensity of the rotational line J of $v(v'-v)$ band, $(\omega_0)_{v'v}$ is the wavenumber of the band origin of $v(v'-v)$, and $R^{v'v}$ is the transition moment. By applying the $N_{v'}$ value to the Boltzmann distribution equation for vibration, the temperature was estimated to be 2800K. This value was a thousand degrees higher than the rotational temperature, suggesting that the vibrational distribution had not yet become equilibrated completely.

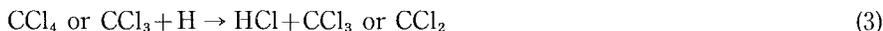
4. Discussion

4.1 Property of infrared emission in the combustion wave

Most of the infrared radiation from a stationary flame has been explained as thermal. However, as reviewed by Gaydon¹²⁾, there have been several old observations which suggested the contribution of emission from chemical processes in the explosion flames, although no satisfactory interpretation has been given as yet. The non-equilibrium in vibrational distribution observed in the present experiment also suggested that the infrared emission in the combustion wave involved not only the thermal radiation from hot products but also the chemiluminescence. This phenomena seemed to be an additional evidence to support the old observations.

4.2 Reaction of HCl formation

The infrared emission spectra indicated that the CCl_4 , which was added for the flame inhibition, decomposed to produce HCl, and that HCl was excited up to the vibrational level $v=3$. The facts that the vibrational distribution had not thermalized completely and that levels higher than $v=3$ were not definitely observed suggested that the highest attainable level of vibration is probably 3 in this flame. Taking into account that the vibrational energy of $v=3$ is 23.7kcal/mol, the following reaction was considered to be the most probable for the HCl formation:



since the exothermic heat of reaction (3) is 24.7kcal/mol. As the other possible reaction of HCl formation, the reaction of the Cl atom with the C_2H_4 molecule can be considered as follows,



It has been reported that reaction (4) occurred with the rate constant $k_4 = 8.4 \times 10^{-14} \exp(-1500/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the inhibited $\text{H}_2\text{-O}_2$ flame where HCl was added as an inhibitor²⁾. In the CCl_4 -added C_2H_4 flame, reaction (4) would be followed by reaction (5). Since the exothermic heat of HCl formation is estimated to be only 5kcal/mol for reaction (5), it probably does not influence the population at higher vibrational levels of HCl.

4.3 Flame inhibition

If reactions from (3) to (5) occur predominantly in the CCl_4 -added flame, the important

chain propagation and branching related to H atom such as,



will be retarded. In order to examine this assumption, it is necessary to compare the rate of each of the reactions described above. The rate constants of reactions (6) and (7) are known as $k_6 = 1.8 \times 10^{-10} \exp(-8500/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ¹³⁾ and $k_7 = 2.0 \times 10^{-7} T^{-0.91} \exp(-16630/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ¹⁴⁾. Thus k_6 was $1.5 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_7 = 1.9 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1750K. The rate constant of reaction (3) has not been reported in previous literatures; therefore, in the present study it was estimated from the following reaction, of which the rate constant was recently determined by Comborieu *et. al.*¹⁵⁾:



The extrapolated value of k_8 to 1750K was $3.1 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which was considerably smaller than that of reaction (6). However, as the steric factor of reaction (3) for CCl₄ is assumed to be larger than that for CH₂Cl₂, reaction (3) is able to compete with reactions (6) and (7), and, consequently, also to retard the reactions involving OH radicals and O atoms such as $\text{OH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{H}_2\text{O}$, $\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{O} + \text{CH}_2$, and $\text{O} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3 + \text{CHO}$, which are the most important reactions in the C₂H₄ oxidation mechanism.

5. Summary

The infrared emission spectra of HCl, which was produced in the combustion wave of CCl₄-added C₂H₄ and O₂ mixture, were investigated by using a rapid scan infrared spectrometer installed in our laboratory. The spectral range scanned was from 3200cm⁻¹ to 2400cm⁻¹. Three band heads due to $\nu(1-0)$, $\nu(2-1)$ and $\nu(3-2)$ were identified. The *P* and *R* branch lines of $\nu(1-0)$ up to $J=18$ and a part of the sequences of $\nu(2-1)$ and $\nu(3-2)$ were also observed.

However, no lines or band heads due to vibrational levels higher than $\nu=3$ were detected. T_{rot} and T_{vib} , which were estimated from the intensities of *P* branch lines, were 1750K and 2800K respectively, this indicated that a thermal equilibrium was not reached in the combustion wave even though the time required for the measurement was much longer than the vibrational relaxation. These results led to the conclusion that predominant reaction for HCl formation is $\text{H} + \text{CCl}_4$ or $\text{CCl}_3 \rightarrow \text{HCl} + \text{CCl}_3$ or CCl_2 , because the vibrational energy of $\nu=3$ is comparable to the exothermic heat of the above reaction. Comparison of the values of the rate constants at flame temperature provided a suggestion that the above CCl₄ reaction could result in the retardation of the important elementary reactions involving H atoms and OH radicals in C₂H₄ oxidation. More direct evidence, for example, the measurement of the rate constant of the reaction CCl₄ and H atom, must be added to confirm this conclusion.

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