

Chemical kinetics of OH radical with HCFC-22 and the residual life time in the troposphere*

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Abstract—The rate constants for the reaction of hydroxyl radical with HCFC-22 in the temperature range of 302–382 K have been determined by using discharge flow resonance fluorescence instrument. The Arrhenius expression in units $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ is given as follows:

$$k(T) = (1.74 \pm 0.2) \times 10^{-12} \exp[-(14.14 \pm 0.32)/RT] .$$

The residual life time of HCFC-22 has been calculated by a competitive method. Methylchloroform was selected as a reference material.

Keywords: hydroxyl radical; HCFC-22; discharge flow resonance fluorescence.

1 Introduction

There is sufficient evidence to suggest that chlorofluorocarbon (CFC) in the stratosphere will photolyze and release chlorine which will deplete ozone layer (Rowland, 1975; Watson, 1977). Therefore, alternatives to CFC are being pursued. Recently hydrofluorocarbons and hydrochlorofluorocarbons (HCFC) are recommended to replace CFC (Ren Zhang, 1990; Anthony, 1991). The presence of H atoms makes those substitutes easily to react with OH in the troposphere. And a large fraction of them are removed before reaching the stratosphere. HCFC-22 (CHClF_2) is one of the interesting HCFC. It is an important candidate to replace CFC-11. The reaction of HCFC-22 with OH radical in the atmosphere seems to be a main path of sink of this compound in the troposphere. Therefore, the rate constant and its temperature

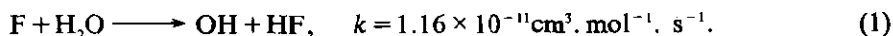
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coefficient of the reaction of HCFC-22 with OH are required to estimate the residual life time and the contribution of HCFC-22 to the depletion of ozone layer.

2 Experimental

By the discharge flow system and the technique of resonance fluorescence monitor of OH, the reaction rate constant of HCFC-22 with OH radical can be determined. The diagram of experimental apparatus is shown in Fig. 1. It mainly consists of five parts: (1) gases passage; (2) flow discharge reaction tube; (3) heating system; (4) generation of OH radical; (5) detection of OH.

Argon was selected as carrier gas. A mixture of Ar and CF_4 was flowing through the micro-wave discharge chamber in order to produce F atom. The produced F atom reacted with water vapor in the reaction tube and OH radical was generated immediately as the following reaction (Lee, 1984):



This reaction is very fast. It will be completed before F atom reaching the reaction region.

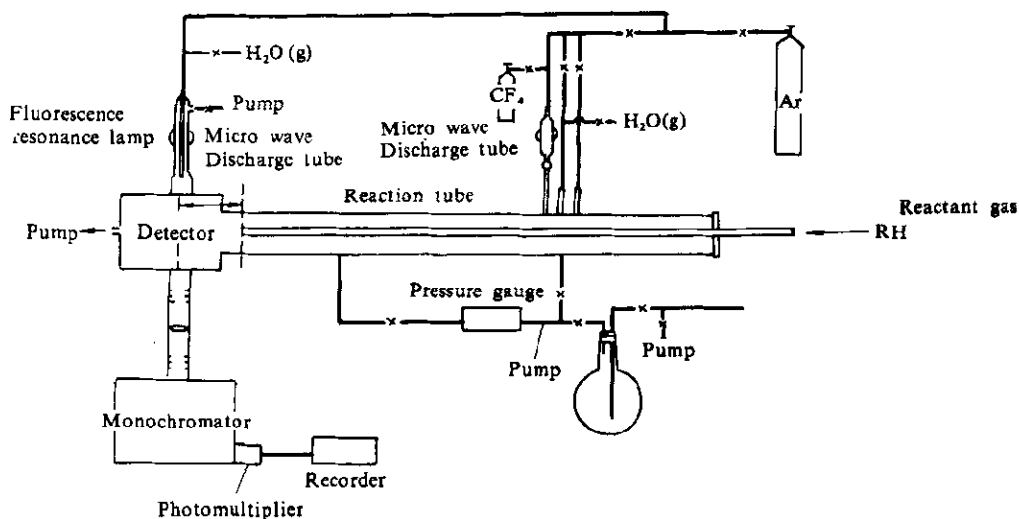


Fig. 1 Diagram of experimental apparatus

A large part of Ar directly entered the reaction tube as carrier gas, so every kinds of reactant gases could be mixed well. Reactant gas ($CHClF_2$) was flowing

through the removable inner tube into reaction tube. The volume of flowing gas was measured by a dp/dt glass flask.

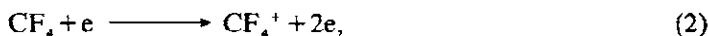
Flowing reaction tube was made by a glass tube. Its inner diameter is 27mm, the length is 100cm. The inner wall of reaction tube was coated by a thin layer of halo-wax to reduce the wall reaction of OH radical. The rate constant of wall reaction will reduce to $k(\text{wall}) < 18\text{s}^{-1}$.

There is a small tube in the center of reaction tube. The reactants are introduced in the system through this small tube. There is a O-ring rubber between small tube and the reaction tube, so the small tube can be moved smoothly. By change the inserted position of small tube, the sign of fluorescence of OH varied with time can be measured. Then the rate constant can be determined. In order to reduce the error from the small tube, the outside wall of the tube was coated by halo-wax.

The temperature of reaction tube was measured by a semiconductor into thermometer, which was controlled by a transformer. The fluctuation of temperature in the inner reaction region (0–40cm) was less than $\pm 2^\circ\text{C}$. During experimental period, the variation of the temperature was less than $\pm 1^\circ\text{C}$. So the heating system is suitable for determining the rate constant of elemental reaction.

2.1 OH radical

The F atom was produced by micro-wave dissociation of CF_4 . And the OH radical was formed as the following processes:



Reaction (5) is very rapid, $k = 1.16 \times 10^{-11} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. When the concentration of H_2O is higher than $5 \times 10^{14} \text{mol} \cdot \text{cm}^{-3}$, all of the F atom will transfer to OH completely within the length of 10cm.

2.2 The OH radical detecting system

The technique of resonance fluorescence system was used to detect the OH radical. This system consisted of resonance lamp, detecting chamber, grating monochromator, photomultiplier, current multiplier, and recorder.

Resonance lamp was made of silica glass. Water vapor was introduced by carrier gas Ar passing through a micro-wave discharge apparatus. At the same time, the spectra of OH was emitted. The light was introduced into the detecting chamber through a silica window. The OH radical which was flowing in the inner tube was excited by the radiation of resonance lamp. Then the fluorescence was emitted, and it was introduced passing through focused lens, monochromator, photomultiplier. The

electric current was multiplier and recorded. It was shown that the electric current was direct in proportion to the concentration of OH radical.

OH radical has a maximum resonance fluorescence peak near 3096Å, therefore, the wavelength of monochromator was set at 3096Å (Carleton, 1976; Kyuman, 1984).

Generally, the reaction of flow discharge system was carried out at pseudo first order condition. In this experiment, [OH] is about in the range of 10^{10} – 10^{11} mol.cm⁻³, [CHClF₂] is 10^{13} – 10^{14} mol.cm⁻³. If [CHClF₂]/[OH]=100, then the concentration of CHClF₂ was considered as constant during reaction period. The kinetics equation was shown as follows:

$$-d [\text{OH}] / dt = k'' [\text{RH}] [\text{OH}] = k' [\text{OH}], \quad (6)$$

here, $k' = k''[\text{RH}]$, k' is pseudo first order reaction rate constant, k'' is second order reaction rate constant.

The key problem in this experiment is how to modulate the signal of OH fluorescence. Usually, we hope to use the limited amount of CF₄ to get the stronger sign..

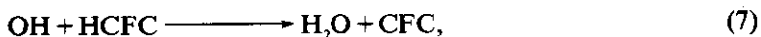
In this report, the following reactants were used:

Ar: purity > 99.98% (Beijing Oxygen Production Factory); CF₄: purity > 99.9% (Tianjin Third Nuclear Institute); CHClF₂: purity > 99.8% (Jinan Chemical Factory).

3 Results and discussions

3.1 Reaction mechanism and kinetics equation

The reaction of hydrochlorofluorocarbon with OH is expressed as follows:



According to the mass action law, we have,

$$-d [\text{OH}]/dt = k'' [\text{OH}] [\text{HCFC}], \quad (8)$$

If [HCFC]/[OH] > 100, the second order reaction can be considered as pseudo first order reaction.

$$-d [\text{OH}]/dt = k' [\text{OH}], \quad (9)$$

$$\text{so, } \ln \frac{[\text{OH}]_0}{[\text{OH}]_t} = k't + C, \quad (10)$$

where, t is the reaction time; k^1 is pseudo first order reaction rate constant; C is integral constant.

Kaufman (Kaufman, 1984) reported that the concentration of OH is direct in proportion to the intensity of resonance fluorescence of OH.

$$[\text{OH}] \propto I, \quad (11)$$

$$\text{so, } \ln I_0/I_t = k^1 t + C'. \quad (12)$$

The reaction time t was determined by the distance which was the path of HCFC flowing apart from small tube into reaction tube to the detector window.

$$dt = dx/v, \quad (13)$$

$$\text{and } \ln(I_0/I_t) = k^1 x/v + C'. \quad (14)$$

Then plot $\ln(I_0/I_t)$ against x , a straight line can be given. The slop of the line is k^1/v . Where, v is flowing rate of gas in the tube.

$$\text{If } P(\pi r^2 v) = n_r RT, \text{ so } v = n_r RT / \pi r^2 P, \quad (15)$$

where, n_r is the mole number of flowing gas in the tube per second; T is temperature (K) of reaction tube; P is pressure (atm.) in the reaction tube; r is inner radius (mm) of reaction tube.

3.2 Reaction rate constant at different temperature

In this report, the reaction rate constants of HCFC-22 with OH radical were determined at the temperature range from 301K to 382K. The decay curves of OH reacting with HCFC-22 at 302K are shown in Fig. 2.

k^1 can be calculated from decay curves. Plotting k^1 against $[\text{CHClF}_2]$, we get k^1 at a given temperature. The curves of k^1 vers $[\text{CHClF}_2]$ at five different temperatures are shown in Fig. 3. k^1 and k^1 determined by the method described above are listed in Table 1.

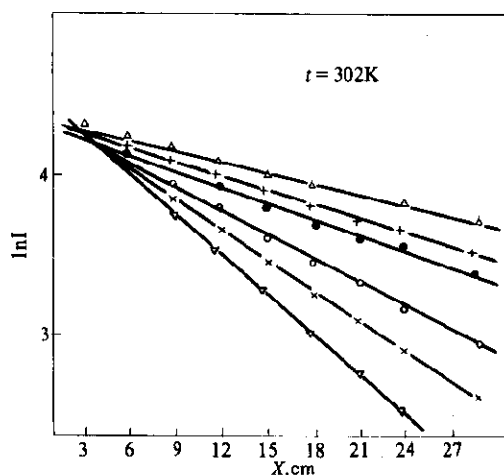


Fig. 2 The decay curves of OH reacting with HCFC-22 at 302K

Table 1 The reaction rate constants of pseudo first order and second order reaction for HCFC-22 with OH radical at different temperature

<i>t</i> , K	HCFC-22, mol. cm ⁻³ . 10 ⁻¹⁵	<i>k</i> ^I , s ⁻¹	<i>k</i> ^{II} , cm ³ . mol ⁻¹ . s ⁻¹ . 10 ⁻¹⁴
302	1.339	32.62	
	3.610	42.61	
	5.420	55.43	
	7.230	66.60	
	9.030	80.07	
	13.850	105.27	0.599
331.8	1.949	50.70	
	2.805	59.98	
	3.200	67.29	
	7.040	107.60	
	9.039	128.80	1.090
345	1.180	46.32	
	1.810	57.93	
	2.489	66.87	
	3.560	78.03	
	4.405	91.01	
	5.810	109.95	
	6.990	120.71	1.280
366	0.447	30.31	
	2.090	56.38	
	3.017	76.22	
	4.834	97.37	
	6.810	133.85	1.600
382	1.250	57.75	
	1.982	73.51	
	2.681	88.50	
	3.841	107.33	
	5.410	142.17	1.992

3.3 Arrhenius equation

A and *E* of Arrhenius equation can be obtained by plotting $\log k^{\text{II}}$ against $1/T$. The results of this experiment are shown in Fig. 4. The linear relationship between $\log k$ and $1/T$ is evident.

$$\log k = \log A - E/2.303RT, \quad (16)$$

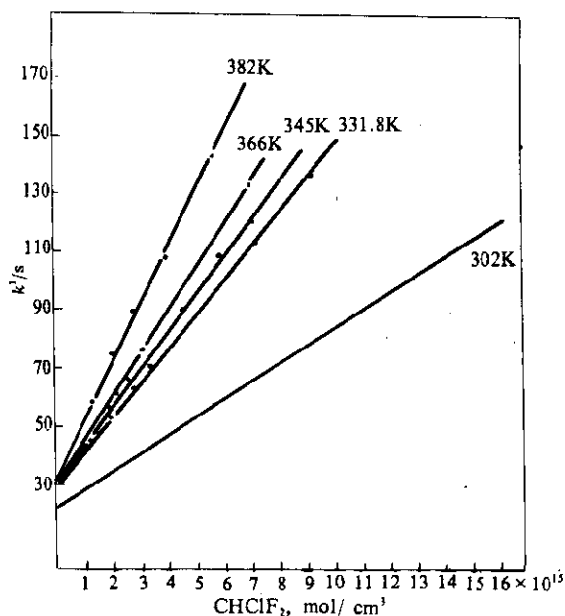


Fig. 3 The curves of k^1 vs CH_2ClF_2 at different temperature

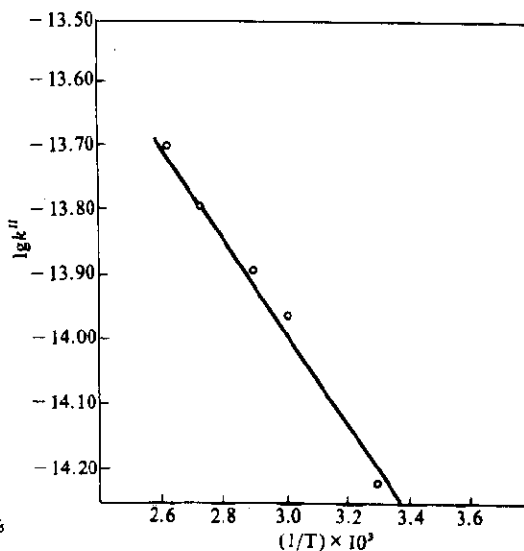


Fig. 4 The curve of $\log k^1$ vs $1/T$

so the Arrhenius equation of HCFC-22 is expressed as follows:

$$k(T) = (1.74 \pm 0.2) \times 10^{-12} \exp [-(14.14 \pm 0.32)/RT]. \quad (17)$$

The results of this work and reference data are presented in Table 2.

Table 2 Comparison of Arrhenius equations

$k(298)$, $\times 10^{15} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	A , $\times 10^{11} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	E kJ/mol	T , K	References
5.8 ± 1.0	1.74 ± 0.2	14.14 ± 0.32	302–382	This work
4.84 ± 0.46	0.925 ± 0.1	13.09 ± 0.59	250–350	Watson 1977
4.1 ± 0.9	9.55 ± 1.17	19.12 ± 0.002	294–426	Michael, 1979
5.3 ± 0.9	2.09 ± 1.32	14.97 ± 0.002	263–373	Handwerk, 1978

3.4 Error analysis

3.4.1 System error of k

$$k = 1.74 \times 10^{-19} \cdot \Phi_T / \Phi_{RH} \times T^2 / p^2 \times 1/\pi R^2 \cdot d \ln I / dX,$$

$$\Delta k / k = [(2 \cdot \Delta \Phi_T / \Phi_T) + (\Delta \Phi_{RH} / \Phi_{RH}) + (2 \times \Delta T / T) + (2 \Delta P / P) + (2 \Delta R / R) + (\Delta \text{slop} / \text{slop})^2]^{1/2}$$

$$= [(2 \times 0.05)^2 + (0.05)^2 + (2 \times 0.01)^2 + (2 \times 0.05)^2 + (2 \times 0.01)^2 + (0.04)^2]^{1/2} = 0.16$$

3.4.2 Error of A

$$A = k \exp(Ea / RT),$$

so $\Delta A / A = |\Delta k / k| + Ea / R |\Delta T / T|,$

$$\Delta A = 0.20 \times 10^{-12} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

3.4.3 Error of E

$$Ea = RT \ln(A / K)$$

$$\Delta Ea / Ea = |\Delta T / T| + RT / Ea |\Delta K / K|,$$

$$\Delta Ea = 0.32 \text{ kJ/mol}.$$

3.5 Wall reaction rate constant at different temperatures

In this reaction system, the ratio of inner surface area and volume of reaction tube is large. So the wall reaction of radical can not be ignored. In order to reduce wall reaction, the inner wall of reaction tube was treated by halo-wax. Generally, the wall reaction rate constant can be determined by the similar procedure as determination of k , but the reactant was instead of Argon and water vapor through the flow tube.

The $k(\text{wall})$ of this reaction system were determined at different temperatures. The results are listed in Table 3. As can be seen from Table 3 that the higher the reaction temperature is, the smaller the $k(\text{wall})_0$ would be, as the inner temperature of the reaction tube is higher than 312K.

Table 3 The $k(\text{wall})$ at different temperatures

$t, ^\circ\text{K}$	298	312	334	347	365
k^w, s^{-1}	18.2	18.4	14.6	12.4	10.3

3.6 Estimation for residual life time of HCFC-22 in the troposphere

At present time, the experimental results for OH concentration in the atmosphere are dispersion. It can not provide a satisfying data of OH concentration. So the average concentration of [OH] was used to estimate the residual life time of HCFC. Obviously, this method appeared some inadequacies. Therefore, we select the method as Prather (Prather, 1990) described to estimate the life time of HCFC reacted with OH radical and select CH_3CCl_3 as reference material. Because the source and sink of CH_3CCl_3 are well know. So we have

$$t(\text{HCFC}) = t(\text{me}) \cdot k(\text{me}, 277\text{K}) / k(\text{HCFC}, 277\text{K}). \quad (18)$$

$t(\text{HCFC})$, $t(\text{me})$ represent the life time of HCFC and CH_3CCl_3 in the atmosphere respectively, $k(\text{me}, 277)$, $k(\text{HCFC}, 277\text{K})$ are the rate constants of CH_3CCl_3 and HCFC with OH radical at 277K. According to the modelling calculation, 277K is the best temperature for the distribution of OH radical. From Arrhenius equation we get $k(\text{HCFC-22}, 277\text{K})$ as follows:

$$k(\text{HCFC-22}, 277\text{K}) = (3.74 \pm 0.092) \times 10^{-15} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

As we know $t(\text{me}) = 6.3\text{yr}$, and $k(\text{me}, 277\text{K}) = 7.704 \times 10^{-15} \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. So we get $t(\text{HCFC-22}) = 13.0\text{yr}$. The data from references are presented in Table 4.

Table 4 Comparison of residual life time of HCFC-22

t , year	13.0	17.2	15.6	14.7	21.3
References	This work	Renzhang, 1990	Watson, 1977	Handwerk, 1978	Micheal, 1979

4 Conclusions

The rate constants of CHClF_2 with OH radical were determined by using flow discharge resonance fluorescence method at five different temperatures in the range from 302K to 382K. The Arrhenius equation expresses as follows:

$$k(T) = (1.74 \pm 0.2) \times 10^{-12} \exp[-(14.14 \pm 0.32)/RT] \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

The residual life time of HCFC-22 in the troposphere was determined to be 13.0 years by a competitive method and CH_3CCl_3 was selected as reference material.

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