B–3.1 Measurements of Rate Constants and Mechanisms of Free Radical Reactions Related to Tropospheric Trace Gases. (Final Report)

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1. Abstract

The following two studies were carried out in order to understand chemical processes among tropospheric trace gases.

[1] Rate Constants for Reactions of Substituted Methyl Radicals with O_2.

Reactions of the substituted methyl radicals CH_2OCH_3, CH_2NH_2, CH_2I, and CH_2CN with O_2 have been studied by a combination of pulsed laser photolysis and photoionization mass spectrometry. The reactivity is greatly enhanced by substituting one of the hydrogen atoms of a methyl radical with the electron–donating substitutents, – OCH_3 and $-NH_2$. The rate constants obtained at 298.5K were $(6.5 \pm 0.7) \times 10^{-12}$ and $(3.5 \pm 0.4) \times 10^{-11}$ in units of cm^3 molecule^{-1} s^{-1} for CH_2OCH_3 and CH_2NH_2, respectively. The reactivity is reduced for CH_2I and CH_2CN, which have the electron–withdrawing substitutents, $-I$ and $-CN$. The rate for the reaction of CH_2I with O_2 was $(1.6 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The reactivity of substituted methyl radicals was discussed by the correlation with ionization potentials and electronegativities of radicals.

[2] Measurements of Rate Constants for HO_2+NO and NH_2+NO Reactions.

Absolute rate constants for HO_2+NO, NH_2+NO reactions were measured by a photoionization mass spectrometry coupled with a laser flash photolysis. HO_2, and NH_2 radicals were photoionized by an Ar resonance lamp and were detected as their parent ions (HO_2^+ and NH_2^+). The rate constants were determined to be

$$k (HO_2 + NO) = (6.5 \pm 2.0)10^{-12} \; cm^3 \; molecule^{-1} \; s^{-1}$$
$$k (NH_2 + NO) = (1.9 \pm 0.3)10^{-11} \; cm^3 \; molecule^{-1} \; s^{-1}$$

Both rates are consistent with those previously reported.

Key Word   Free Radical, photoionization Mass Spectrometry, Rate Constant, HO_2, NH_2, Substituted Methyl Radical
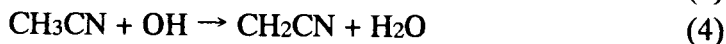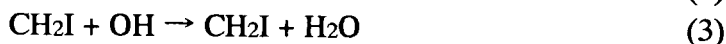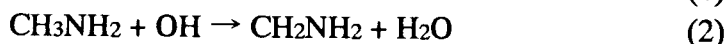
2. Research Objective

In this research project, elementary reactions involving following important free radicals were investigated.

[1] Rate Constants for Reactions of Substituted Methyl Radicals (CH_2OCH_3, CH_3NH_2, CH_2I, and CH_2CN) with O_2.

Substituted methyl radicals, such as CH_2OCH_3, CH_2NH_2, CH_2I, and CH_2CN are

produced primary by reactions of CH_3OCH_3, CH_3NH_2, CH_3I, and CH_3CN with OH radicals in the tropospheric atmosphere.

$$CH_3OCH_3 + OH \rightarrow CH_2OCH_3 + H_2O \tag{1}$$

$$CH_3NH_2 + OH \rightarrow CH_2NH_2 + H_2O \tag{2}$$

$$CH_2I + OH \rightarrow CH_2I + H_2O \tag{3}$$

$$CH_3CN + OH \rightarrow CH_2CN + H_2O \tag{4}$$

Among above reactions, reaction(3) is thought to be important in chemistry of marine atmosphere, and reactions(2) and(4) are important as pimary reaction of biogenic hydrocarbons. Radicals produced by reactions (1)–(4) might react with oxygen molecule in the atmosphere.

$$R\bullet + O_2 + M \rightarrow RO_2 + M \tag{5}$$

In this study , reaction (5) for R = CH_2OCH_3, CH_2NH_2, CH_2I, and CH_2CN are reported.

[2] Measurements of Rate Constants for HO_2 + NO and NH_2 + NO Reactions.

The reactions of HO_2 radicals with NO, reaction (6) is one of the most important process to convert NO to NO_2 in the atmosphere.

$$HO_2 + NO \rightarrow OH + NO_2 \tag{6}$$

For HO_2 radicals insensitive methods(e.g. ultraviolet absorption and LMR method) are known, further sensitive and selective detection methods are necessary for accurate measurement of rates of reactions involving HO_2 radicals.

In this research project, detection sensitivity of a photoionization mass spectrometry has been improved drastically, more than 50 times as sensitive as those of conventional equipments, and high sensitivity detection of HO_2 radicals has been accomplished. With this method, rate constants of reaction (6) was measured.
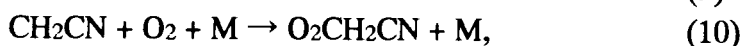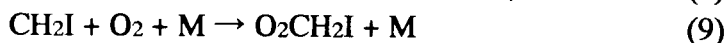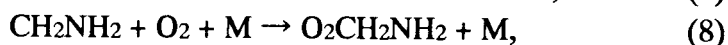
3. Research
[1] Rate Constants for Reactions of Substituted Methyl Radicals (CH_2OCH_3, CH_2NH_2, CH_2I, and CH_2CN) with O_2.

1. Introduction

There have been numerous kinetic studies on termolecular reactions of alkyl type free radicals with molecular oxygen. Rate constants for these reactions range from 1 to 30 $\times\ 10^{-12}\ cm^3\cdot molecule^{-1}\cdot s^{-1}$ at room temperature. The limiting high–pressure rate constants for alkyl radicals + O_2 reactions are known to correlate with the ionization potentials of the radicals ; a radical whose ionization potential is low tends to react with a large rate constant. Recently, we proposed a similar correlation for rates of reactions of hydroxyalkyl radicals with O_2. Since hydroxyl is an electron–donating substituent, ionization potentials of hydroxyalkyl radicals are relatively lower than those of alkyl radicals, and the reaction rate constants with O_2 increase.

In the present study, the rate constants for the reactions of methoxymethyl, aminomethyl, iodomethyl, and cyanomethyl radicals with O_2 have been measured :

$$CH_2OCH_3 + O_2 + M \rightarrow O_2CH_2OCH_3 + M, \tag{7}$$

$$CH_2NH_2 + O_2 + M \rightarrow O_2CH_2NH_2 + M, \tag{8}$$

$$CH_2I + O_2 + M \rightarrow O_2CH_2I + M \tag{9}$$

$$CH_2CN + O_2 + M \rightarrow O_2CH_2CN + M, \tag{10}$$

–OCH_3 and –NH_2 are typical electron–donating substituents, while –I and –CN are

electron–withdrawing substituents. The present study focused on (i) measuring the kinetics of these four new radicals and (ii) examining how fast the rate constants of the above four reactions are, since the ionization potentials of the former two radicals are expected to be lower and the latter two higher than the unsubstituted methyl radical.

2. Experimental

The radical precursors and O_2 were introduced to a tubular Pyrex reactor (13 mm i.d.) with N_2 as carrier gas. Pulsed 193 nm radiation from an ArF excimer laser (Lambda Physik, LPX 120 icc) was directed along the axis of the reactor. CH_2OCH_3 was generated by 193 nm pulse photolysis of CCl_4 followed by the H atom abstraction reaction of Cl atom with CH_3OCH_3 :

$$CCl_4 + h\nu\ 193 \rightarrow CCl_3 + Cl, \tag{11}$$
$$CCl_2 + 2Cl, \tag{12}$$
$$CH_3OCH_3 + Cl \rightarrow CH_2OCH_3 + HCl. \tag{13}$$

CH_2NH_2 was generated by pulsed photo–dissociation of ethylenediamine, $NH_2CH_2CH_2NH_2$, using the ArF laser :

$$H_2NCH_2CH_2NH_2 + h\nu\ 193 \rightarrow 2CH_2NH_2, \tag{14}$$

CH_2I and CH_2CN were produced by the photodecomposition of chlorinated precursor molecules by ArF laser pulse.

$$CH_2ClI + h\nu\ 193 \rightarrow CH_2I + Cl \tag{15}$$
$$ClCH_2CN + h\nu\ 193 \rightarrow CH_2CN + Cl \tag{16}$$
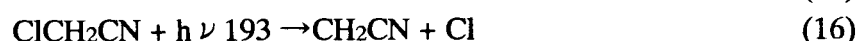
Part of the gas in the reactor was sampled through a Pyrex orifice (ϕ = 0.3 mm) located in the wall of the reactor, and the time dependences of the radical concentrations were recorded directly by photoionization mass spectrometry. A Xe resonance lamp having a sapphire window (8.44 eV) was used to ionize CH_2OCH_3 and CH_2NH_2. A Kr resonance lamp with a MgF_2 window (10.3 and 10.64 eV) and an Ar resonance lamp having a LiF window (11.62 and 11.83 eV) were used to ionize CH_2I and CH_2CN, respectively. The rate constants for reactions (7) − (10) were determined by measuring the decay rates of the time dependences of radical concentration under various O_2 concentrations. All the measurements were carried out at 298 ± 5.

3. Results and Discussion

The reactivity is greatly enhanced by substituting one of the hydrogen atoms of a methyl radical with the electron–donating substitutents, $-OCH_3$ and $-NH_2$. The rate constants obtained at 298.5K were $(6.5 \pm 0.7) \times 10^{-12}$ and $(3.5 \pm 0.4) \times 10^{-11}$ in units of cm^3 molecule^{-1} s^{-1} for CH_2OCH_3 and CH_2NH_2, respectively, and no pressure dependence was observed between 0.6–6Torr(80–800Pa) of N_2 as a bath gas. The reactivity is reduced for CH_2I and CH_2CN, which have the electron–withdrawing substitutents, $-I$ and $-CN$. The rate for the reaction of CH_2I with O_2 was independent on the total pressure between 2–15Torr (270–2000Pa) of N_2, and the rate constant was determined to be $(1.6 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate constants of CH_2CN with O_2 depended on the total pressure, and were 6.8–11.0×10^{-15} cm^3 molecule^{-1} s^{-1} for total pressures 2–6Torr (270–800Pa) of N_2 + O_2.

The present results agree qualitatively with the correlation noted previously between the rate constants at the high–pressure limit and the ionization potentials of radicals. For CH_2OCH_3 and CH_2NH_2 radicals having electron–donating substituents(–

OCH₃ and –NH₂), the ionization potentials are low (6.94 and 6.3 eV, respectively) and the reaction rates with O_2 are enhanced compared to CH_3+O_2. On the other hand, for CH_2I and CH_2CN radicals having electron–withdrawing substitutents (–I and –CN), the ionization potentials are high (8.4 and 10–11eV, respectively and the rates of reaction with O_2 are slower.

In figure 1, the limiting high–pressure rate constants obtained in the present work plotted against the ionization potentials of radicals together with previous results for alkyl and hydroxyalkyl radicals. As can be seen in Figure 1, the CH_2NH_2 radical falls close to the correlation line while CH_2OCH_3 and CH_2I radicals does not.

Recently, Seetula et al. used a so–called TSED parameter as an indicator of the reactivity of substituted methyl radicals with halogen molecules. TSED parameters are calculated by the simple algebraic sum of the Pauling electronegativities of the atoms or groups attached to the radical carbon, and they indicate the strengths of the dipole–induced dipole interaction in the R+O₂ reaction.

In figure 2, the limiting high–pressure rate constants are plotted against the TSED parameters. The TSED parameter for $CX_1X_2X_3$ was calculated as

$$\Delta EN(CX_1X_2X_3) = \Sigma(ENxi-EN_H). \tag{17}$$

Where ENxi represents Pauling's electronegativity of Xi.

$$D(H-X) = [D(X-X) + D(H-H)]/2 + 23(ENxi-EN_H)^2 \tag{18}$$

Here, values of 104.2 kcal mol⁻¹ and 2.1 were used for D(H–H) and EN$_H$, respectively. The signs (+, –) of the TSED parameter were determined by whether Hammett's empirical parameter is positive (electron–donating) or negative (electron–withdrawing). As can be seen in Figure 2, the correlation is not satisfactory only for the CH_2NH_2 radical.

The above results show that the reactivities of substituted methyl radicals are not just a function of the ionization potentials and electronegativities of radicals. Further studies of substituted methyl radicals, such as CH_2NO_2, CH_2F, CH_2Cl, CH_2Br, $CH_2(CO)CH_3$, are desirable. A dermination of the limiting high–pressure rate constant of very slow reactions, such as $CH_2CN + O_2$, would be especially important.
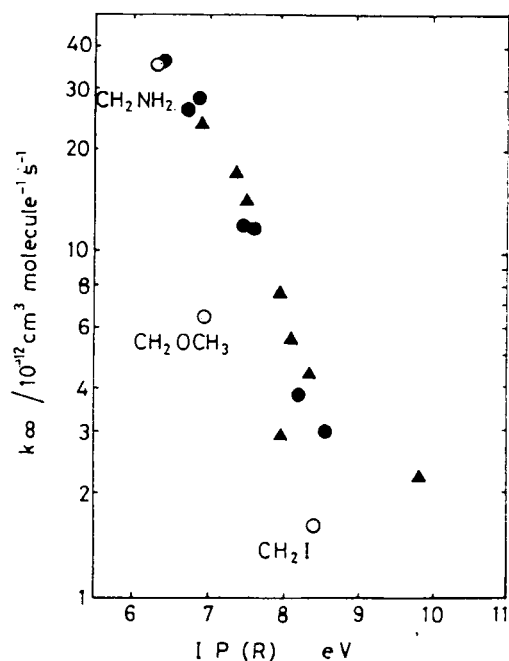

Fig.1 Plots for k∞ vs. IP

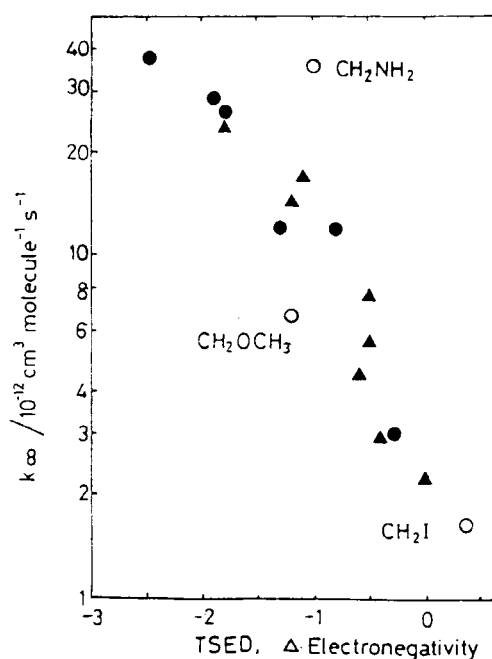Fig.2 Plots for k∞ vs. TSED parameter

[2] Measurements for Rate Constants for HO_2 + NO and NH_2 + NO reactions.

1. Introduction

Photoionization mass spectrometry (PIMS) is a method to detect reaction intermediates directly with adequate selectivity and sensitivity. PIMS is capable of combining with a laser flash photolysis technique as well as discharge flow and have been widely applied to kinetic studies of free radicals, atoms, and metastable molecules in the gas phase. Recently, in this laboratory, the detection sensitivity of PIMS has been improved by a factor of about 50 [1]. This enabled to detect the CH_3O_2 as the parent ion ($CH_3O_2^+$) with sufficient sensitivity to measure the rate constant for the CH_3O_2 + NO reaction. In this work, the detection of HO2 radicals by PIMS was challenged.

The HO_2 is the simplest peroxy radicals and the reaction of HO_2 radicals with NO, reaction (6), is important to control the concentration of OH radicals in the atmosphere.

Laser magnetic resonance (LMR) spectroscopy is well known as a method to detect HO_2 directly with high sensitivity [2-4]. Discharge flow reactor coupled with a LMR spectrometer has been used to determine the rate of reaction (6)[3-7]. The rate constant recommended by the IUPAC Subcommittee is $(8.3 \pm 2.2) \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ at 298 K[8]. There has been an attempt to detect HO_2 by PIMS, and it has been reported that the detection of HO_2 by PIMS was possible but the quantitative analysis of the HO_2^+ ion signal was difficult because the signal was extremely weak. In the present study, the intensity of the ionizing light of PIMS was greatly enhanced and hence the HO_2 radical was able to be detected directly as the parent ion of HO_2^+.

The reaction of NH_2 radicals with NO, reaction(19) has been known as a thermal de-NOx process in combustion and atmospheric chemistry.

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{19}$$

The rate constant for reaction (19) has been measured by several methods to measure NH_2 directly[9-7]. The rate constant recommended by the IUPAC Subcommittee is (1.6 ± 0.9) $10^{-11} cm^3 molecule^{-1} s^{-1}$ at 298 k[8]. There has been no measurement of NH_2 radicals by the method of PIMS.

2. Experimental

In the present study, rate constants for reactions of HO_2 and NH_2 radicals with NO were measured by PIMS coupled with pulsed laser photolysis. The experimental set-up of the photoionization mass spectrometer was described in detail elsewhere [1]. Briefly, NH_3 diluted in O_2 was flowed through a Pyrex tubular reactor and was coaxially irradiated by a 193nm ArF excimer laser (Lambda Physik LPX120i) to generate H atoms and NH_2 radicals by reaction (20).

$$NH_3 + h\nu \ (\ 193nm \ ) \rightarrow H + NH_2 \tag{20}$$

HO_2 radicals were produced by the association reaction of H atoms with O_2 by reaction (21).

$$H + O_2 + M \rightarrow HO_2 + M \tag{21}$$

The radicals, HO_2 and NH_2, were sampled through a thin Pyrex pinhole (ϕ = 0.3mm) to ionization region and were photoionized by an Ar resonance lamp with a LiF window (11.62 and 11.83eV). The Ar resonance lamp was powered by a microwave (2450 MHz) discharge. In order to achieve high sensitivity, the microwave cavity of the lamp was placed as close as possible (about 30mm) to the ionization region. A typical sensitivity for the NO molecule was 1×10^6 counts $mTorr^{-1} s^{-1}$ when 1mTorr of NO (0.005% of NO/N_2

mixture) was in the reactor.

3.Results and Discussion

HO2 radicals were produced by reactions (20) and (21). Transient ion signals were observed at m/e = 33 when the Ar resonance lines(11.83 and 11.62eV) were used as the photoionization light source. The maximum intensity of the signals was observed within 1 ms after the photolysis laser (193nm) flash .The rate constant for reaction(21) was reported to be 1.1×10^{-14} cm^3 molecule^{-1}s^{-1} at 6 Torr of O2 or N2[8]. The rise time of the HO2 formation by reaction (4) is, then, calculated to be 0.5ms at the O2 pressure of 6 Torr. The rise time of the ion signals observed at m/e=33is consistent with the rate of the HO2 formation considering the gas diffusion in the reactor and effusion to the ionization region. The ion detected at m/e = 33 could be attributed to the parent ion (HO2$^+$) of the HO2.

The decay rate obtained from the time profile of the HO2$^+$ ion signal with out NO was 293 s^{-1}. Rapid decay can be attributed to the depletion of HO2 by the reaction with NO, reaction(6). The typical decay profile of HO2 radicals with NO is shown in Fig 3.
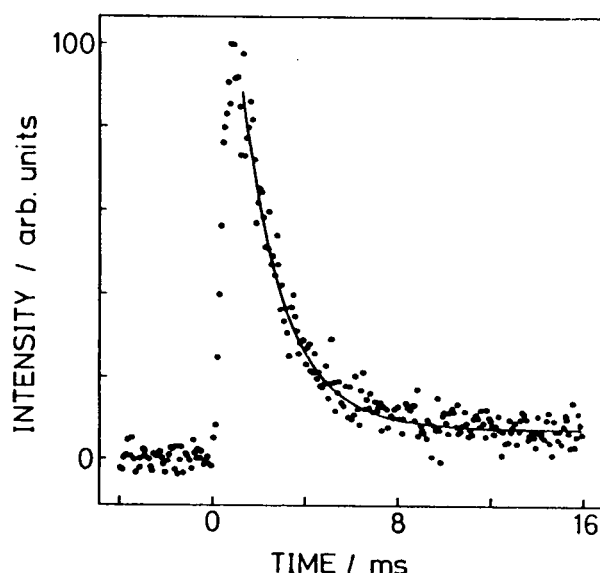

Figure 3.
Typical time profile of the ion signals at m/e=33.
The conditions were
[HO2]0 = 2.4×10^{11} molecule cm^3,
[O2] = 6.0Torr ,and [NO] = 1.21 mTorr. The solid curve represents result of the best fitting of eq.(22)

The decay profiles of the ion signals can be written by the following exponential decay equation having fitting parameters A and B.

$$I(t)=A \cdot \exp(-k' \cdot t)+B \qquad (22)$$

where,

$$k' = k_0 + k_6 [NO] \qquad (23)$$

Here k_6 is the second order rate constant for reaction (6) ,and k_0 is the sum of all other processes, including pumpout from the cell, loss on the walls and reactions with parent molecules or with impurities.

In the case shown in Fig.3, the solid curve shows the best fit curve of the signal fitted to eq.(22), and the decay rate (k') determined is 546 s^{-1}. The values of k' were determined under various NO concentrations and were plotted against the NO concentration as shown in Fig.4. The value of k_6 can be obtained from the slope of the Stern-Volmer plots according to eq.(23). The value of the slope of the Stern-Volmer plots shown in Fig.4 is $(6.5 \pm 2.0) \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} at 6 Torr of O2. Error limits due to the scatter of the Stern-Volmer plots were calculated by least-squares fitting with

95% confidence limits. The value of k_6 obtained in this work is about 20% smaller than the value recommended by IUPAC, which is $(8.3 \pm 2.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Considering the error limits of both values, however, values are in agreement.
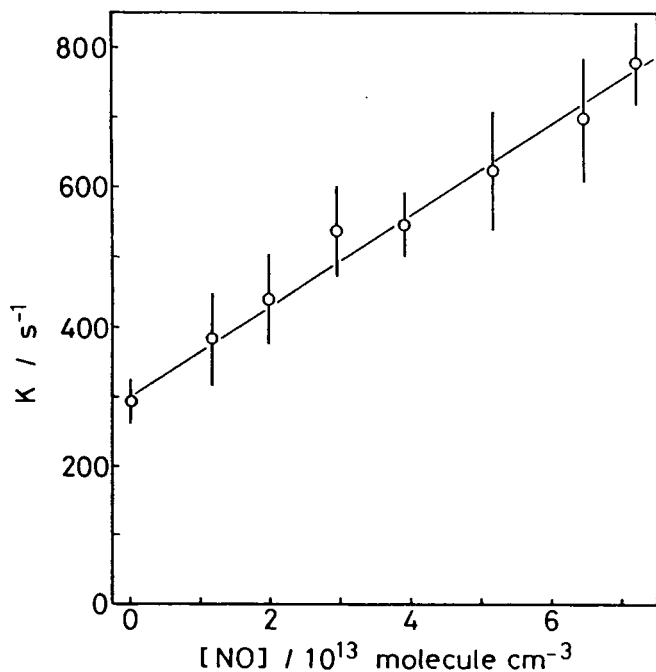

Figure4
Decay rates of HO$_2$ radicals as a function of NO concentration.

The decay rates of NH$_2$ radicals (k') were obtained at the total pressure (mostly O$_2$) of 6 Torr as a function of the NO concentration. From the slope of the plots, the value $(1.9 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained as the rate constant for reaction (19). The rate constant for reaction (19) obtained in this work is in good agreement with the previous recommended value, $(1.6 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} .

In conclusion, the rate constant for the reaction of HO$_2$+NO was measured by monitoring the HO$_2$ directly by PIMS coupled with the laser flash photolysis. The rate constant was determined to be $(6.5 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, which is agreement with those obtained by discharge flow technique within the error limit. The rate constant for the reaction of NH$_2$+NO was also determined to be $(1.9 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This is good agreement with the previous recommended value.

References

1. A. Masaki, S. Tsunashima and N. Washida, Chem. Phys. Lett., **218**, 523 (1994).
2. M. S. Zahniser and C. J. Howard, J. Chem. Phys., **73**, 1620 (1980).
3. C. J. Howard and K. M. Evenson, Geophys. Res. Lett., **4**, 437 (1977).
4. C. J. Howard, J. Chem. Phys., **71**, 2352 (1979).
5. W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner and K. Hoyermann, Int. J. Chem. Kinet., **12**, 851 (1980).
6. B. A. Thrush and J. P. T. Wilkinson, Chem. Phys. Lett., **81**, 1 (1981).
7. A. A. Jemi–Alade and B. A. Thrush, J. Chem. Soc. Faraday Trans., **86**, 3355 (1990).
8. R. Atkinson, D.L. Baulch, R.A Cox, R.F. Hampson Jr., J. A. Kerr, and J. troe, J. Phys. Chem. Ref. Data, **21** 1125 (1992). 16.
9. G. Hancock, W. Lange, M. Lenzi and K. H. Welge, Chem. Phys. Lett., **33**, 168 (1975).
10. R. Lesclaux, P. V. Khe, P. Dezauzier and J. C. Soulignac, Chem. Phys. Lett., **35**, 493 (1975).
11. L. J. Stief, W. D. Brobst, D. F. Nava, P. R. Borkowski and J. V. Michael, J. Chem. Soc. Faraday Trans. II , **78**, 1391 (1982).
12. A.R. whyte and L.F. Phillips, Chem. phys .lett., 451 (1983).
13. B. Atakan, A. Jacobs, M. Wahl, R. Weller and J. Wolfrum, Chem. Phys. Lett., **155**, 609 (1989).
14. V. P. Bulatov, A. A. Ioffe, V. A. Lozovsky and O. M. Sarkisov, Chem. Phys. Lett., **161**, 141 (1989).
15. J. A. Silver and C. E. Kolb, J. Phys. Chem., **86**, 3240 (1982).
16. J. B. Jeffries, J. A. McCaulley and F. Kaufman, Chem. Phys. Lett., **106**, 111 (1984).
17. T. Yu and M.C. Lin, J. phys. Chem., **98** ,2105 (1994)