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ATMOSPHERIC CHEMISTRY OF ORGANIC SULFUR AND NITROGEN COMPOUNDS
First annual progress report 1988 (EV4V-0067-C)

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Abstract. The work carried out during the first year of a four year Danish-Irish contract with the European Economic Community is described. The reactions of OH radicals with dialkyl sulfides and nitroalkanes have been studied applying both an absolute technique of pulse radiolysis with kinetic spectroscopy and a relative rate method using conventional smog chamber facilities. The reactions of OH with dimethyl sulfide and nitromethane have been investigated in special detail. Rate constants for reaction of Cl atoms with the same compounds have been determined using the relative rate method.

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1. INTRODUCTION

This report describes the work carried out in the first year of the four year contract (EV4V-0067-C EDB) between the European Economic Community (EEC), and University College Dublin (UCD), Dublin Institute of Technology (DIT) and Risø National Laboratory (RNL).

At RNL absolute rate studies are performed using pulse radiolysis combined with kinetic UV spectroscopy. Radical species, in this case OH radicals, are monitored under pseudo first order conditions.

At UCD and DIT relative rate studies have been done using conventional smog chamber facilities.

The groups in both countries have developed expertise and invested heavily in equipment in order to carry out photochemical and kinetic studies on reactions of importance in atmospheric chemistry.

The Danish group's activities are concentrated on direct monitoring of radical species in the reaction, whereas the Irish work is more concerned with substrate decay and final product analysis. The two techniques are complementary and information from both methods is invaluable in evaluating the kinetics and mechanisms of complex systems as those pertaining in atmospheric chemistry.

The joining of the two groups under the auspices of an EEC contract has enabled members of each group to share their results and accumulated experience. Personnel from Risø have spent time carrying out research in Dublin, and those from Dublin at Risø. In particular graduate students from the two Dublin institutes have spent extended periods of time up to 6 months working on projects at Risø. This has important benefits in their research training and is a valuable spin-off of the scientific cooperation between the two groups. It is interesting to note that this exchange of students has had full support of the relevant authorities in both countries, who have had the foresight to realize the benefits of shared expertise particularly for the smaller countries in the EEC.

In this report the experimental setups are described first. Then in the next four chapters the results for the OH reactions with dimethyl sulfide (DMS), dialkyl sulfides (R_2S), nitromethane and nitroalkanes (RNO_2) are presented and discussed. Finally some conclusions are made and future work is mentioned.

2. EXPERIMENTAL

2.1. Absolute method

The apparatus is shown schematically in Figure 1 and has been described in detail elsewhere [1,2]. Single pulses of 30 ns duration of 2 MeV electrons from a Febetron 705B field emission accelerator were used to irradiate mixtures of 15 mbar H_2O and Ar to 1 atm. Excited Ar atoms, Ar*, are formed initially by the pulse radiolysis. OH radicals are produced through the reaction

(2) $Ar^* + H_2O \rightarrow OH + H + Ar$

Formation of OH is rapid relative to the time scale of the OH decay. In the absence of added compounds in the system, the second order decay of OH is governed by the reactions

(3) $OH + OH + M \rightarrow H_2O_2 + M$

(4) $H + OH + M \rightarrow H_2O + M$

where M is a third body, here Ar and H_2O. The OH decay is described to a good approximation by the differential equation

(I) $-d[OH]/dt = 2k_3[OH]^2[M] + k_4[OH][H][M]$

Introducing a substrate compound, S, reacting with OH

(5) $S + OH \rightarrow \text{products}$

a term must be added to equation (I), $k_5[S][OH]$. Over a sufficiently large range of concentrations, [S], the following pseudo-first-order rate conditions can be obtained:

(II) $k[S] >> 2k_3[OH][M] + k_4[H][M]$

In this case k_5 can be determined from a plot of reciprocal OH half life versus concentrations of S, with a slope equal to $\ln(2)/k_5$.

A more rigorous procedure which allows a clear distinction between first and second-order kinetics is to plot the logarithm of the absorbance versus time. Such a plot is linear in the pseudo-first order approximation. Plotting the slopes of the log plots, k′, versus [S] gives a linear plot with slope equal to k_5. All absolute experimental data were analysed using both the reciprocal OH half life plot and the log plots, and the obtained rate constants were identical within the limits of uncertainties.

The irradiation cell is a 1 liter stainless steel cell mounted directly onto the accelerator. A set of White mirrors provide variable optical path lengths. Each substrate compound was premixed with Ar in a 50 liter FEP Teflon bag, since if the substrate compound was admitted directly to the cell part of it could be adsorbed on the walls of the cell. H_2O and Ar were admitted directly one at a time and the partial pressures read using an MKS Baratron 170 absolute membrane manometer with a resolution of 10^{-5} bar. The analyzing light source is a pulsed 150 W high pressure Xenon arc lamp. A Hilger and Watts grating spectrograph, a Hamamatsu photomultiplier, and a Biomation-8100 waveform digitizer detect and record the light intensity at the desired wavelength. Transfer and storage of raw data on a mainframe computer is controlled by a PDP11 minicomputer.

The kinetics of the OH radicals were studied by monitoring the transient absorbance of one of the rotational lines at 309 nm, using a modified version of Beer's law, $A = (\epsilon \times l \times c)^n$ [1]. The observed transient absorbance is a direct measure of the OH concentration at any time during the decay. The kinetics of methyl radicals were studied by monitoring the transient absorption at 216 nm.

2.2. Relative rate method

OH radicals are generated by photolysis of methyl nitrite in air at wavelenghths longer than 290 nm:

(6) $CH_3ONO + h\nu \rightarrow CH_3O + NO$

(7) $CH_3O + O_2 \rightarrow CH_2O + HO_2$

(8) $HO_2 + NO \rightarrow OH + NO_2$

Experiments were carried out at 730-750 torr in a 50 liter FEP Teflon cylindrical reaction chamber. The chamber was surrounded by 20 fluorescent lamps (10 blacklamps, Philips TL 20/08 and 10 sunlamps, Philips TL 20/09) giving a photolytic half-life for CH_3ONO of about 30 minutes. All pressure measurements were made using an MKS Baratron capacitance manometer (MKS 220A). Measured amounts of the reactants were flushed from pyrex bulbs by a stream of ultra-zero air (BOC) or ultra pure nitrogen (BOC) into the reaction chamber, which was then filled to the full volume. All quantitative analyses were made by gas chromatography. Series of experiments were carried out in which CH_3ONO/NO/substrate/reference compound/air mixtures were photolysed. Typically the concentrations were in the range 1-20 ppm. The OH radicals generated via reactions (6)-(8) react with the substrate and the reference hydrocarbon:

(5) OH + S -> products

(9) OH + RH -> products

Providing the substrate and the reference hydrocarbon are consumed only by reaction with OH radicals, k_5 can be determined:

(III) $\ln([S]_0/[S]_t) = (k_5/k_9)\ln([RH]_0/[RH]_t)$.

Chlorine atoms were generated directly from either the photolysis of chlorine or phosgene. In certain systems molecular chlorine is an unsuitable Cl atom source due to fast dark reaction with the substrate compounds. The experimental arrangement for the chlorine atom studies was identical to that described above.

2.3. Materials

Argon (AGA 99.9 %), phosgene and Cl_2 (Matheson 99.9 %), and NO (BOC 99.9 %) were used as received. DMS and DMDS (Merck 99 %), dialkyl sulfides (Fluka better than 98 %), and nitroalkanes (Merck 99 %) were degassed and purified by trap-to-trap distillations on the vaccum system prior to use without further purification. Methyl nitrite was prepared by dropwise addition of 50 % H_2SO_4 to methanol saturated with sodium nitrite. In all cases the H_2O was triply distilled.

3. THE REACTION OF OH WITH DMS

3.1. Introduction

The recent suggestion of reduced sulfur compounds being involved in a feedback mechanism in the earth's ecosystem and climate [3], has caused more emphasis to be put on studying the atmospheric chemistry of these compounds. On a global scale anthropogenic and biogenic emissions of sulfur compounds are thought to be approximately equal [4]. DMS is the most important of the reduced sulfur compounds emitted both by terrestrial and marine biota. Emissions of reduced sulfur compounds from the sea are almost exclusively in the form of DMS and constitute a major global flux of sulfur to the atmosphere. The most important daytime homogeneous loss process for DMS in the atmosphere is known to be reaction with OH radicals.

Fourteen investigations have appeared reporting kinetic data for the reaction of DMS with OH [4-17]. A further 6 papers deal with product studies only [18-23]. Kinetic studies have been carried out using a wide variety of absolute and relative techniques. Absolute measurements have been done using conventional flash photolysis [5,6,8,15], pulsed laser photolysis [14], and discharge flow techniques [9,12,16]. The investigation by Hynes et al. [14] is the only absolute study done both in the absence and presence of O_2. All the relative rate constant studies [4,7,11,15,17] except one [15] were carried out using photolysis techniques to generate OH radicals. Wallington et al. [15] used a relative technique where OH radicals were generated from the dark reaction of O_3 with N_2H_4 [25]. Two of the relative studies were done only in the presence of O_2 [4,7], whereas the studies by Barnes et al. [11,17] and Wallington et al. [15] investigated the OH + DMS reaction both in the presence and absence of O_2. Among the rate constants measured in the absence of O_2 as well as among those measured in the presence of O_2 significant discrepancies exist.

Two possible reaction pathways, abstraction and addition, have been suggested.

(1a) $CH_3SCH_3 + OH \rightarrow CH_3SCH_2 + H_2O$

(1b,1b-) $CH_3SCH_3 + OH + M \leftrightarrow CH_3S(OH)CH_3 + M$

Hynes et al. [14] and Barnes et al. [17] have suggested from product studies that reaction (1b) is only important when the adduct is removed by further reaction with O_2, indicating that the addition channel is negligible in the absence of O_2. There have been three determinations of the branching ratio for abstraction, $k_{1a}/(k_{1a}+k_{1b})$ [12,14,17]. Martin et al. [12] estimate a lower limit for the branching ratio of 0.3 at room temperature in the absence of O_2. In 1 atm. of air Hynes et al. [14] found a monotonically increasing branching ratio from 0.24 to 0.87 over the temperature range 250-310 K with a room temperature value of 0.67. Recent work by Barnes et al. [17] gives a branching ratio of 0.55 under the same experimental conditions.

The purpose of this work was to provide further information on the reaction channels for the OH+DMS reaction and also to rationalize the discrepancies in the reported rate data.

3.2. Results

All experiments in this work using the absolute technique were performed under pseudo-first-order conditions. Concentrations of DMS were in large excess relative to the initial OH concentration. The OH decay with and without added DMS is shown in Figure 2. The corresponding log-plots are also shown in Figure 2. DMS was premixed in suitable concentrations with Ar in a 50 liter FEP Teflon bag and allowed to mix for 30 minutes before use. Different partial pressures of the mixture were added to 15 mbar of H_2O and backed up with Ar to a total pressure of 1 atm. The plot of reciprocal OH half-lives versus concentrations are shown in Figure 3. The rate constant derived from a least squares fit of the straight lines is: $k=(3.5\pm0.2) \times 10^{-12}$ $cm^3molecule^{-1}s^{-1}$. The error limits are $\pm2\sigma$ of the fit. The intercept of the straight line corresponds to the decay rate via reactions (3) and (4) in the absence of added DMS.

The concentration-time data from the relative experiments are shown plotted in the form of eq. (III) in Figure 4. As can be seen these plots did not give the expected straight lines. It is also seen that curvature increases with increasing concentrations of added NO. It is not possible to extract a rate constant for the reaction of OH with DMS from these plots.

3.3. Discussion

The value of k_1 obtained in the present study is compared with results previously reported in the literature in Table 1. The high value of McLeod et al. [9] has been explained by Martin et al. [12] to be in error due to heterogeneous wall reactions. The only possible explanation for the high values reported by Atkinson et al. [5] and Kurylo [6] is the presence of reactive impurities in their DMS samples. The remaining values of k_1 determined in the absence of O_2 agree almost within their stated experimental uncertainties giving an average value of 3.5×10^{-12} $cm^3molecule^{-1}s^{-1}$ somewhat lower than Atkinson's [24] recommendation of 4.28×10^{-12} $cm^3molecule^{-1}s^{-1}$.

In this work it was possible to monitor the formation kinetics of CH_3 radicals generated following the reaction of OH radicals with DMS. In the absence of O_2 the fate of a possible DMS-OH addition adduct could be subsequent decomposition:

(10) $CH_3S(OH)CH_3 \rightarrow CH_3SOH + CH_3$

or

(11) $CH_3S(OH)CH_3 \rightarrow CH_3S + CH_3OH$

A formation rate constant k_{10} of $(9.1\pm1)x10^{-14}$ $cm^3molecule^{-1}s^{-1}$ was determined from the CH_3 radical appearance data. This corresponds to a branching ratio for abstraction of 0.97 in the absence of O_2. When compared to the previously determined branching ratios, this means that reaction (10) is a negligible pathway for the fate of the DMS-OH addition adduct and provides support for the conclusion by Hynes et al. [14] that the addition channel in only important in the presence of O_2.

Curvature of the plots in Figure 4 from the relative measurements has previously been reported by Cox and Sheppard [7] and by Atkinson et al. [26]. Cox and Sheppard [7] attributed this curvature to reaction of DMS with oxygen atoms, which are formed during photolysis. Atkinson et al. [26] suggested that an additional reason for this curvature was the formation of NO_3 under conditions where O_3 generation was significant. We have confirmed these explanations in the present work by photolyzing NO_2 in DMS/c-C_6H_{12}/air mixtures. The DMS was observed to decay quite rapidly while the c-C_6H_{12} concentration remained virtually constant. Furthermore, DMS has a high decay rate in O_3/NO_2/air mixtures in the dark. However, the above explanation cannot be used to rationalize the apparent dependence of the rate constant for the OH+DMS reaction on the NO concentration. High concentrations of added NO would suppress O_3 formation and hence the presence of the NO_3 radical cannot be responsible for the curvature in Figure 4.

There seems to be a general agreement [11,13,15,17] that relative techniques using systems containing NO give erroneous rate constant data for the reaction of OH with DMS due to unknown secondary reactions in these systems. The CH_3S radical has been suggested as an important intermediate in the oxidation of DMS [4,11,20,22] through the following reactions:

(1a) $CH_3SCH_3 + OH \rightarrow CH_3SCH_2 + H_2O$

(12) $CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2O_2 + M$

(13) $CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$

(14) $CH_3SCH_2O \rightarrow CH_3S + HCHO$

In order to test whether CH_3S radicals play an important role in the additional loss of DMS in the presence of NO_x and O_2 dimethyl disulfide (DMDS) was used as a photolytic source of CH_3S radicals in our experiments. The results show that photolysis of DMDS in the presence of DMS in either pure N_2 or air does not result in loss of DMS. However, when the photolysis was carried out in air with NO present rapid removal of DMS occurred. Further increase in DMS decay was observed with increasing addition of NO. Hence, it is concluded that the presence of O_2 and NO_x in the system will lead to unreliable rate constant data for the OH+DMS reaction. It is of interest to note that the recently reported relative rate data by Barnes et al. [17] carried out in the absence of O_2 and NO_x provides rate constant data in excellent agreement with recent absolute values.

Recently rate constants for the reactions of CH_3S with O_2, NO, and NO_2 have been determined at 298 K, $k(O_2)<2x10^{-17}$, $k(NO)=3.8x10^{-11}$, and $k(NO_2)=1.1x10^{-10}$ $cm^3 molecule^{-1} s^{-1}$, respectively [27]. Since CH_3S by itself does not remove DMS and since the reaction with O_2 is too slow to be dominant with NO and NO_2 present, CH_3SNO and CH_3SO formed by reaction of CH_3S with NO and NO_2 respectively, must be responsible for the additional loss of DMS. CH_3SNO has indeed been observed in product studies [20]. The mechanism for the additional loss of DMS by CH_3SNO and CH_3SO, and their influence on observed final products SO_2 and CH_3SO_3H is still unknown and requires further investigation.

4. THE REACTION OF OH AND Cl ATOMS WITH DIALKYL SULFIDES

4.1. Introduction

Organic sulfur compounds have recently been suggested to be involved in a feedback mechanism in the earth's ecosystem [3]. The different natural sulfur source strengths are ill defined and arise mainly from emissions of organic sulfur compounds produced by biological activity in soil, water, and vegetation [28]. H_2S, DMS, CS_2, and OCS are the most important of the reduced sulfur compounds emitted both by terrestrial and marine biota [4]. However, DES has recently been detected in coastal areas [29]. The most important daytime homogeneous loss process for organic sulfur compounds in the atmosphere is reaction with OH radicals [24,30].

Rate data for the reaction of OH with DES have been reported in three different investigations [11,12,14]. Martin et al. [12] used an absolute discharge flow technique and determined a value of $k_1=(12\pm1.4)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$. Hynes et al. [14] found in flash photolysis resonance fluorescence experiments an absolute value $k_1=(15.4\pm2.2)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$. The most recent data for the OH+DES reaction were reported by Barnes et al. [11]. They used a relative technique with H_2O_2 as the source of OH and obtained a value of $k_1=(11\pm2)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$. In the same study Barnes et al. [11] reported the only rate constant for the OH+DPS reaction, $k_2=(19\pm2)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$, available in the literature. These values for the rate constants of OH with the dialkyl sulfides were all determined in the absence of O_2. Hynes et al. [14], Barnes et al. [11], and Wallington et al. [15] all observed that the rate constant for the OH+DMS reaction increases in the presence of O_2. This is the first rate measurement of the OH+DBS reaction. To our knowledge there have been no previous investigations on the reactions of Cl atoms with dialkyl sulfides. The aim of the present study was to extend the data base for these reactions in order to provide more mechanistic information.

4.2. Results

All experiments using the absolute technique were performed under pseudo-first-order conditions. Concentrations of the dialkyl sulfides were in large excess relative to the initial OH concentration. The OH decay with and without added R_2S is shown in Figure 5 along with the corresponding log-plots. Each dialkyl sulfide was premixed in suitable concentrations with Ar in a 50 liter FEP Teflon bag and allowed to mix for 30 minutes before use. Different partial pressures of the mixture were added to 15 mbar of H_2O and backed up with Ar to a total pressure of 1 atm. The log slope plots are shown in Figure 6. The rate constants derived from a least squares fit of the straight lines are given in Table 2 together with literature data. The error limits are $\pm 2\sigma$ of the fit and the intercept of the straight line corresponds to the decay rate via reactions (9) and (10) in the absence of added R_2S.

Mixtures of the dialkyl sulphides and reference hydrocarbon with phosgene were stable in the dark for several hours in the Teflon reaction chamber. Over the time period of the kinetic experiments the sulfides and the reference hydrocarbon showed no significant decay due to photolysis. For each compound at least 5 runs were carried out with cyclohexane as the reference hydrocarbon. In order to test the internal consistency of the rate constant ratio data each compound was also run against another member of the series. In all cases the relative rate constant values were in excellent agreement with the results obtained using cyclohexane as the reference hydrocarbon. The rate constants for the reactions of Cl atoms with dialkyl sulfides were derived using a value of $k(OH+c\text{-}C_6H_{12})=31.1\times10^{-11}$ $cm^3 molecule^{-1} s^{-1}$ [31] and are given in Table 2. The errors quoted are twice the standard deviation arising from the measurement of the rate constant ratios and do not include an estimate of the error in the reference rate constant.

As a check on the experimental technique used in this work, particularly with respect to the use of $COCl_2$ as the Cl atom source, we determined the ratio for the reaction of Cl atoms with different hydrocarbons using both Cl_2 and $COCl_2$. The two sets of results were identical within the experimental uncertainties and gave rate constant ratios essentially the same as those found by Atkinson and Aschmann [31], and lends confidence to the experimental method employed.

4.3. Discussion

Rate constant data for the OH+DES reaction in the absence of O_2 obtained in this work is in satisfactory agreement with the two previously reported results from absolute rate studies [12,14]. Martin et al. [12] used the discharge flow - EPR technique to investigate this reaction at 0.5 Torr of helium. They obtained reproducible results when the reactor was coated with a halocarbon wax in order to minimize heterogeneous wall reactions. Hynes et al. [14] studied the reaction at pressures up to 50 Torr of argon over a temperature range of 255-370 K using a conventional flash photolysis - resonance fluorescence technique. Our values of the rate constants for the OH+DES and OH+DPS reactions are also within the stated experimental uncertainties of those reported by Barnes et al. [11]. They employed a relative rate method in which OH radicals were generated from H_2O_2 photolysis in 1 atm. of N_2. Relative rate measurements of rate constants for OH reactions with sulfides and thiols have generally been shown to be unreliable due to secondary reactions in the system [15,17,32]. However, it is now clear that these secondary reactions are unimportant if NO_x is excluded from the system [17,32].

The reaction of OH radicals with dialkyl sulfides may involve hydrogen atom abstraction or addition to the sulfur atom:

(15) $OH + RSR \rightarrow RSR_{-H} + H_2O$

(16) $OH + RSR + M \leftrightarrow RS(OH)R + M$

On the basis of a significant deuterium isotope effect and a small positive activation energy for the $OH+CH_3SCH_3$ reaction Hynes et al. [14] suggested that in the absence of O_2, H atom abstraction is the major reaction channel. Recently we have shown that for the $OH+CH_3SCH_3$ reaction decomposition of the addition complex via methyl radical loss is also negligible [15]. The absence of any pressure effect on the reported rate constants for the $OH+CH_3SCH_3$ reaction (0.5-760 Torr) provides additional support for the dominance of the abstraction process. When O_2 is added to the system an increase in the effective rate constant for OH removal has been observed [14,17,32]. This suggests that the addition complex is sufficiently stable to enable reaction with O_2 to compete effectively with decomposition.

It seems reasonable to assume that H atom abstraction will also be the dominant channel for reaction of OH radicals with the higher members of this homologous series in the absence of O_2. Reactions of Cl atoms with dialkyl sulfides occurs via a H atom abstraction mechanism and since Cl atoms and OH radicals are both electrophilic it is expected that there would be a correlation in the reactivities of these species. The plot in Figure 7 of Cl versus OH reactivity shows essentially linear correlation indicating mechanistically similar reactions.

Assuming the C-H bond strength in CH_3SCH_3 is similar to that in CH_3OCH_3 [33] and to secondary C-H bonds in alkanes the increased reactivity for the OH+DMS reaction relative to the $OH+C_2H_6$ reaction would be expected. However, it can be seen from the data in Table 2 that the rate constants increase linearly with the alkyl chain length. Thus, the CH_2 groups in these molecules show similar reactivities which appear to be a factor of 3 higher than in the corresponding alkanes. It is unlikely that the presence of a sulfur atom will change the C-H bond energy in the β and γ positions. Hence, the increase in reactivity must result from some other mechanistic effect, In order to quantify the effect we have assigned overall rate constants for abstraction from CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9 groups attached to the S atom in R_2S. Within the quoted experimental uncertainties the rate constant for the $OH+CH_3SC_2H_5$ reaction [14] is the average of the rate constants for the $OH+CH_3SCH_3$ and $OH+C_2H_5SC_2H_5$ reactions. Such behaviour suggests that the reactivities of the aliphatic chains on either side of the S atom are essentially independent and additive. We can thus assign an overall rate constant for each side chain equal to half of the measured rate constant. Figure 8 shows a plot of the increase in the overall rate constant for the alkyl group in R_2S relative to that observed for the corresponding group in n-alkanes as a function of the number of CH_2 groups. Such a plot should reach a plateau when the addition of a CH_2 group to the alkyl side chain has the same effect as that observed in n-alkanes. Clearly the activating effect of the S atom extends at least to the γ C atom. We have also treated the reported OH rate constants for straight chain aliphatic ethers [34] in a similar manner. As shown in Figure 8 and previously indicated by Wallington et al. [34] the activating effect of the O atom in dialkyl ethers is operative over 3 tc 4 C atoms. These conclusions cannot be explained purely in terms of bond energy or inductive effects and indicate an alternative reaction pathway to the direct concerted H atom abstraction pathway observed in n-alkanes. Further mechanistic and product studies for the reactions of OH radicals with dialkyl sulfides and ethers are required to resolve these problems.

5. THE REACTION OF OH AND Cl ATOMS WITH CH_3NO_2 AND CD_3NO_2

5.1. Introduction

There was only one previous rate constant measurement of the $OH+CH_3NO_2$ reaction by Campbell and Goodmann [35]. Problems associated with the relative technique employed by Campbell and co-workers have been suggested by Tuazon et al. [36]. This was one of the reasons why we undertook this investigation. Another reason was that an investigation of the $OH+CH_3NO_2$ reaction might give a basis for comparison with the $OH+CH_3ONO$ and $OH+CH_3ONO_2$ reactions which are of the outmost importance in investigations of atmospheric chemistry. The rate constant for the reaction of OH with CD_3NO_2 was measured to reveal whether the mechanism is primarily H-atom abstraction or addition. The results of this investigation have recently been published elsewhere [37]. The relative rate data previously reported [37] was in error by about a factor of 2 due to incorrect calibration in the analytical procedure and has accordingly been amended. The results from both our pulse radiolysis and continuous photolysis studies are now in agreement within the experimental uncertainties.

5.2. Results

All experiments using the absolute technique were performed under pseudo-first-order conditions at 295±3 K. Concentrations of CH_3NO_2 and CD_3NO_2 were in large excess relative to the initial OH concentration. The OH decay with and without added substrate is shown in Figure 9. Corresponding log plots are also shown in Figure 9. Various concentrations of CH_3NO_2 and CD_3NO_2 were mixed with 15 mbar of H_2O and backed up with Ar to a total pressure of 1 atm. The plots of reciprocal OH half-lives versus concentrations and the plots of log slopes versus concentrations are shown in Figure 10. The rate constants derived from a least-squares fit of the straight lines are given in Table 3. The error limits are $\pm 2\sigma$ of the fit. The intercept of the straight lines corresponds to the OH decay rate via reactions (3) and (4) in the absence of added CH_3NO_2 or CD_3NO_2.

The concentration-time data from the relative experiments are show plotted in the form of eq. (III) in Figure 11. Taking the recommended value of $k(OH+C_2H_6)=2.74\times10^{-13}$ $cm^3molecule^{-1}s^{-1}$ [24] for the reference reaction provides the values of the rate constants for the reaction of OH with CH_3NO_2 and CD_3NO_2 given in Table 3. The error limits are twice the standard deviation. A value of $k(Cl+CH_3NO_2)=(6\pm2)\times10^{-15}$ $cm^3molecule^{-1}s^{-1}$ was obtained using a value of $k(Cl+CH_4)=1.0\times10^{-13}$ $cm^3molecule^{-1}s^{-1}$ [38].

5.3. Discussion

For $k(OH+CH_3NO_2)$ there is a factor of 6 difference between the average value of $(1.4\pm0.1)\times10^{-13}$ $cm^3molecule^{-1}s^{-1}$ obtained in the present investigation and the value of $(9.1\pm0.1)\times10^{-13}$ $cm^3molecule^{-1}s^{-1}$ reported by Campbell and Goodmann [35]. The same paper [35] reports a value $k(OH+CH_3ONO)$ which is a factor 7 higher than that reported by Tuazon et al. [36]. Our results support the suggestion by Tuazon et al. that there are problems associated with the relative technique used by Campbell and co-workers [35], which leads to consistently high values for the measured rate constants.

Our value for $k(OH+CH_3NO_2)$ is similar to the value recommended by Atkinson [24] for $k(OH+C_2H_6)$. This suggests that the replacement of a methyl group by a nitro group in ethane has very little effect on the OH reactivity. If this reaction involved mainly H atom abstraction the presence of the strongly electron-withdrawing NO_2 group would be expected to considerably decrease the rate constant for abstraction by the electrophilic OH radical. The strongly electron-withdrawing nitrate group has previously been shown to significantly reduce the rate of H atom abstraction by OH radicals from alkyl groups bonded to the ONO_2

group [39-41]. The rate constant $k(Cl+CH_3NO_2)$ determined in this work shows a decrease of about four orders of magnitude compared to the value of $k(Cl+CH_3CH_3)=5x10^{-11}$ $cm^3molecule^{-1}s^{-1}$ [38] indicating a marked decrease in the importance of the abstraction reaction channel following substitution by the nitro group. Also the small isotope effect found for the reaction of OH with CD_3NO_2 provides support for this suggestion since the abstraction channel would be expected to show a larger isotope effect. Hence, the reaction between OH radicals and nitromethane may involve both hydrogen abstraction and OH addition followed by rapid decomposition of the adduct:

(17) $OH + CH_3NO_2 \rightarrow CH_2NO_2 + H_2O$
$\Delta H^0(17) \approx -20$ kcal mol^{-1}

(18) $OH + CH_3NO_2 \rightarrow CH_3(OH)NO_2 \rightarrow CH_3 + HNO_3$
$\Delta H^0(18a) = 11.4$ kcal mol^{-1}

(18) $OH + CH_3NO_2 \rightarrow CH_3(OH)NO_2 \rightarrow CH_3OH + NO_2$
$\Delta H^0(18b) = -31.6$ kcal mol^{-1}

Reaction channels (17) and (18b) are both appreciably exothermic [42]. The evidence presented above shows that for the $OH+CH_3NO_2$ reaction at 295±3 K and atmospheric pressure the addtion channel predominates and the abstraction pathway is of minor importance. Thus for the reaction of electrophilic OH radicals the presence of the strongly electron withdrawing nitro group appeared to have little effect on the CH_3 reactivity compared to that found in C_2H_6, whereas reactivity with the electrophilic Cl atoms was decreased almost by 4 orders of magnitude. It is interesting to compare the results for the reactions of OH radicals and Cl atoms with CH_3NO_2 to those obtained for reactions with CH_3CN. Poulet et al. [43] have shown that the reactions of both OH and Cl with CH_3CN involve only H atom abstraction. In this case the electron withdrawing CN group greatly reduces both rate constants compared to those for the reactions with C_2H_6, $k(OH+CH_3CN)=2.1x10^{-14}$ $cm^3molecule^{-1}s^{-1}$ and $k(Cl+CH_3CN)= 8.9x10^{-15}$ $cm^3molecule^{-1}s^{-1}$, despite a considerable reduction in C-H bond dissociation energy ($D(C_2H_5$-H)=98.2 kcal mol^{-1} [44], D($CNCH_2$-H)=93 kcal mol^{-1} [44]).

Zabarnick et al. [45] have recently employed the technique of laser photolysis - laser induced fluorescence to investigate the kinetics of the $OH+CH_3NO_2$ reaction at low pressures in argon as a function of temperature. At 300 K they report a rate constant of $(1.41\pm0.30)x10^{-14}$ $cm^3molecule^{-1}s^{-1}$ in substantial agreement with a preliminary value $k=1.7x10^{-14}$ $cm^3molecule^{-1}s^{-1}$ obtained by Kurylo et al. [46] using flash photolysis - resonance fluorescence at 298 K in 50 Torr of Argon. On the basis of the measured activation energy of 2.7 kcal mol^{-1} and an isotope effect of close to 2 for the $OD+CD_3NO_2$ reaction Zabernick et al. [45] suggested, that under their experimental conditions, the $OH+CH_3NO_2$ reaction involves an abstraction mechanism. The similarity of the rate constant for $OH+CH_3NO_2$ at low pressures to that for the $OH+CH_3CN$ [43] supports this suggestion. Hence, at atmospheric pressure the $OH+CH_3NO_2$ reaction involves mainly the addition channel whereas at lower pressures the addition complex is unstable and the major reaction channel is abstraction. Further evidence for the addition channel can be seen from a comparison of the rate data for OH radicals and Cl atoms with the higher nitroalkanes.

6. THE REACTION OF OH AND Cl ATOM WITH NITROALKANES

6.1. Introduction

Reaction with hydroxyl radicals is the primary oxidative step for the majority of compounds in atmospheric and combustion processes [30]. Atmospheric modelling relies heavily on accurate OH rate data. Over the last 20 years this has led to a considerable scientific effort involving the investigation of OH reactions with a large number of compounds using a wide variety of both absolute and relative rate techniques [24]. Even rate data for compounds not present in the atmosphere are of high interest because these data add to our general predictive data base.

The reaction of OH with the first member of the homologeous series of nitroalkanes, nitromethane, was dealt with in chapter 5. In order to further elucidate our surprising result that an addition process is the major reaction channel for $OH+CH_3NO_2$, we have measured for the first time the rate constants for the reaction of OH with $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$. All the OH rate constant measurements were carried out by both an absolute method using pulse radiolysis combined with kinetic spectroscopy and a conventional relative rate method. In order to provide more mechanistic data the rate constants for reaction of Cl with all the nitroalkanes were determined using the relative rate method.

6.2. Results

All experiments using the absolute technique were performed under pseudo-first-order conditions at 295±3 K. Concentrations of RNO_2 were in large excess relative to the initial OH concentration. The OH decay with and without added substrate is shown in Figure 12. Corresponding log-plots are also shown in Figure 12. Various concentrations of RNO_2 were mixed with 15 mbar of H_2O and backed up with Ar to a total pressure of 1 atm. The plots of OH half-lives versus concentrations are shown in Figure 13. The rate constants are derived from a least squares fit of the straight lines and are given in Table 4. The error limits are $\pm 2\sigma$ of the fit. The intercept of the straight lines corresponds to the decay rate via reactions (2) and (3) in the absence of added compounds.

The concentration-time data from the relative OH and Cl experiments are shown plotted in the form of eq. (III) in Figures 14-16. The derived OH and Cl rate constants are given in Table 4.

6.3. Discussion

As it can be suggested from the results presented in chapter 5 the reaction between OH radicals and nitroalkanes may involve both hydrogen abstraction and OH addition followed by rapid decomposition of the adduct. Further evidence for the addition channel can be seen from a comparison of the rate data for OH radicals and Cl atoms with the higher nitroalkanes. Both OH and Cl are electrophilic species and a linear relationship between the logarithm of their rate constants would be expected.

The measured rate constant for each nitroalkane will have an abstraction and addition component, $k_{obs}=k_{abs}+k_{add}$. Assuming that addition is the major channel for the $OH+CH_3NO_2$ reaction at atmospheric pressure it is possible to estimate the rate constant for the abstraction process for the each member of the higher nitroalkanes. A value of k_{add} for the $OH+CH_3NO_2$ reaction may be derived from the experimental data. Taking $k_{abs}=0.14x10^{-13}$ $cm^3molecule^{-1}s^{-1}$ from the low pressure investigation of the $OH+CH_3NO_2$ reaction a value of $k_{add}=1.3x10^{-13}$ $cm^3molecule^{-1}s^{-1}$ is calculated for CH_3NO_2 ($k_{obs}=1.4x10^{-13}=0.14x10^{-14}+k_{add}$). It is unlikely that the length of the alkyl chain will influence the rate constant for the addition process. Hence, the rate constant for abstraction for the nitroalkanes is derived from $k_{abs}=k_{obs}-1.3x10^{-13}$ $cm^3molecule^{-1}s^{-1}$. Values of k_{abs} are given in Table 5 and the resulting linear free energy plot shown in Figure 17. There appears to be an essentially linear correlation between the reactivities of OH radicals and Cl atoms toward the nitroalkanes as expected if both processes involve a simple direct H atom abstraction.

It is apparent from the rate constant data for H atom abstraction by OH radicals in the nitroalkanes given in Table 5 that the NO_2 group has a strong deactivating effect for abstraction of H atoms positioned α and β to the NO_2 group of the nitroalkane. Bond dissociation energies are not available for these C-H bonds but it is unlikely that the NO_2 group will change the C-H bond energy at the β position from the C-H bond energy found in unsubstituted alkanes. Thus the reduction in reactivity at the β C atom and at least in part at the α C atom must result from inductive effects in the transition state involving polar repulsion between the electrophilic OH radical and the abstracted H atom. In order to quantify this deactivation in terms of the number of C atoms over which the effect is operative we have plotted in Figure 18 the reduction in the overall rate constant for the alkyl group in nitroalkanes relative to that observed for the corresponding group in the n-alkanes as a function of the number of CH_2 groups. The plot shows clearly that the deactivating effect of the NO_2 group extends to the α and β C atom.

We have also treated the reported OH rate constants for n-alkyl alcohols [47,48] in a similar manner. As seen in Figure 18 and as pointed out by Wallington et al. [47,48] the activating effect of the OH group in the alcohol is operative over 3 to 4 C atoms. This cannot be explained purely in terms of an inductive effect and indicates an alternative reaction pathway to the H atom abstraction process operative for the n-alkanes. Clearly further mechanistic and product studies for the reactions of OH with both nitroalkanes and aliphatic alcohols are needed to resolve these points.

7. FUTURE WORK

Future work will concern product studies of some of the reactions investigated in this work. Also reactions of OH with nitrites and nitrates will be studied. Finally it is planned to try to obtain spectral data for the CH_3S radical.

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APPENDIX I : Tables

Table 1. Summary of reported rate constants for OH+DMS at 298±2 K

k[a]	technique[b]	pressure torr	M	Authors
10.0±1.0	CP-GC (rel)	735	air	Atkinson et al. [4]
9.8±1.2	FP-RF (abs)	50-98	Ar	Atkinson et al. [5]
8.3±0.9	FP-RF (abs)	10-50	Ar/SF_6	Kurylo 1978 [6]
9.1±1.4	CP-GC (rel)	760	air	Cox et al. 1980 [7]
4.3±0.6	FP-RF (abs)	50	Ar	Wine et al. 1981 [8]
10.4	DF-EPR (abs)	0.5	He	McLeod 1983 [9]
4.4±0.4	CP-GC (rel)	760	N_2	Barnes [11/17]
8.0±0.5	CP-GC (rel)	760	air	Barnes [11/17]
3.2±0.2	DF-EPR (abs)	0.5	He	Martin et al. [12]
4.8±0.2	PLP-PLIF (abs)	40-700	N_2	Hynes et al. [14]
6.3±0.1	PLP-PLIF (abs)	750	air	Hynes et al. [14]
3.6±0.2	FP-RF (abs)	50	Ar	Wallington [15]
10.5±0.3	DS-GC (rel)	740	O_2	Wallington [15]
5.5±1.0	DF-RF (abs)	0.8	He	Hsu et al. [16]
3.5±0.2	PR-KS (abs)	760	Ar	this work

[a]units: $10^{12}cm^3molecule^{-1}s^{-1}$

[b] CP = Continuous Photolysis; GC = Gas Chromatography; FP = Flash Photolysis; RF = Resonance Fluorescence; DF = Discharge Flow; EPR = Electron Paramagnetic Resonance; PLP = Pulsed Laser Photolysis; PLIF = Pulsed Laser Induced Fluorescence; DS = Dark Source of OH; PR = Pulse Radiolysis; KS = Kinetic Spectroscopy.

Table 2. Rate constants for the OH+RSR and Cl+RSR reactions

Reaction	$10^{12}k^a$	Technique[b]	Reference
OH+DES	12 ±1.4	DF-EPR (abs)	Martin et al [7]
	15.5±2.2	LP-LIF (abs)	Hynes et al. [6]
	11 ±2	CP-GC (rel)	Barnes et al. [9]
	11.6±2.5	PR-KS (abs)	This work
OH+DPS	19 ±2	CP-GC (rel)	Barnes et al. [9]
	21.5±3	PR-KS (abs)	This work
OH+DBS	37.4±5	PR-KS (abs)	This work
Cl+DMS	322 ±30	CP-GC (rel)	This work
Cl+DES	441 ±40	CP-GC (rel)	This work
Cl+DPS	518 ±40	CP-GC (rel)	This work
Cl+DBS	604 ±37	CP-GC (rel)	This work

[a] in units of $cm^3 molecule^{-1} s^{-1}$

[b] DF = Discharge Flow; EPR = Electron Paramagnetic Resonance; LP = Laser Photolysis; LIF = Laser Induced Fluorescence; CP = Continuous Photolysis; GC = Gas Chromatography Source; PR = Pulse Radiolysis; KS = Kinetic Spectroscopy.

Table 3. OH rate constants[a] for reaction with CH_3NO_2 and CD_3NO_2

Reaction	halflife plot	log slope plot	mean	relative
$OH+CH_3NO_2$	1.45±0.07	1.67±0.01	1.56±0.12	1.1±0.1
$OH+CD_3NO_2$	1.13±0.09	0.78±0.09	0.96±0.11	0.9±0.1

[a] in units of 10^{13} $cm^3molecule^{-1}s^{-1}$

Table 4: Rate constants[a] for the reaction of Cl and OH with RNO_2

Compound	k_{Cl}(rel)	k_{OH}(rel)	k_{OH}(abs)	k_{OH}(av)
CH_3NO_2	0.06±0.02[b]	1.1±0.1	1.6±0.5[b]	1.4
CD_3NO_2	0.02±0.01	0.9±0.1	1.0±0.2[b]	1.0
$CH3CH_2NO_2$	1.7±0.1	1.5±0.1	1.5±0.5	1.5
$CH_3CH_2CH_2NO_2$	99 ±6	5.5±0.8	3.4±0.8	4.5
$CH_3CH_2CH_2CH_2NO_2$	619 ±20	17.3±1.1	15.5±0.9	16.4
$CH_3CH_2CH_2CH_2CH_2NO_2$	1377 ±58	32.7±1.5	33.0±0.5	32.9

[a] in units of $10^{13}cm^3molecule^{-1}s^{-1}$

[b] taken from ref [37]

Table 5: H atom abstraction reactivity in linear aliphatic chains

R	k_{OH} in RCH_3[a]	k_{OH} in RNO_2[b]	Δk[c]	k_{OH} in ROH[d]	Δk[e]
CH_3	1.4	0.1	-1.3	8.61	+7.2
C_2H_5	10.4	0.2	-10.2	33.3	+22.9
C_3H_7	23.9	3.2	-20.7	53.4	+29.5
C_4H_9	39.2	15.1	-24.1	83.1	+43.9
C_5H_{11}	54.4	31.6	-22.8	108	+54
C_6H_{13}	71.6	-	-	124	+52
C_7H_{15}	85.8	-	-	136	+50

all in units of $10^{13}cm^3molecule^{-1}s^{-1}$

[a] Calculated from OH rate constant data of n-alkanes [3] minus contribution from a terminal CH_3 group ($k(CH_3)=\frac{1}{2}k(C_2H_6)$).

[b] Calculated from OH rate constant data of the nitroalkanes min contribution from the addition channel, $k_{abs}=k_{obs}-1.3$, see text detailed explanation.

[c] $\Delta k=k(RNO_2)-k(RCH_3)$

[d] Data from ref [47] and [48].

[e] $\Delta k=k(ROH)-k(RCH_3)$

APPENDIX II : Figures

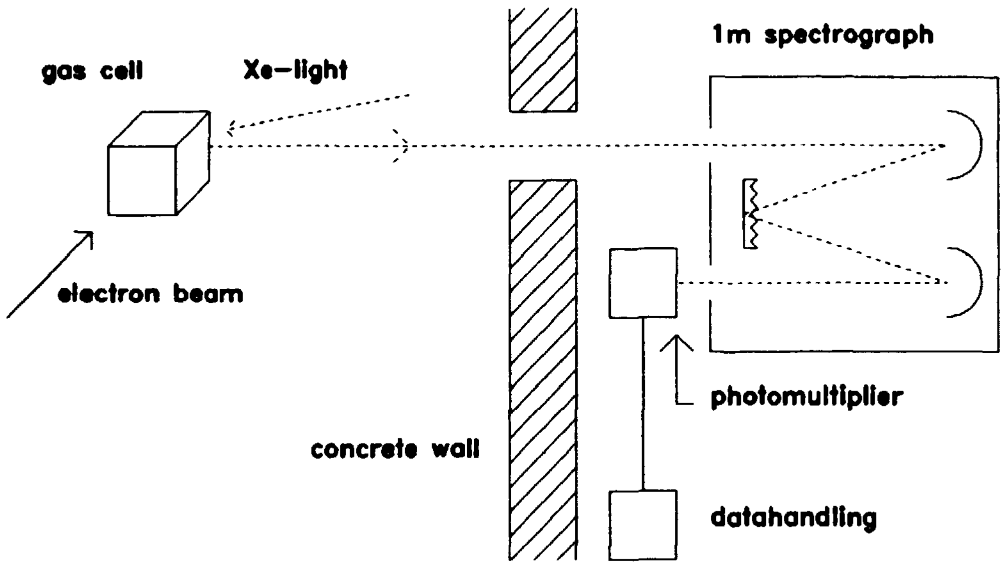

Fig. 1. Schematic diagram of the experimental apparatus.

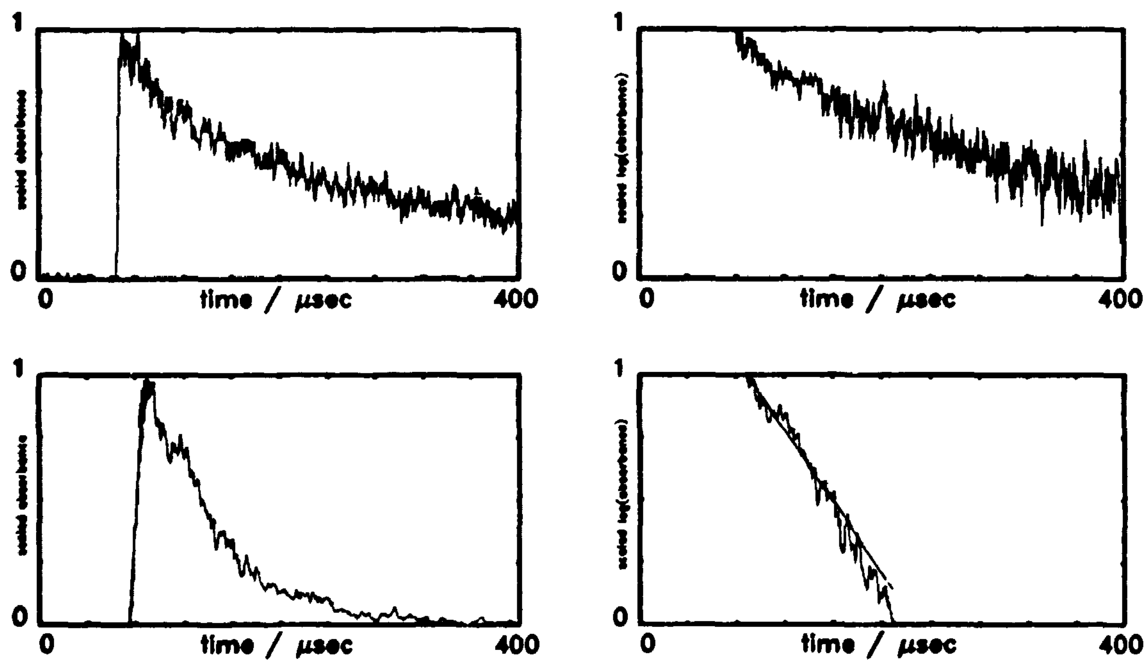

Fig. 2. Experimental OH kinetics. Upper left: 15 mbar H_2O with Ar to 1 atm. Lower left with 1.9 mbar DMS added. The right-hand figures are the logarithmic plots.

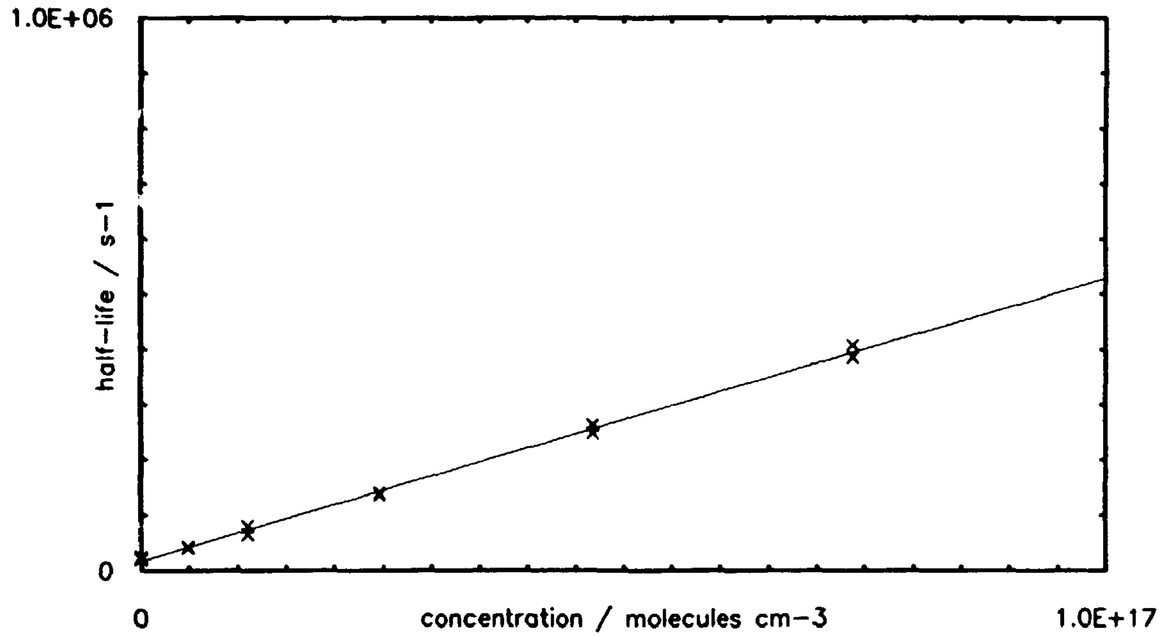

Fig. 3. Plot of OH reciprocal half-lives versus [DMS]

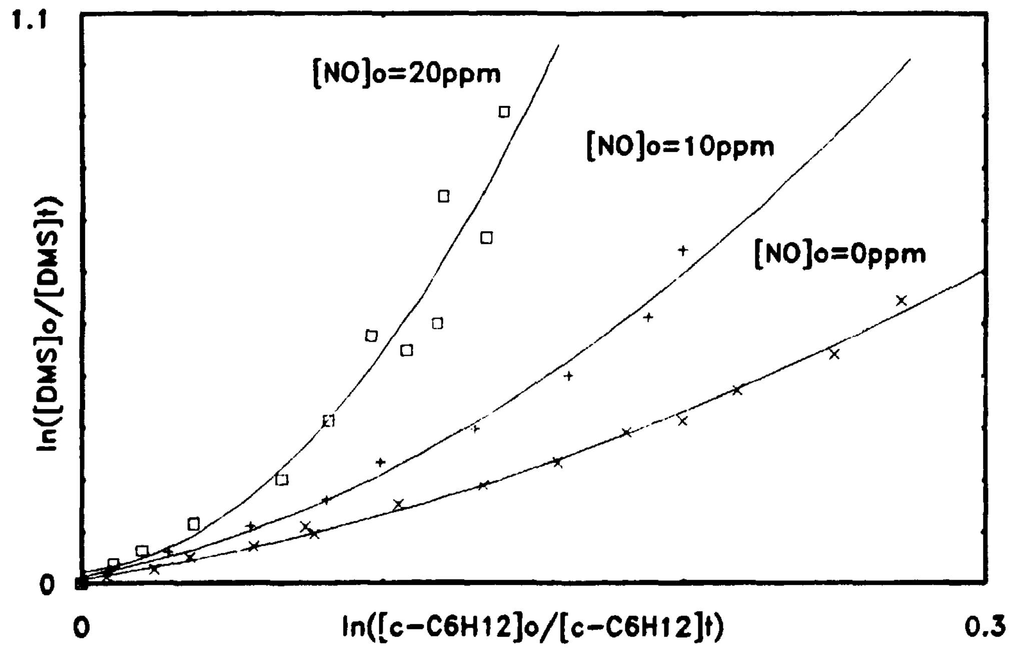

Fig. 4. Concentration-time data from the relative experiments.

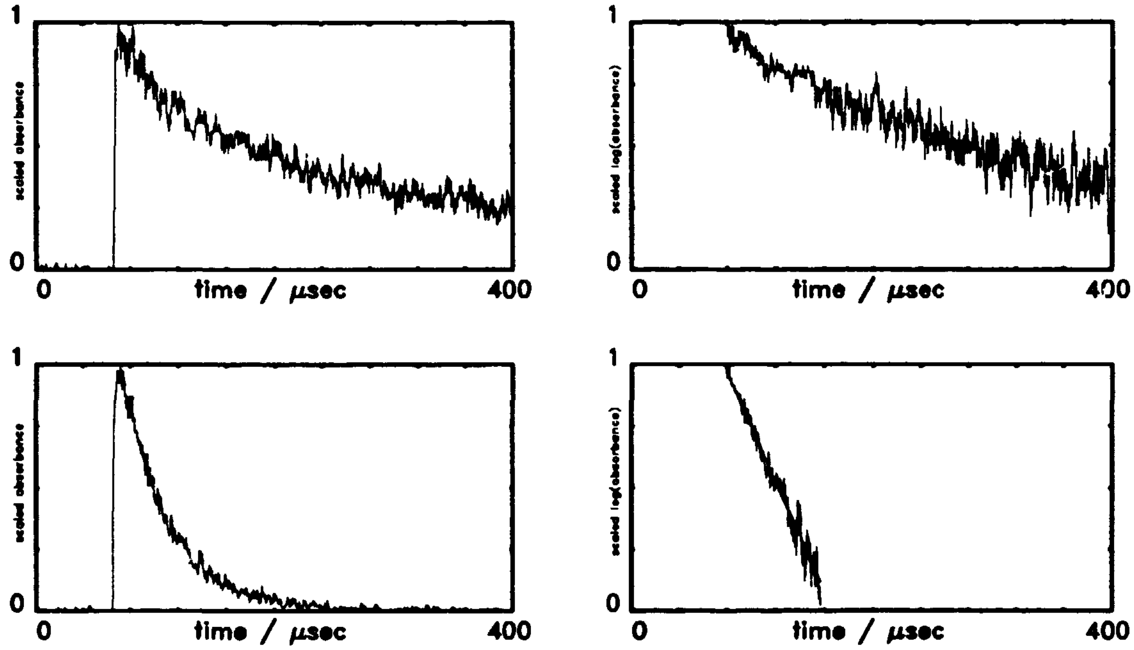

Fig. 5. Experimental OH kinetics. Upper left: 15 mbar H_2O with Ar to 1 atm. Lower left with 0.025 mbar DES added. The right-hand figures are the logarithmic plots.

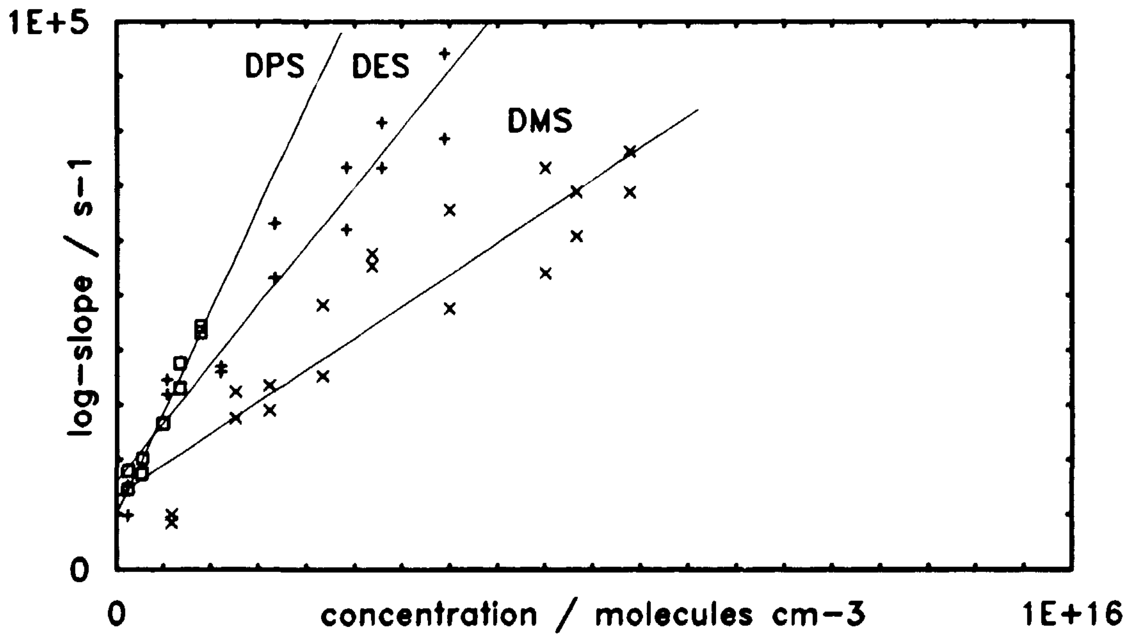

Fig. 6. Plot of log slopes versus reactant concentration.

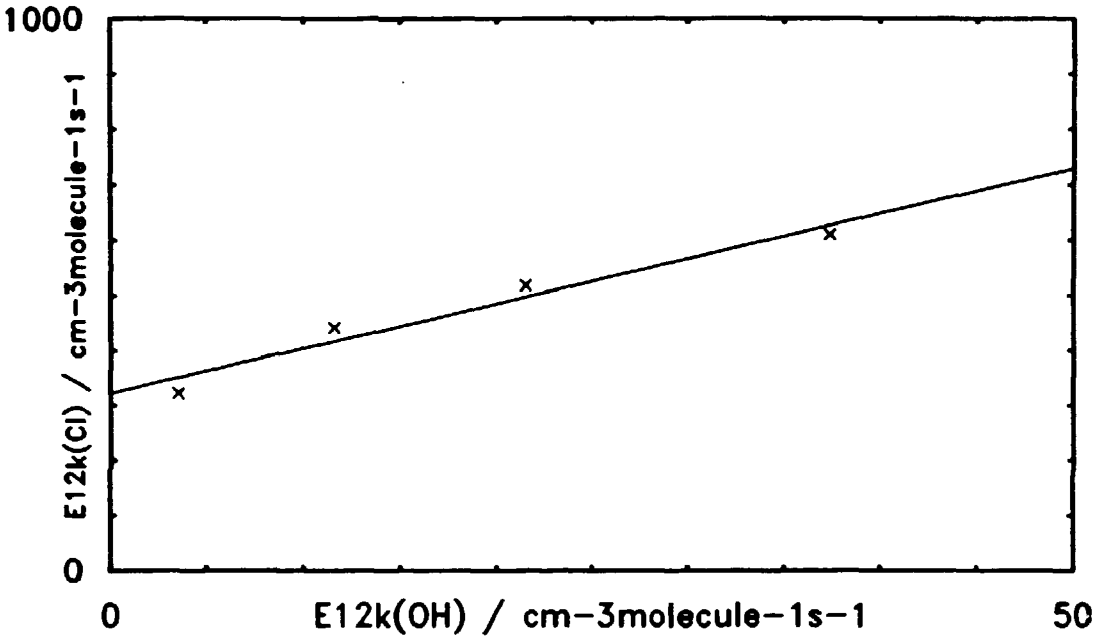

Fig. 7. k_{Cl} versus k_{OH} for DMS, DES, DPS and DBS

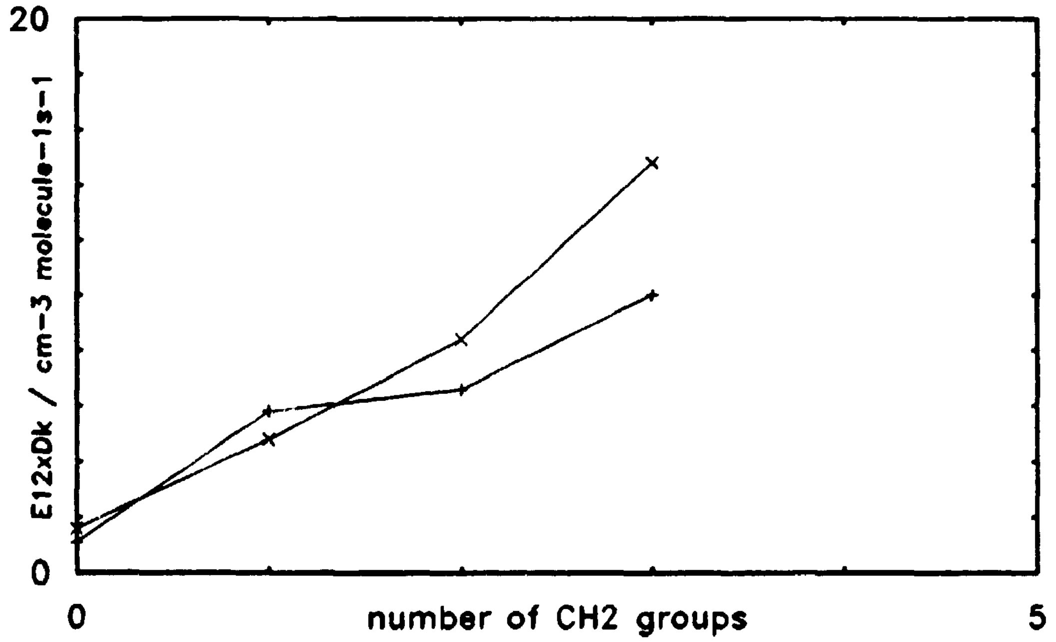

Fig. 8. k_{OH} versus number of CH_2 groups for sulfides (x) and ethers (+)

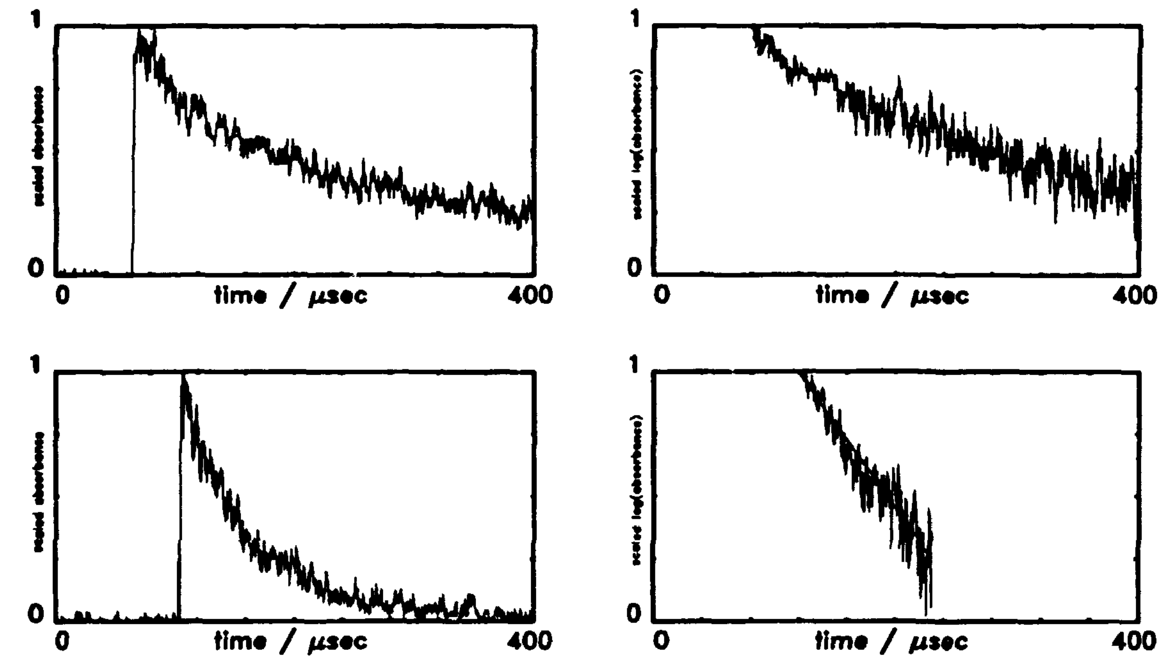

Fig. 9. Experimental OH kinetics. Upper left: 15 mbar H_2O with Ar to 1 atm. Lower left with 4.0 mbar CH_3NO_2 added. The right-hand figures are the logarithmic plots.

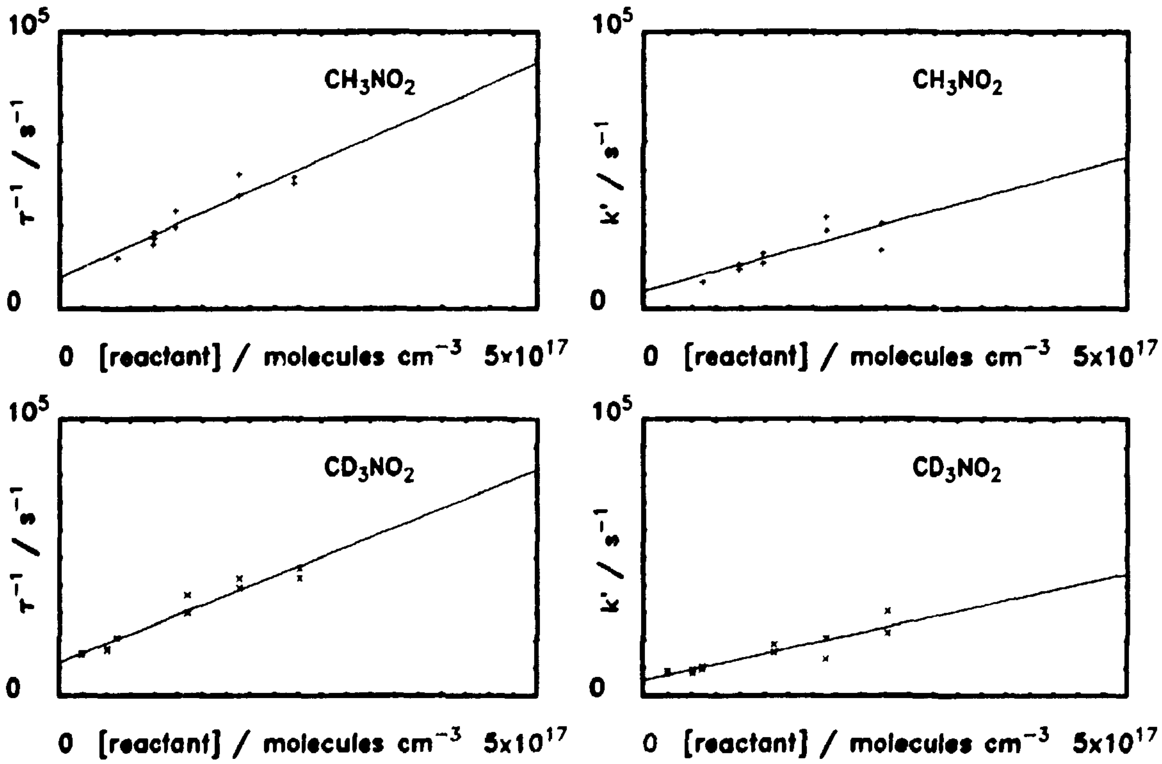

Fig. 10. Left-hand side: Plots of OH reciprocal half-lives versus reactant concentrations. Righ-hand side: The corresponding plots of the log slopes versus reactant concentrations.

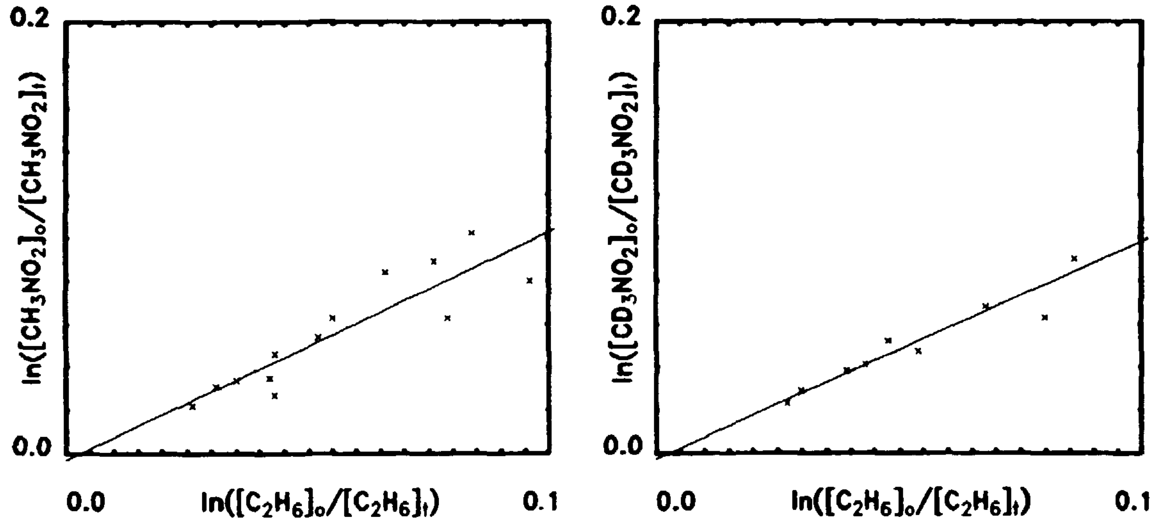

Fig. 11. Concentration-time data from the relative experiments.

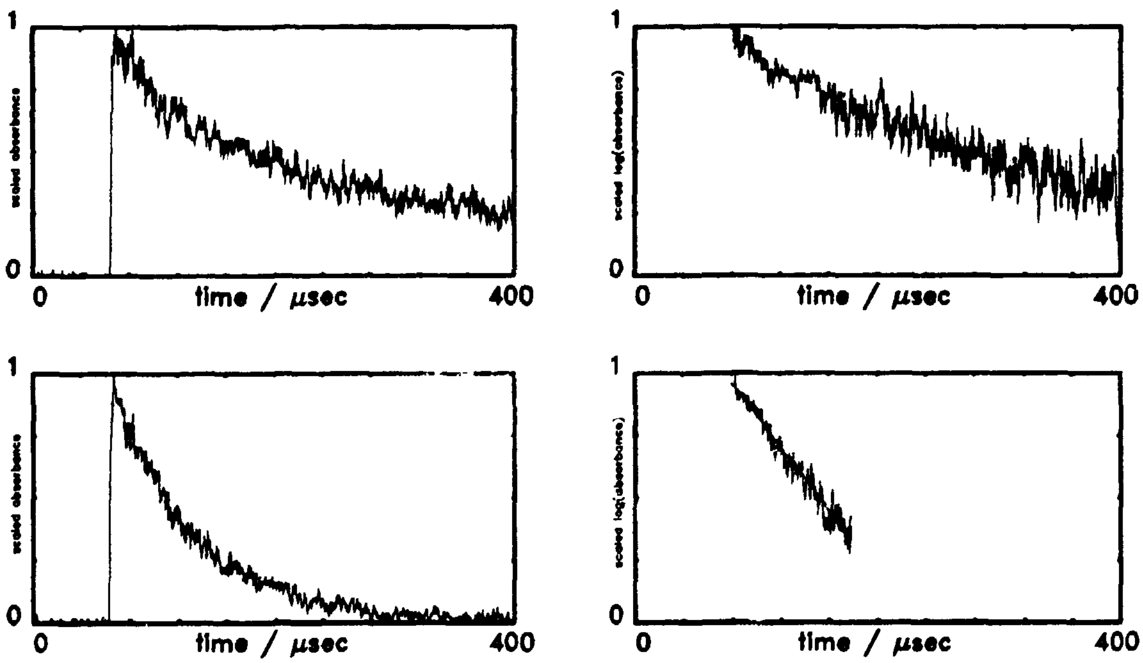

Fig. 12. OH kinetics in the pulse radiolysis. Upper left: Pure H_2O with Ar to 1 atm. Lower left: with 1.5 mbar $CH_3CH_2NO_2$ added. The right-hand figures are the corresponding logarithmic plot.

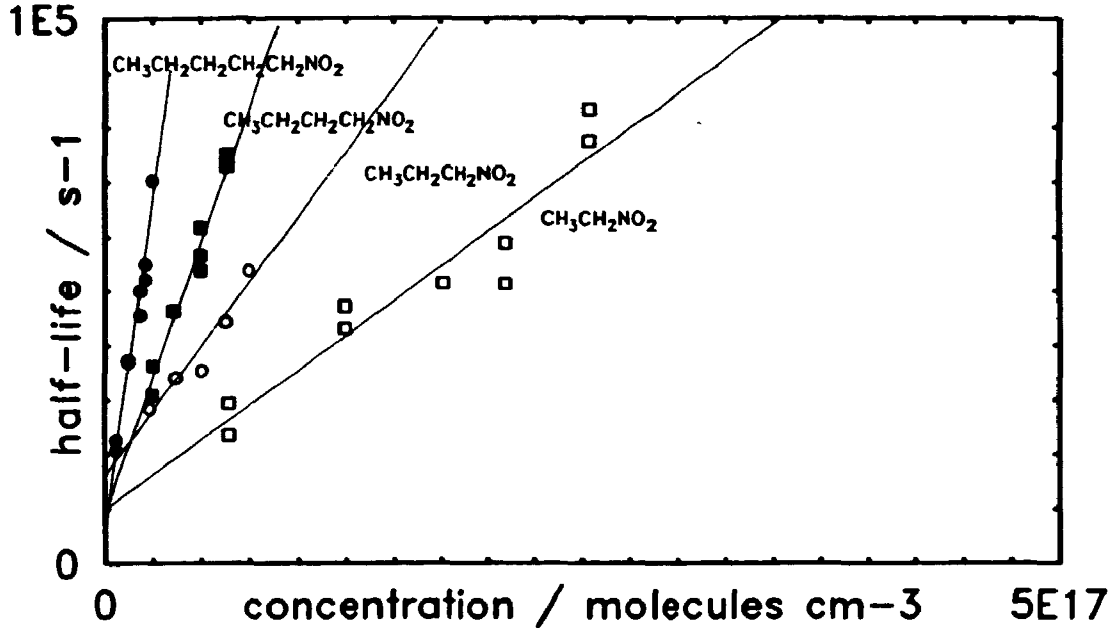

Fig. 13. Plots of OH reciprocal half-lives versus reactant concentrations for $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$, respectively with increasing slopes of the straight lines.

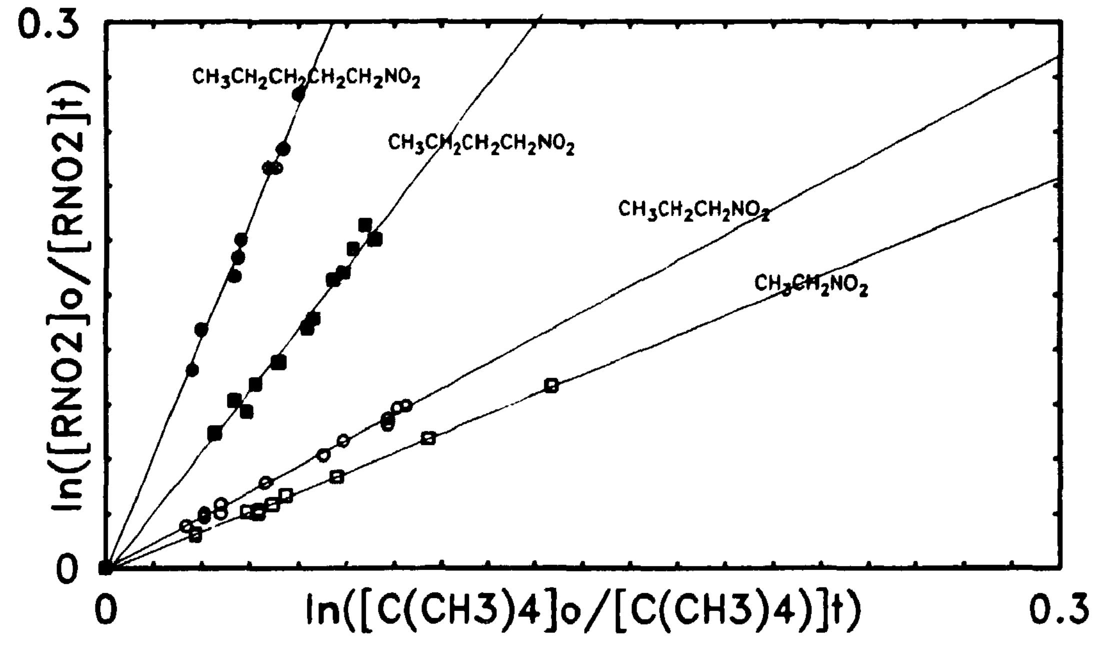

Fig. 14. Plot of the results of the relative OH experiments. $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$, respectively with increasing slopes of the straight lines.

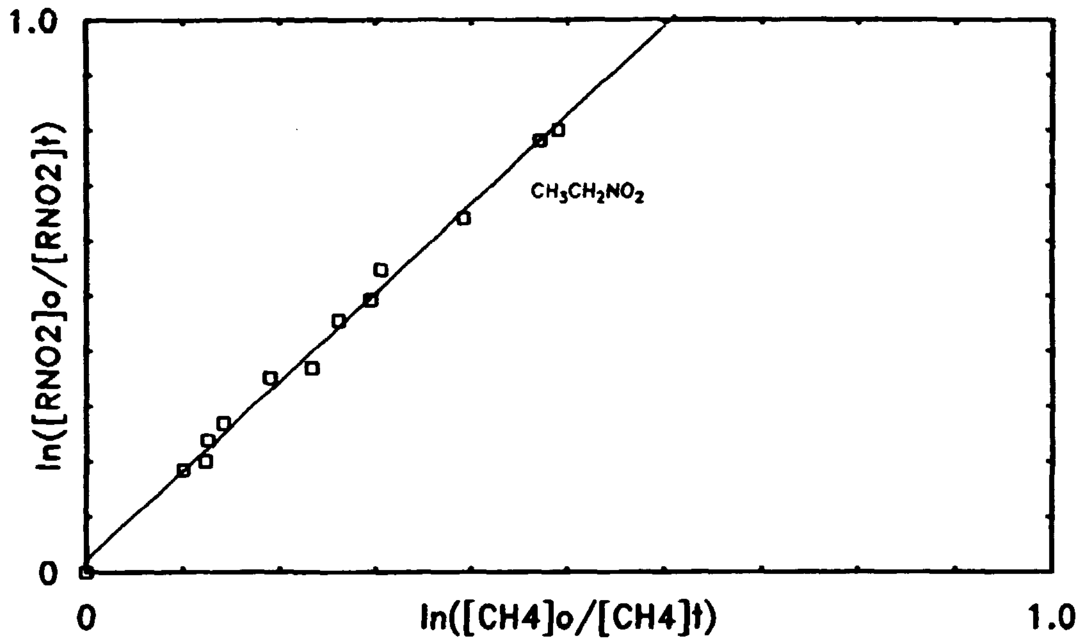

Fig. 15. Plot of the results of the relative Cl experiment for $CH_3CH_2NO_2$ relative to CH_4.

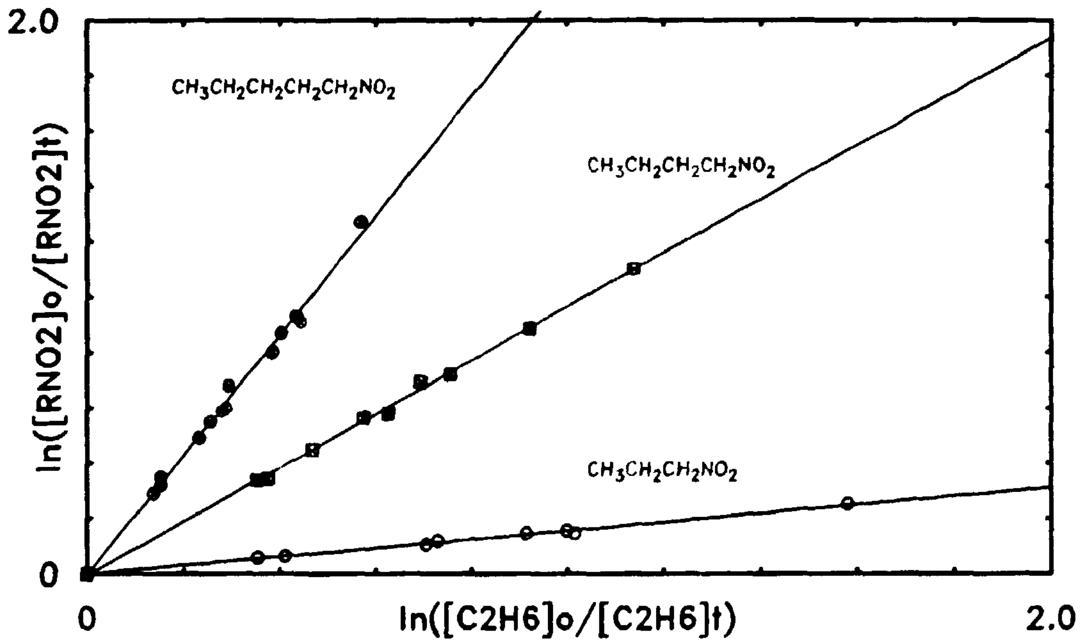

Fig. 16. Plot of the results of the relative Cl experiments. $CH_3CH_2CH_2NO_2$, $CH_3CH_2CH_2CH_2NO_2$, and $CH_3CH_2CH_2CH_2CH_2NO_2$, respectively with increasing slopes of the straight lines (relative to C_2H_6)

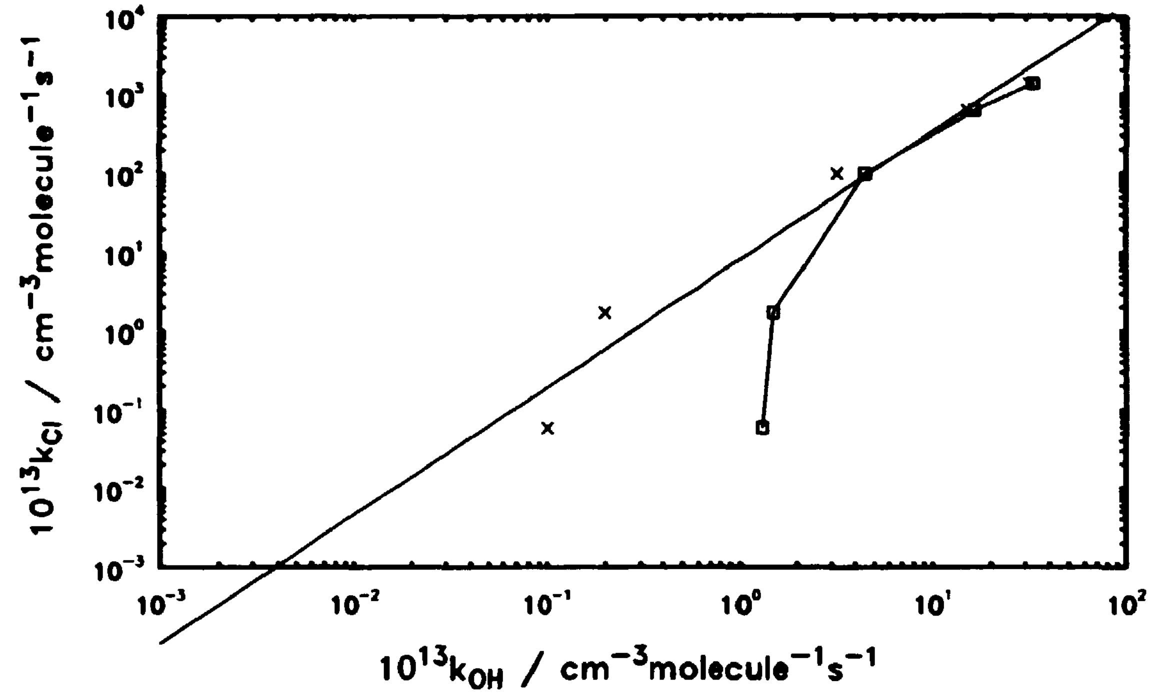

Fig. 17. Linear free energy plot of log(k_{Cl}) versus log(k_{OH}) for both observed values of k_{OH} (□) and values of k_{OH} corrected for addition (X)

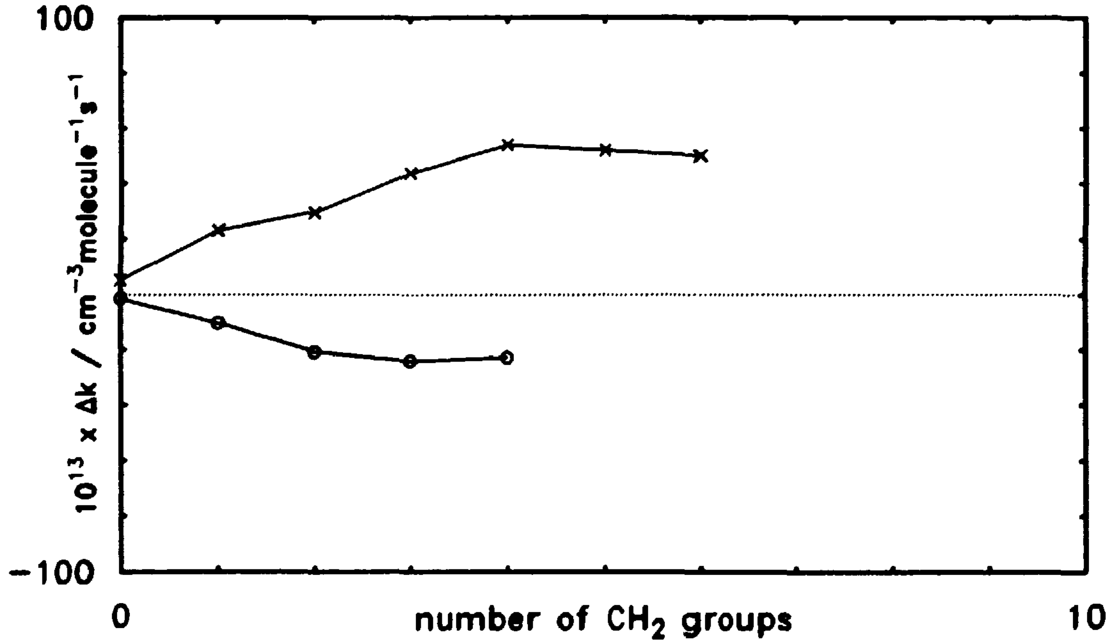

Fig. 18. Plot of the increase in the overall OH rate constant for reaction with a series of alcohols (X) (ref. [47,48]) relative to the n-alkanes (ref. [24]) versus number of CH_2 groups, and of the decrease in the overall OH rate constant for reaction with the nitroalkanes (O) (this work) relative to the n-alkanes (ref. [24]) versus number of CH_2 groups.

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Abstract (Max. 2000 char.)

Abstract. The work carried out during the first year of a four year Danish-Irish contract with the European Economic Community is described. The reactions of OH radicals with dialkyl sulfides and nitroalkanes have been studied applying both an absolute technique of pulse radiolysis with kinetic spectroscopy and a relative rate method using conventional smog chamber facilities. The reactions of OH with dimethyl sulfide and nitromethane have been investigated in special detail. Rate constants for reaction of Cl atoms with the same compounds have been determing using the relative rate method.

Descriptors

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