

Kinetics of the OH and Cl reactions with *N*-methylformamide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide

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Abstract

A relative kinetic technique was used in combination with long-path Fourier transform infrared spectroscopy to study the kinetics of the reactions of *N*-methylformamide (HC(O)NHCH₃), *N,N*-dimethylformamide (HC(O)N(CH₃)₂) and *N,N*-dimethylacetamide (CH₃C(O)N(CH₃)₂) with OH radicals and Cl atoms at 298 ± 2 K and atmospheric pressure 1000 ± 10 mbar of air. The measured OH and Cl reaction rate coefficients (in units of cm³ molecule⁻¹ s⁻¹) were, respectively, (0.86 ± 0.24) × 10⁻¹¹ and (0.97 ± 0.17) × 10⁻¹⁰ for *N*-methylformamide, (1.4 ± 0.3) × 10⁻¹¹ and (1.9 ± 0.3) × 10⁻¹⁰ for *N,N*-dimethylformamide, (1.9 ± 0.3) × 10⁻¹¹ and (2.5 ± 0.4) × 10⁻¹⁰ for *N,N*-dimethylacetamide. The results are presented and discussed in terms of structure–activity relationships and the atmospheric impact of the amides.

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Keywords: Amides; Kinetics; Rate coefficients; OH radical; Cl atom; Structure–activity relationship

1. Introduction

Amides are widely used as organic solvents, starting materials or intermediates in different industries (e.g. synthetic polymers, manufacture of dyes, synthesis of pesticides) [1–3]. Their industrial use results in emissions of the compounds into the atmosphere and, in addition they are also formed in situ as intermediate products in the degradation of amines [2–4]. As for other volatile organic compounds, once released to the atmosphere these compounds can undergo photolysis and chemical reactions with OH and NO₃ radicals and O₃ [5,6]. Kinetic and mechanistic studies on the gas phase atmospheric chemistry of amides are presently limited to two investigations [7,8] and the available structure–activity relationships used for rate coefficient estimations are based on a very limited kinetic data base for amines and no amides. More studies are required to properly characterize the gas phase degradation processes of amides in the atmosphere.

The aim of this work was to expand the kinetic data base for amides through measurements of rate coefficients for the reactions of OH radicals and chlorine atoms with three amides: *N*-methylformamide (MF, HC(O)NHCH₃), *N,N*-dimethylformamide (DMF, HC(O)N(CH₃)₂) and *N,N*-dimethylacetamide (DMA, CH₃C(O)N(CH₃)₂). *N,N*-Dimethylformamide is a high volume chemical with production exceeding 1 million pounds annually in the US. Its main use is as an organic solvent in many industrial applications such as microelectronics, pharmaceuticals, fibers and textiles. Its presence in water and air has been reported [9]. In the year 2000 the worldwide production volume of *N,N*-dimethylacetamide was estimated to be between 50,000 and 60,000 tonnes year⁻¹. It is mainly used for polymer dissolution in the man-made fibre production industry and in the fine chemical industry. The only study reported so far in the literature for the three amides investigated in this work is a determination by Koch et al. [8] of the rate coefficient for the reaction of OH radicals with *N,N*-dimethylacetamide at two temperatures (300 and 384 K) using flash photolysis/resonance fluorescence (FP-RF).

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These authors also reported rate coefficients for the reaction of OH with *N*-methylacetamide, *N*-methylpropamide and *N,N*-dimethylpropamide.

The results obtained in this work are presented and discussed in terms of structure–activity relationships and the potential atmospheric impact of the amides investigated.

2. Experimental

Experiments were conducted using two different systems in Wuppertal and Orléans. The experimental systems and procedures used in the present study were the same as those described in other papers from both laboratories and hence are only briefly summarized here.

The chamber of Wuppertal consists of a 480 L cylindrical Duran glass vessel (3 m in length, 45 cm in diameter) closed at both ends by aluminum end flanges. The metal flanges contain ports for the introduction of bath gases and reactants into the chamber. A mixing fan and a capacitance manometer are also located on the flanges. Arranged concentrically around the outside of the reactor are 20 superactinic lamps (Philips TLA 40 W, $300 \leq \lambda \leq 450$ nm, $\lambda_{\text{max}} = 360$ nm). The chamber can be evacuated down to 10^{-3} Torr by means of a turbomolecular pump backed by a double stage rotary fore pump. The chamber is equipped with an internally mounted White mirror system operated at an optical path length of 51.6 m which is coupled to an FTIR spectrometer (Nicolet Magna 520) for the acquisition of infrared spectra at a resolution of 1 cm^{-1} . The chamber is described in detail elsewhere [10].

The set-up of Orléans used consists of a 200 L FEP Teflon bag surrounded by six lamps (Sylvania, G 300 W) emitting at 254 nm. The photolytic light intensity was controlled by the number of lamps that were turned on (usually 1 lamp), while the temperature was maintained at 298 ± 2 K by flowing air around the Teflon bag. Analyses of reactants were performed using a Nicolet FTIR spectrometer (Magna 550) with a path length of 10 m (spectra were taken at 1 cm^{-1} resolution) and a gas phase chromatograph coupled with a flame ionization detector (GC-FID).

At Wuppertal the reaction rate coefficients of OH radicals and Cl atoms with *N*-methyl formamide ($\text{C}_2\text{H}_5\text{NO}$, MF), *N,N*-dimethyl formamide ($\text{C}_3\text{H}_7\text{NO}$, DMF) and *N,N*-dimethylacetamide ($\text{C}_4\text{H}_9\text{NO}$, DMA) were determined at room temperature ($T = 298 \pm 2$ K) and atmospheric pressure ($P = 1000 \pm 10$ mbar) in synthetic air. At Orléans only the reaction rate coefficient of OH with DMF was measured at 298 K and atmospheric pressure. The photolysis of H_2O_2 was used at Orléans as the OH radical source while at Wuppertal the photolysis of CH_3ONO was employed as the OH source and photolysis of Cl_2 as the Cl atom source.

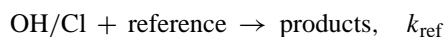
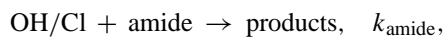
In Wuppertal authentic samples of the investigated amide compounds were added to the chamber in a heated air stream; all reference compounds were introduced by direct injection of the required amount using a calibrated syringe. The concentration–time behavior of the amides and reference

compounds were monitored using FTIR. A subtraction procedure in combination with calibrated reference spectra was used for quantification of the compounds. The IR spectral features used for the analysis were $1130\text{--}1305 \text{ cm}^{-1}$ for MF, $1025\text{--}1130 \text{ cm}^{-1}$ for DMF, $970\text{--}1105$ or $1120\text{--}1305 \text{ cm}^{-1}$ for DMA, $2800\text{--}3000 \text{ cm}^{-1}$ for cyclohexane, $850\text{--}1050 \text{ cm}^{-1}$ for propene and $800\text{--}1100$ or $2900\text{--}3200 \text{ cm}^{-1}$ for ethene. Depending on the system the concentration–time profiles of the investigated compounds were monitored over irradiation periods ranging between 5 and 120 min leading to a consumption of 30–70% of the initial concentrations of the organic compounds.

Test experiments on the amide/reference/air mixtures in the 480 L reactor showed that losses to the wall or via photolysis accounted for between 10 and 20% for DMF and DMA and up to 50% in the case of MF for both processes. These losses were measured prior to introduction of the OH or Cl precursor and were taken into account in the kinetic analysis as indicated below. Test experiments were also performed in which amide/reference/air/ CH_3ONO or Cl_2 mixtures were kept in the dark for a time period longer than that of the experiment to test for possible complications due to dark chemical reactions. No complications were observed. The initial reactant concentrations (in units of molecule cm^{-3}) were in the ranges $(1.7\text{--}3.9) \times 10^{14}$ for MF, $(1.5\text{--}5.2) \times 10^{14}$ for DMF, and $(0.12\text{--}2.5) \times 10^{15}$ for DMA while initial concentrations of CH_3ONO and Cl_2 were in the range of $(1.5\text{--}3) \times 10^{14}$.

At Orléans loss of DMF by photolysis and wall loss was measured to be less than 10% per hour (using 1 lamp). DMF and reference compound concentrations were monitored for a period of 2–3 h leading to a consumption of 50–80% of the initial reactant concentrations.

The reaction rate coefficients for both the OH and Cl reactions were determined using the relative rate technique in which the relative disappearance rate of the amides and that of different reference compounds whose rate coefficients with OH and Cl are well established, were monitored in the presence of OH radicals/Cl atoms:



The reaction rate coefficients can be derived from the following equation:

$$\begin{aligned} \ln([\text{amide}]_0/[\text{amide}]_t) - k_w t \\ = k_{\text{amide}}/k_{\text{ref}} \ln([\text{reference}]_0/[\text{reference}]_t) \end{aligned}$$

where $[\text{amide}]_0$ and $[\text{reference}]_0$ represent the concentrations of MF, DMF and DMA and the reference compounds, respectively, at reaction time t_0 ; $[\text{amide}]_t$ and $[\text{reference}]_t$ the corresponding concentrations at time t ; and k_{amide} and k_{ref} are the rate coefficients of the reaction of OH/Cl with the investigated compound and the reference, respectively. k_w represents the loss rate of the amides (wall loss), which was measured in the dark prior to exposing the mixture to

irradiation. The loss rates of the reference compounds were found to be negligible.

2.1. Materials

The purity of the chemicals used as stated by the manufacturer were: from Aldrich, MF (99+%) and propene (99+%); from Sigma–Aldrich DMF (99.9+%), DMA (99.9+%) and cyclohexane (99.9+%); from Messer Griesheim, ethene (99.95 vol.%); 1,3-dioxolane (99.99%) was from Lambiotte Company; acetaldehyde (>99.5%) and acrolein (95%) from Fluka.

3. Results

3.1. Rate coefficients for the reaction of OH radicals with MF, DMF and DMA

At Wuppertal, the rate coefficient measurements for the reaction of OH with MF, DMF and DMA were investigated relative to three reference compounds (with k_{OH} in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units): cyclohexane ($k_{OH} = 7.21 \times 10^{-12}$ [11]), propene ($k_{OH} = 3.01 \times 10^{-11}$ [12]) and ethene ($k_{OH} = 9 \times 10^{-12}$ [12]). At Orléans the rate coefficient for the reaction of OH with DMF was measured relative to three different compounds (with k_{OH} in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units): 1,3-dioxolane ($k_{OH} = 1.11 \times 10^{-11}$ [13]), acetaldehyde ($k_{OH} = 1.53 \times 10^{-11}$ [14]) and acrolein ($k_{OH} = 1.99 \times 10^{-11}$ [15]).

Representative plots of the kinetic data for the reaction of OH with *N*-methylformamide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide are displayed in Figs. 1–3, respectively. The experimental conditions, number of runs, the measured rate coefficient ratios and the values of the rate coefficients for the reaction of the amides with OH, obtained with the different reference compounds and put on absolute basis using the literature values for the reference reactions, are summarized in Table 1. Generally good linear plots were obtained for all the amides with all of the different reference compounds. The values of the rate coefficients, obtained for each amide with each individual reference, are largely in agreement within the combined 2σ standard errors given in Table 1. Since consistent results were obtained using three reference compounds in the cases of MF and DMA and six in the case of DMF averaged values can be given for the reaction rate coefficients. The following averaged values with error limits that encompass the extremes of the 2σ error of the individual determinations have been obtained:

$$k_{MF+OH} = (0.86 \pm 0.24) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{DMF+OH} = (1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{DMA+OH} = (1.9 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

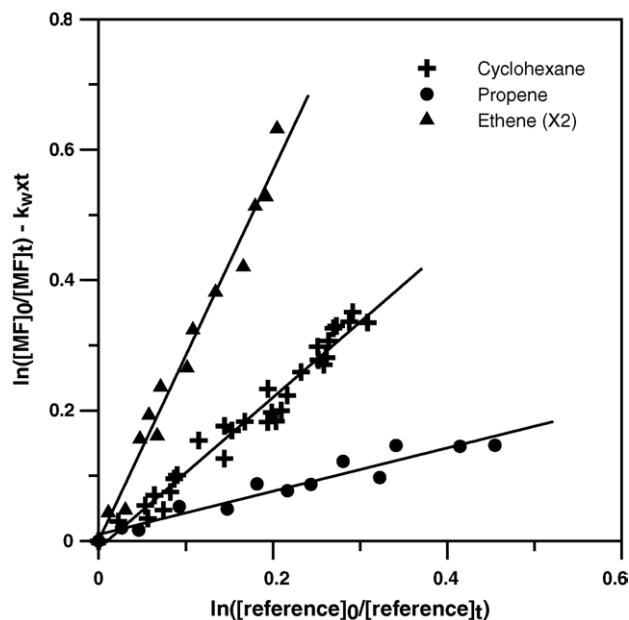


Fig. 1. Relative losses of MF obtained vs. that of cyclohexane, ethene and propene in the presence of OH radicals.

In addition to the above investigations, an experiment was conducted to measure the decay of DMF against DMA in the presence of OH radicals. This experiment resulted in the rate coefficient ratio $k_{DMF+OH}/k_{DMA+OH} = 0.79 \pm 0.07$ which is in very good agreement with the value of 0.74 obtained using the measured rate coefficients for these two compounds with other reference compounds as described above. Due to the much higher wall loss of MF compared to that of DMF or DMA it was not possible to measure accurately the loss of MF versus that of DMF or DMA in the presence of OH radicals.

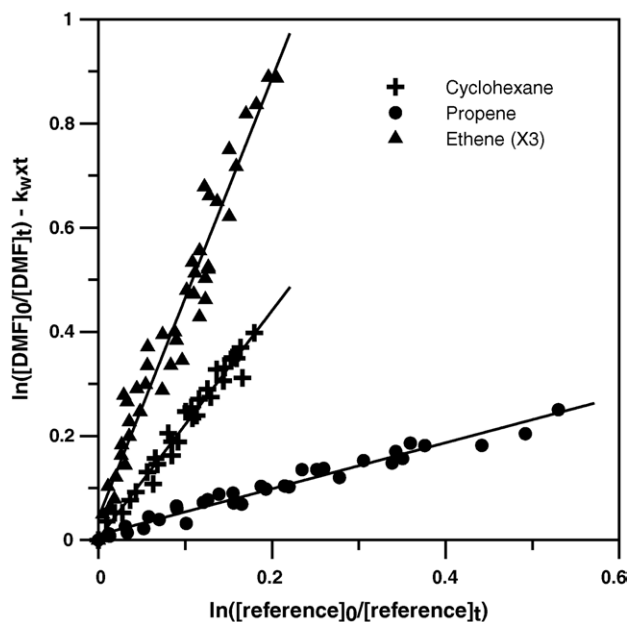


Fig. 2. Relative losses of DMF obtained vs. that of cyclohexane, ethene and propene in the presence of OH radicals.

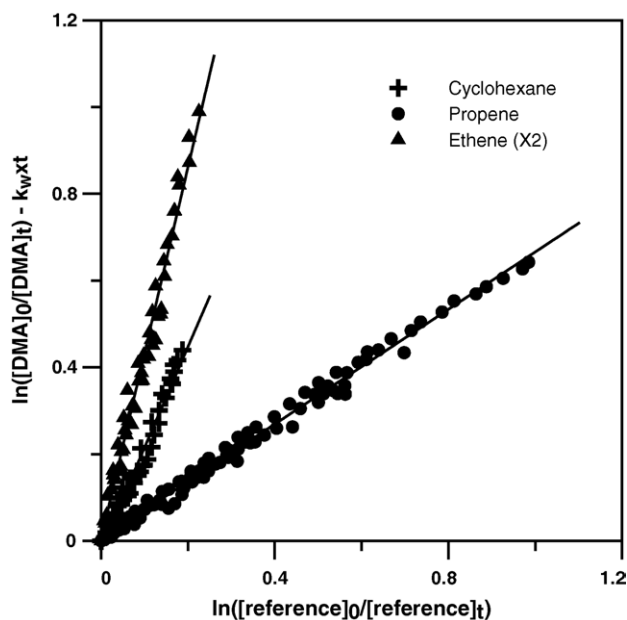


Fig. 3. Relative losses of DMA obtained vs. that of cyclohexane, propene and ethene in the presence of OH radicals.

3.2. Rate coefficients for the reaction of Cl atoms with MF, DMF and DMA

The rate coefficients for reaction of Cl atoms with MF, DMF and DMA were determined at Wuppertal using three reference compounds (with k_{Cl} in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units): cyclohexane ($k_{\text{Cl}} = 3.07 \times 10^{-10}$ [16]), propene ($k_{\text{Cl}} = 2.63 \times 10^{-10}$ [12]) and ethene ($k_{\text{Cl}} = 1.1 \times 10^{-10}$ [17]). Representative plots of the kinetic data for the reaction of Cl atoms with *N*-methylformamide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide are displayed in Figs. 4–6, respectively. Table 2 summarizes the experimental conditions, the number of runs, the measured rate coefficient ratios and the values of the rate coefficients for the reactions of the

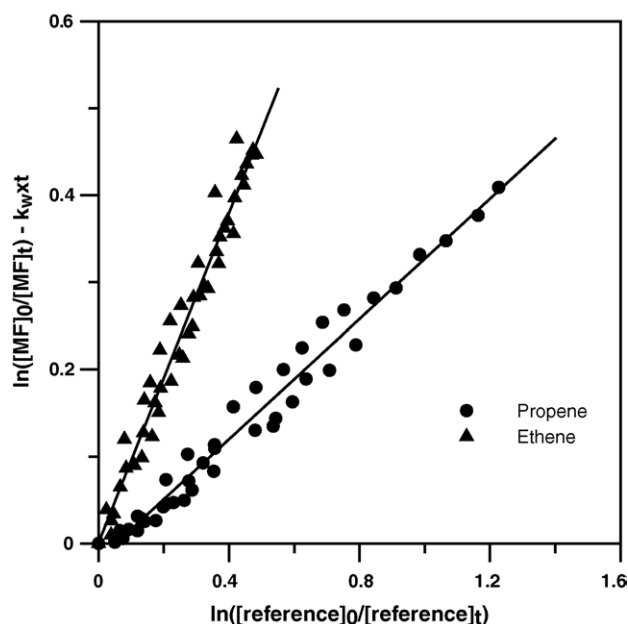


Fig. 4. Relative losses of MF obtained vs. that of propene and ethene in the presence of Cl atoms.

amides with Cl obtained with the different reference compounds and put on absolute basis using the literature rates for the reference reactions.

Good linear plots were obtained for the reaction of Cl atoms with all the amides and different reference compounds and reasonable agreement was found between the values of the rate coefficients obtained using the different reference compounds. Since consistent results were obtained using two reference compounds in the case of MF and three in the cases of DMF and DMA we prefer to give averaged values for the reaction rate coefficients of Cl with the amides. The following averaged values with error limits that encompass the extremes of the 2σ error of the individual determinations have been

Table 1

Summary of the rate coefficient determinations for reaction of OH radicals with *N*-methylformamide (MF), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA)

Amide	[Amide] ^a	Reference	[Reference] ^a	No. of runs	$k_{\text{amide}}/k_{\text{ref}}$	$k(\text{amide})^b (\times 10^{-11})$
MF	$(2.3\text{--}4.2) \times 10^{14}$	Cyclohexane	$(0.15\text{--}0.6) \times 10^{14}$	3	1.10 ± 0.25	0.79 ± 0.18
	2.1×10^{14}	Propene	3.6×10^{14}	1	0.29 ± 0.07	0.88 ± 0.19
	$(1.7\text{--}2.3) \times 10^{14}$	Ethene	$(3.6\text{--}4.1) \times 10^{14}$	3	1.01 ± 0.10	0.91 ± 0.09
DMF (Wuppertal)	$(1.5\text{--}4.5) \times 10^{14}$	Cyclohexane	$(0.4\text{--}0.52) \times 10^{14}$	3	2.07 ± 0.18	1.49 ± 0.13
	$(1.5\text{--}4.5) \times 10^{14}$	Propene	$(4\text{--}5.2) \times 10^{14}$	3	0.44 ± 0.03	1.32 ± 0.09
	$(1.5\text{--}5.2) \times 10^{14}$	Ethene	$(1\text{--}4) \times 10^{14}$	2	1.41 ± 0.05	1.27 ± 0.05
DMF (Orléans)	$(1.2\text{--}2.5) \times 10^{15}$	1,3-Dioxolane	$(0.9\text{--}1.2) \times 10^{15}$	2	1.31 ± 0.19	1.45 ± 0.42
	$(1.2\text{--}2.5) \times 10^{15}$	Acetaldehyde	$(0.9\text{--}1.6) \times 10^{15}$	2	0.93 ± 0.13	1.42 ± 0.40
	$(1.2\text{--}2.5) \times 10^{15}$	Acrolein	$(0.9\text{--}1.1) \times 10^{15}$	2	0.76 ± 0.15	1.51 ± 0.30
DMA	$(1.5\text{--}3) \times 10^{14}$	Cyclohexane	0.55×10^{14}	3	2.32 ± 0.12	1.67 ± 0.09
	$(1.2\text{--}3) \times 10^{14}$	Propene	$(2\text{--}5) \times 10^{14}$	3	0.66 ± 0.02	1.99 ± 0.06
	$(1.5\text{--}2) \times 10^{14}$	Ethene	$(4\text{--}5.2) \times 10^{14}$	3	2.14 ± 0.09	1.93 ± 0.08

The errors are the 2σ standard deviation.

^a In units of molecule cm^{-3} .

^b In units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Table 2

Summary of the rate coefficient determinations for reaction of Cl atoms with *N*-methylformamide (MF), *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA)

Amide	[Amide] ^a	Reference	[Reference] ^a	No. of runs	$k_{\text{amide}}/k_{\text{ref}}$	$k(\text{amide})^b (\times 10^{-10})$
MF	$(2.7\text{--}3.9) \times 10^{14}$	Propene	$(2\text{--}3) \times 10^{14}$	2	0.32 ± 0.02	0.86 ± 0.06
	$(2.1\text{--}3.4) \times 10^{14}$	Ethene	$(1.2\text{--}3) \times 10^{14}$	4	1.04 ± 0.06	1.08 ± 0.06
DMF	$(1.5\text{--}1.9) \times 10^{14}$	Cyclohexane	$(0.8\text{--}1) \times 10^{14}$	2	0.60 ± 0.06	1.84 ± 0.07
	$(1.5\text{--}3) \times 10^{14}$	Propene	$(2.6\text{--}4.1) \times 10^{14}$	2	0.65 ± 0.02	1.72 ± 0.06
	1.5×10^{14}	Ethene	4.1×10^{14}	1	1.95 ± 0.06	2.15 ± 0.06
DMA	$(1.5\text{--}2.5) \times 10^{14}$	Cyclohexane	$(0.6\text{--}1) \times 10^{14}$	3	0.83 ± 0.05	2.55 ± 0.16
	$(2\text{--}2.5) \times 10^{14}$	Propene	$(2\text{--}3.6) \times 10^{14}$	4	0.82 ± 0.06	2.16 ± 0.16
	$(2.2\text{--}2.5) \times 10^{14}$	Ethene	$(5\text{--}10) \times 10^{14}$	3	2.42 ± 0.14	2.66 ± 0.14

The errors are the 2σ standard deviation.

^a In units of molecule cm^{-3} .

^b In units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

obtained:

$$k_{\text{MF}+\text{Cl}} = (0.97 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{\text{DMF}+\text{Cl}} = (1.9 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_{\text{DMA}+\text{Cl}} = (2.5 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Similar to the OH radical investigations a series of experiments were conducted to measure the relative decay of the amides against each other in the presence of Cl atoms. The following ratios were obtained: $k_{\text{MF}+\text{Cl}}/k_{\text{DMA}+\text{Cl}} = 0.50 \pm 0.04$ and $k_{\text{DMF}+\text{Cl}}/k_{\text{DMA}+\text{Cl}} = 0.85 \pm 0.04$. The errors represent the 2σ standard deviation on the slope analyses. The ratios can be compared with the ratios of $k_{\text{MF}}/k_{\text{DMA}} = 0.39$ and $k_{\text{DMF}}/k_{\text{DMA}} = 0.76$ calculated from the rate coefficients obtained from the reference compounds. The agreement is satisfactory considering that significant

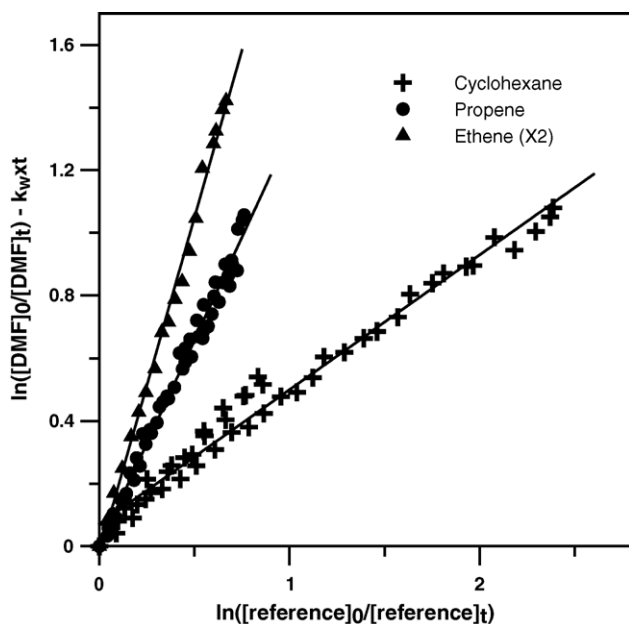


Fig. 5. Relative losses of DMF obtained vs. that of cyclohexane, ethene and propene in the presence of Cl atoms.

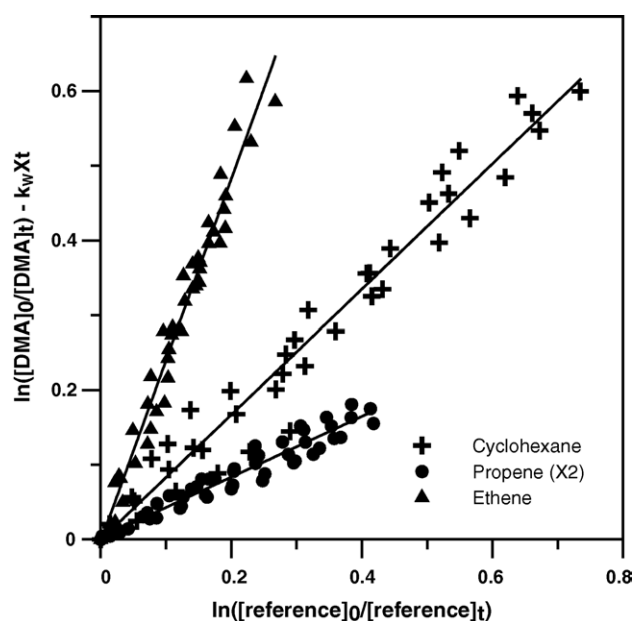


Fig. 6. Relative losses of DMA obtained vs. that of cyclohexane, ethene and propene in the presence of Cl atoms.

corrections for wall loss have to be applied for all the amides.

4. Discussion

To date the measurements reported here constitute the first determination of the rate coefficients for the reactions of OH radicals with MF and DMF and of Cl atoms with MF, DMF and DMA. The rate coefficient of $k = 1.9 \pm 0.3 \times 10^{-11}$ obtained in this study for the reaction of OH with DMA is in satisfactory agreement with the value of $1.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Koch et al. [8] at 300 K using the absolute FP-RF method. Both reactions of OH and Cl with the amides take the reactivity order $k_{\text{MF}} < k_{\text{DMF}} < k_{\text{DMA}}$, i.e. an increase in reactivity towards electrophilic attack with increasing methyl substitution due

to the positive inductive effect of these groups. The OH reactivity of the amides investigated here is considerably lower than that of the corresponding amines reported by Atkinson et al. [18] and Carl and Crowley [19].

For the reaction of OH/Cl with MF an overall H-atom abstraction reaction is possible from three sites: $-\text{CO}-\text{H}$, $-\text{NHCH}_2-\text{H}$ and $-\text{N}(\text{CH}_3)-\text{H}$. For DMF and DMA there are two possible non-equivalent sites, $\text{H}-\text{CO}-$ and $-\text{N}(\text{CH}_3)\text{CH}_2-\text{H}$ and $\text{H}-\text{CH}_2\text{CO}-$ and $-\text{N}(\text{CH}_3)\text{CH}_2-\text{H}$, respectively. Koch et al. [8] observed a negative activation energy ($E/R = -400$ to -600 K) for the gas phase reactions of OH with the amides which they investigated: *N*-methylacetamide (MA, $\text{CH}_3\text{CONHCH}_3$), *N*-methylpropamide (MPA, $\text{C}_2\text{H}_5\text{CONHCH}_3$), *N,N*-dimethylacetamide (DMA, $\text{CH}_3\text{CON}(\text{CH}_3)_2$) and *N,N*-dimethylpropamide (DMPA, $\text{C}_2\text{H}_5\text{CON}(\text{CH}_3)_2$). Although the observed negative activation energy does not totally exclude a direct abstraction mechanism it was taken as an indication of an addition reaction mechanism with the addition being mainly at the amide group with products resulting from a subsequent H-atom abstraction from an adjacent carbon. The studies did not give any indication as to which carbon the abstraction was occurring at.

As indicated above for the amides investigated here H-atom abstraction from the $\text{H}-\text{CO}-$ and $\text{H}-\text{CH}_2\text{CO}-$ moieties is a possibility. The $\text{H}-\text{CO}-$ and $\text{CH}_3-\text{CO}-$ entities in formates and acetates ($\text{R}-\text{CO}-\text{OR}$, $\text{R} = \text{H}$ or CH_3) are not very reactive [20] and by analogy a similar low reactivity might be expected for the HCO group in the formamides and acetamides. However, Hayon et al. [21] have used pulse radiolysis and kinetic absorption spectrophotometry to investigate the sites of attack of OH radicals on amides in aqueous solution. For formamide (HCONH_2) and acetamide (CH_3CONH_2) they observed attack at the $\text{HCO}-$, $\text{CH}_3\text{CO}-$ and $-\text{NH}_2$ groups. For the other *N*-methylated amides investigated in their study (MF, DMF, NMA, DMA) attack with OH was found to occur mainly at the *N*-methyl groups which supports the suggestions of Koch et al. [8]. At present, it is not possible to exclude or confirm a gas phase H-atom abstraction reaction from the $\text{HCO}-$ or $\text{CH}_3\text{CO}-$ groups. However, it is worth mentioning that the mechanistic study of the OH-initiated oxidation of 1-methyl-2-pyrrolidone ($\text{C}_5\text{H}_9\text{NO}$) conducted by Aschmann and Atkinson has shown that H-atom abstraction from the amine side of the molecule ($\text{>N}-$) leads almost exclusively to formation of *N*-methyl succinimide ($\text{C}_5\text{H}_7\text{NO}_2$) and 1-formyl-2-pyrrolidinone ($\text{C}_5\text{H}_7\text{NO}_2$) [7]. Addition of OH to the amide group with a sterically favourable van der Waals' interaction might facilitate H-atom abstraction from these groups.

As stated previously there are no other studies on the kinetics of the reaction of Cl with amides. To our knowledge, there are also no kinetic studies on the reactions of Cl with amines from which inferences on reactivity patterns can be drawn. Preliminary results from our laboratories on the Cl-initiated oxidation of the three studied amides in the absence of NO_x have shown that the main observed products are $\text{HC}(\text{O})\text{N}(\text{CH}_3)\text{CHO}$ for DMF, and $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)\text{CHO}$

for DMA. These data indicate that the mechanism of the Cl reaction with amides goes mainly through H-atom transfer from the $-\text{N}(\text{CH}_3)_2$ site. Rudic et al. [22] have studied the product branching and dynamics of the reaction of Cl atoms with methylamine (CH_3NH_2) and found a yield branching ratio for $\text{C}-\text{H}:\text{N}-\text{H}$ abstraction of 0.48:0.52, i.e. nearly equal H-atom abstraction from both the methyl and amine entities.

The evidence presented above suggests that, in the gas phase reactions of OH and Cl with amides, an overall mechanism involving addition followed by subsequent H-atom abstraction is most likely operational. Abstraction can occur from all the sites containing an H-atom but the major channel appears to be abstraction from methyl groups on the amine group. Detailed product studies on the reaction of OH radicals and Cl atoms with all of the amides are necessary in order to elucidate the relative importance of the various reaction channels and validate the mechanistic deductions discussed above.

Other possible loss processes for the amides in the gas phase are reaction with O_3 , NO_3 radicals or photolysis. Some tests performed with MF, DMF and DMA showed negligible reactivity of these compounds towards ozone (i.e. their loss in the presence of O_3 was not distinguishable from wall loss). An upper limit of $<1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate constant of the reaction of O_3 with 1-methyl-2-pyrrolidone has been reported by Aschmann and Atkinson [7] indicating that reaction of amides with ozone is a minor loss process for these compounds in the atmosphere. Measurement of the ultraviolet spectra of DMF and DMA showed no absorption in the actinic region, thus photolysis loss of these compounds will be a negligible atmospheric loss process [23]. Using the laser photolysis-absorption technique, El Dib et al. [24] have recently reported rate constants of 4.4×10^{-14} and $1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reactions of NO_3 with DMF and DMA, respectively.

The contributions of OH, NO_3 , and Cl to the atmospheric oxidation of amides can be assessed by estimating the lifetimes of the amides with respect to reaction with each oxidant. The tropospheric lifetime have been estimated according to the relationship $\tau = 1/k[\text{X}]$ where $[\text{X}]$ represents the average concentration of the oxidant and k the rate coefficient for the reaction of the amide with the oxidant. The rate coefficients obtained in this work and those of El Dib et al. [24] for the NO_3 reactions have been used in combination with a 12-h daytime average global tropospheric OH radical concentration of 10^6 cm^{-3} [25], a peak value for Cl atom of $1 \times 10^5 \text{ cm}^{-3}$ early morning coastal region [26] and a 12 h average nighttime NO_3 radical concentration of $5 \times 10^8 \text{ molecule cm}^{-3}$ [27] for the calculations. The derived lifetimes are less than 1 day for all processes; therefore, fugitive emissions of amides will only be expected to have an atmospheric impact on local and regional scales where degradation with OH and NO_3 will dominate. Reaction with Cl atoms will only be of significance in coastal areas with elevated Cl concentrations or in areas with industrial emissions of chlorine.

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