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Kinetics and mechanisms for the reaction of hydroxyl radicals with trifluoroacetic acid under atmospheric conditions

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Abstract

The rate constant for the gas-phase reaction of the hydroxyl radical with trifluoroacetic acid has been determined over the temperature range 283-323 K using a relative rate technique. The results provide a value of $k(OH+CF_3C(O)OH) = 2.0 \times 10^{-13} \exp(-146 \pm 500/T)$ cm³ molecule⁻¹ s⁻¹ based on $k(OH+C_2H_6) = 7.8 \times 10^{-12} \exp(-1020 \pm 100/T)$ cm³ molecule⁻¹ s⁻¹ based on $k(OH+C_2H_6) = 7.8 \times 10^{-12} \exp(-1020 \pm 100/T)$ cm³ molecule⁻¹ s⁻¹ based on $k(OH+C_2H_6) = 7.8 \times 10^{-12} \exp(-1020 \pm 100/T)$ cm³ molecule⁻¹ s⁻¹ for the rate constant of the reference reaction. The OH-radical initiated oxidation of CF₃C(O)OH was investigated at 298 K in oxygen at 1 atm total pressure using Fourier-transform infrared spectroscopy. The major carbon-containing products were $C(O)F_2$, CF₃O₃CF₃ and CO₂, suggesting that the dominant reaction channel for loss of the CF₃C(O)O radical, formed by hydrogen atom abstraction, is carbon-carbon bond cleavage. The results indicate that the gas-phase reaction of OH radicals with trifluoroacetic acid may provide a sink for this compound in the troposphere that cannot be neglected.

1. Introduction

It is now well established that chlorofluorocarbons are responsible for catalytic ozone loss in the stratosphere [1–4]. This information has led to the development of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) as possible replacement compounds [3–5]. The HFCs and HCFCs have similar physical and chemical properties to the CFCs; however, since they contain at least one hydrogen atom, they are susceptible to attack in the troposphere, primarily by the hydroxyl radical [5]. The subsequent atmospheric degradation of certain HFCs and HCFCs, for example CF₃CH₂F (HFC-134a), CF₃CHCl₂ (HCFC-123) and CF₃CHClF (HCFC-124), can lead to the formation of the acetyl halides CF₃C(O)F (from HFC-134a [6–9] and HCFC-124 [9,10]) and CF₃C(O)Cl (from HCFC-123 [10–12]). In the case of HFC-134a, the average tropospheric yield of CF₃C(O)F from the intermediate alkoxy species, CF₃CHFO, has been estimated from atmospheric modelling calculations to be in the range 30%–40% [6,13,14], whereas the alkoxy radicals formed from HCFC-123 and HCFC-124, CF₃CCl₂O and CF₃CClFO, yield 100% CF₃C(O)Cl and CF₃C(O)F respectively.

Homogeneous removal of the acetyl halides by reaction with OH has been shown to be of negligible importance, although photolysis of $CF_3C(O)Cl$ can take place in the upper troposphere [3]. The major removal process for both $CF_3C(O)F$ and $CF_3C(O)Cl$ is uptake in water droplets and subsequent hydrolysis, giving trifluoroacetic acid [3], which in aqueous solution is almost completely dissociated into $CF_3C(O)O^-$ and H^+ [15]. Rodriguez et al. [13] have suggested that upon evaporation of cloud water. all the trifluoroacetate ions will be released into the gas phase in the form of undissociated trifluoroacetic acid (TFA). The fraction of cloud water which evaporates rather than precipitating will depend on local conditions, but is expected to be high. Removal of gas-phase TFA occurs either through re-incorporation in rainwater, or by surface/ocean deposition. The concentrations of TFA in rainwater, resulting from emission of CF₃CH₂F (HFC 134a) have been calculated by Rodriguez et al. [13] from modelling studies, in which it was assumed that the rainout removal rate for gas-phase TFA is equal to that for nitric acid and that the surface/ocean deposition rate is controlled by aerodynamic factors. These calculations use a tropospheric washout lifetime for TFA of around 12 days and a surface uptake lifetime of the order of 20 days. Most available evidence suggests that TFA is stable with respect to both abiotic and biotic degradation and would therefore be expected to accumulate in the environment [15]. Recent studies have nevertheless shown that TFA can be degraded to methane in the presence of certain methanogenic sediments under anearobic conditions [16]. The significance of this sink on a global scale has however, not yet been assessed. Although photolysis of TFA is not possible at wavelengths penetrating the troposphere, gas-phase removal of TFA by reaction with OH has not previously been considered as an important sink for this species.

The purpose of the present work was to measure the rate constant for the reaction of OH with trifluoroacetic acid as a function of temperature and to determine the mechanism for the reaction under atmospheric conditions. It was intended that the results should provide information concerning the possible importance of this homogeneous sink for $CF_3C(O)OH$ in the atmosphere and hence allow an estimate of the eventual ground level concentrations of TFA.

2. Experimental

Relative rate and product studies were carried out in an FEP teflon cylindrical reaction vessel (volume $\approx 50 \ \ell$) surrounded by 20 Philips TU 15W germici-

dal lamps, which produce 254 nm radiation. The vessel and lamps were housed in a thermostatically controlled chamber which allowed reactions to be studied over the temperature range 283-323 K. A uniform reaction temperature was achieved by the use of fans positioned below the reaction vessel and the temperature was monitored by a chromel/alumel thermocouple placed within the chamber. All pressure measurements were made using MKS capacitance manometers. Measured amounts of the reagents were flushed from calibrated pyrex bulbs into the teflon reaction vessel by a stream of medical-grade oxygen (Air Products) which was then filled to its full capacity with O₂ at 760 Torr. Reaction mixtures were allowed to equilibrate for at least 30 min prior to photolysis. Quantitative analyses were carried out using FTIR spectroscopy (Mattson, Galaxy 5000) and gas chromatography (Shimadzu 14A, with FID detector). Infrared spectra were obtained using an evacuable 2 & teflon-coated Wilks cell, containing a multipass White mirror arrangement, mounted in the cavity of the spectrometer. After various periods of photolysis, the reaction mixtures were expanded into the cell through 3 mm inner diameter teflon tubing. Spectra were recorded using 3-10 m pathlengths and at 2 min intervals. The spectral range was 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and the spectra were derived from 64 scans. Reference spectra and calibration curves for each compound were obtained by expanding known pressures of authentic samples of the compounds into the cell. For the kinetic experiments, the loss of reactants was determined by monitoring the following bands for each species: CF₃C(O)OH, 3560-3600 cm⁻¹ and 1100-1140 cm⁻¹; C₂H₆, 2860-3040 cm⁻¹; C₃H₈, 2860-3026 cm^{-1} . The concentrations of C₂H₆ and C₃H₈ were also monitored by gas chromatography. Samples of the reaction mixtures were drawn through a Valco gas sampling valve for GC analysis. Ozone concentrations were determined by a Monitor Labs Model 8810 UV photometric ozone analyser.

Trifluoroacetic acid (Aldrich, >99%) and deuterated trifluoroacetic acid (Aldrich, 99.5 atom% D) were vacuum distilled prior to use. Ethane and propane were research-grade from Air Products (>99.5%) and were used as received. Ozone was produced by passing medical-grade oxygen through an ozone generator (Monitor Labs) directly into the of reaction could account for the relatively large decrease in reactivity shown by CF₃C(O)OH compared to CH₃C(O)OH. Assuming that the reactions involve hydrogen atom abstraction, the transition states involve a hydrogen atom positioned between the attacking electrophilic OH radical and the $CX_3C(O)O$ radical. Fluorine substitution of the CH_3 group will reduce the electron density on the H atom and thus destabilize the transition state compared to that formed with $CH_3C(O)OH$. A similar reduction in reactivity has previously been observed for the reaction of OH with CF₃CHO compared to reaction with CH₃CHO [25], although in this case the decrease in reactivity is far more pronounced. Presumably the presence of the oxygen atom between the carbon and the abstracted hydrogen atom attenuates the electron-withdrawing effect of the fluorine atoms.

The major products identified in the photolysis of $O_3/H_2O/CF_3C(O)OH$ mixtures in oxygen at 1 atm and 298 K were $C(O)F_2$, $CF_3O_3CF_3$ and CO_2 . The experimental data can be rationalized in terms of the following reactions:

 $OH + CF_3C(O)OH \rightarrow CF_3C(O)O + H_2O,$ (1)

$$CF_3C(0)O \rightarrow CF_3 + CO_2,$$
 (8)

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M, \tag{9}$$

 $2CF_3O_2 \rightarrow 2CF_3O + O_2, \tag{10}$

$$CF_3O + CF_3O_2 \rightarrow CF_3O_3CF_3, \tag{11}$$

$$CF_3O+CF_3C(O)OH\rightarrow CF_3OH+CF_3C(O)O,$$
 (12)

$$CF_3OH \rightarrow C(O)F_2 + HF.$$
 (13)

The mechanism for reaction of OH radicals with CF₃C(O)OH, process (1), may involve initial formation of an OH-CF₃C(O)OH adduct, followed by decomposition to give H₂O and CF₃C(O)O, or it may be a direct H-atom abstraction process. In a recent study, Wallington et al. [26] showed that the CF₃C(O)O radical undergoes C-C bond scission rapidly at 296±2 K to give CF₃ and CO₂. In order to provide information on the details of the reaction of OH with CF₃C(O)OH, the rate constant for reaction of OH with CF₃C(O)OD was also determined relative to that for reaction with ethane. The data are plotted in the form of Eq. (5) in Fig. 1 and give a value of k_1 (CF₃C(O)OD)/ k_2 (C₂H₆)=0.39±0.07. The calculated value of k_1 (OH+CF₃C(O)OD)= $(0.98 \pm 0.18) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K is approximately 1.2 times lower than that observed for CF₃C(O)OH, suggesting a relatively weak kinetic isotope effect. This isotope effect is considerably less than that observed for the reaction of OH radicals with C₂H₆ and C₂D₆ [27] where the ratio $k_{\rm H}/k_{\rm D}$ is around five at 298 K. This result provides some support for the suggestion that, in the transition state for the reaction of OH radicals with trifluoroacetic acid, there is some interaction between the OH radical and the carbonyl group. Similarly, the observation of a temperature dependence of the rate constant that is essentially zero indicates that the reaction does not involve a simple direct H-atom abstraction process.

4. Atmospheric implications

The atmospheric removal of $CF_3C(O)F$ and $CF_3C(O)Cl$, formed from the degradation of CF₃CH₂F, CF₃CHFCl and CF₃CHCl₂, is largely dominated by uptake in cloud droplets and subsequent hydrolysis to give trifluoroacetic acid [3]. Assuming that all the TFA in cloud droplets is re-evaporated into the gas phase, then the concentration of TFA in rainwater, for a given source strength, will be determined by the competition between removal by uptake in rainwater, surface/ocean deposition and gas-phase reaction with OH radicals. Rodriguez et al. [13] have estimated tropospheric lifetimes of around 12 and 10-30 days for rain-out and surface uptake, respectively. The results of the present study provide an average tropospheric lifetime for TFA with respect to reaction with OH radicals of around 100 days. Thus, the homogeneous gas-phase reaction with OH radicals could constitute up to 10% of the loss of TFA from the troposphere. In this estimate it is assumed that TFA, formed in cloud droplets by hydrolysis of $CF_3C(O)F$ and $CF_3C(O)Cl$, is transferred into the gas phase on evaporation of the droplets. This assumption requires experimental verification, since the trifluoroacetate ion may remain associated with solid inorganic components of the cloud droplets after the bulk of the water has evaporated. Moreover, the washout and surface loss processes need to be more precisely characterized and quantified in order to assess the importance of the gas-phase reaction of OH with TFA as a sink process.

Under tropospheric conditions, reaction of OH with TFA leads to the formation of $CF_3C(O)O$ radicals, which will decompose to yield CF_3 radicals. Previous work from our laboratories and elsewhere has shown that CF_3 radicals are efficiently converted to $C(O)F_2$ in the troposphere, and that $C(O)F_2$ is removed in cloud water to give CO_2 and HF [15]. Reaction of OH with TFA therefore leads to degradation of the acid into relatively benign species.

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reaction vessel. Triply distilled water was injected in liquid form into the reaction vessel.

3. Results and discussion

The rate constant for reaction of OH radicals with $CF_3C(O)OH$ was determined relative to that for the reaction with $C_2H_{6_2}$

 $OH+CF_3C(O)OH \rightarrow products$, (1)

$$OH+C_2H_6 \rightarrow products$$
. (2)

Hydroxyl radicals were generated from the photolysis of ozone in the presence of water vapour,

$$O_3 + h\nu(\lambda = 254 \text{ nm}) \rightarrow O(^1D) + O_2$$
, (3)

$$O(^{1}D) + H_{2}O \rightarrow 2OH.$$
⁽⁴⁾

Providing that the reactant and reference compound are consumed only by reaction with OH radicals, it can be shown that

$$\ln\{[CF_{3}C(O)OH]_{0}/[CF_{3}C(O)OH]_{t}\}$$

= k₁/k₂ ln([C₂H₆]₀/[C₂H₆]_t), (5

where the subscripts 0 and t indicate concentrations before irradiation and at time t, respectively. Direct photolytic loss of $CF_3C(O)OH$ or C_2H_6 was unimportant and the reaction mixtures were stable in the dark for at least 5 h.

Mixtures of O₃/H₂O/CF₃C(O)OH/C₂H₆ in oxygen were photolysed for approximately 15 min at 298 ± 2 K with [CF₃C(O)OH]₀ and [C₂H₆]₀=50-200 ppm; $[O_3]_0 = 100 - 1000$ ppm; $[H_2O]_0 = 2000 - 1000$ 10000 ppm (1 ppm= 2.46×10^{13} molecules cm⁻³ at 298 K and 760 Torr total pressure). With the reaction conditions employed, the substrate and reference compound were found to decay by around 50% during the experiments. Data for the runs are plotted in the form of Eq. (5) in Fig. 1 and show the expected linear relationship. The rate constant ratio $k_1/$ $k_2 = 0.47 \pm 0.04$, (the error is 2σ and represents precision only), was independent of reaction time, relative reactant concentration and light intensity, in agreement with the proposed mechanism. The loss of $CF_3C(O)OH$ was determined from measurements on two different infrared bands and the concentrations of C_2H_6 and C_3H_8 were measured using both infrared



Fig. 1. Concentration-time data for the reaction of OH radicals with $CF_3C(O)OH/C_2H_6$, $CF_3C(O)OH/C_3H_8$ and $CF_3C(O)OD/C_2H_6$ mixtures at 298 K.

spectroscopy and gas chromatography. At the low concentrations of CF₃C(O)OH employed dimerization of the acid is expected to be negligible, as was confirmed by the absence of the dimer features in the IR spectra [17]. The rate constant ratios derived from each analytical method were indistinguishable within experimental error, indicating that complications arising from product interferences in the spectra or chromatograms were absent. A possible source of error in the experiments is the reaction of $O(^{1}D)$ with $CF_3C(O)OH$ and C_2H_6 . However, the rate constant for the reaction of O(¹D) with H₂O, $k_4 = 2.2 \times 10^{-10}$ cm^3 molecule⁻¹ s⁻¹ [18] is sufficiently large that under the experimental conditions employed, with $[H_2O]_0 \ge 100 [CF_3C(O)OH]_0 \text{ or } [C_2H_6]_0, O(^1D)$ is effectively scavenged in reaction (4). Variations in the water vapour pressure from 2-10 Torr had no measurable effect on the value of k_1/k_2 , thus providing support for this assumption. As discussed later in this work, the reaction of OH radicals with $CF_3C(O)OH$, reaction (1), can lead to formation of CF₃O radicals. CF₃O radicals may also contribute to the loss of $CF_3C(O)OH$ and C_2H_6 ,

 $CF_3O + CF_3C(O)OH \rightarrow products$, (6)

$$CF_3O + C_2H_6 \rightarrow \text{products}$$
. (7)

Recent relative rate studies in our laboratory provide a value for $k_5/k_6=0.7\pm0.2$ [19] indicating that the relative reactivities of CF₃O and OH radicals towards CF₃C(O)OH and C₂H₆ are quite similar. Hence, possible errors in the OH-radical relative rate measurements arising from the additional removal of CF₃C(O)OH and C₂H₆ by CF₃O radicals will be relatively small. For most experiments, the ratio $[CF_3C(O)OH]_0/[C_2H_6]_0$ was kept less than five, in order to reduce any possible effects of CF₃O radical reactions, although rate data obtained from runs carried out with $[CF_3C(O)OH]_0/[C_2H_6]$ close to unity gave values of k_1/k_2 within experimental error of those determined in excess C₂H₆.

In order to test the consistency of the experimental technique, the rate constants for the reaction of OH with $CF_3C(O)OH$ relative to that for reaction with propane was also determined. The data from these experiments are also shown in Fig. 1 and give a value of $k(OH+CF_3C(O)OH)/k(OH+C_3H_8) =$ 0.11 \pm 0.02. Combination of the values of k_1/k_2 obtained in this work at 298 K with the evaluated rate data for the OH radical reactions with ethane, $k(OH+C_2H_6) = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18], and propane, $k(OH+C_3H_8)=1.14\times10^{-12}$ cm^3 molecule⁻¹ s⁻¹ [18], provides values of $k_1(OH+CF_3C(O)OH) = 1.18 \times 10^{-13}$ and 1.25×10^{-13} 10⁻¹³ cm³ molecule⁻¹ s⁻¹ from relative rate experiments using C_2H_6 and C_3H_8 respectively. Agreement between both these estimates is excellent and gives an average value of $k_1 = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹ at 298 K with an estimated overall uncertainty of $\pm 25\%$. This value is within the experimental error limit of that recently obtained by Nielsen and Wallington [20] using both absolute and relative rate techniques, $k_1 = (1.6 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹.

The ratio of rate constants for the reaction of OH radicals with CF₃C(O)OH and C₂H₆ was determined at five different temperatures over the range 283 to 323 K. The values of k_1/k_2 shows little variation with temperature and are plotted in Arrhenius form in Fig. 2. A linear least-squares fit of the data $k_1(OH+CF_3C(O)OH)/k_2(OH+C_2H_6) =$ gives $0.025 \exp(874 \pm 400/T)$. Taking a vale of $k_2(OH + C_2H_6) = 7.8 \times 10^{-12} \exp(-1020 \pm 100/T)$ cm³ molecule⁻¹ s⁻¹ [18] provides an estimate of $k_1(OH+CF_3C(O)OH) = 2.0 \times 10^{-13} \times$ $\exp(-146 \pm 500/T)$ cm³ molecule⁻¹ s⁻¹. Thus, the lifetime of CF₃C(O)OH at an average tropospheric temperature of 277 K with a 24 h average global tropospheric [OH] = 8.7×10^5 molecule cm⁻³ [21] is approximately 110 days.

The value of the rate constant determined in this



Fig. 2. Arrhenius plot for the ratio of rate constants, k_1/k_2 , obtained from the reaction of OH radicals with CF₃C(O)OH and C₂H₆.

work for the reaction of OH with trifluoroacetic acid is somewhat higher than might be expected by analogy with the reactions of OH with alkanes. The O-H bond strength in CF₃C(O)OH has not been reported. However, the analogous bond in acetic acid has a bond dissociation energy of about 106 kcal mol^{-1} [22] and it is unlikely that fluorine substitution at the CH₃ group will lead to a significant change in the O-H bond strength in CF₃C(O)OH. Thus, despite hydrogen atom abstraction from $CF_3C(O)OH$ being around 6 kcal mol⁻¹ less exothermic than abstraction from C_2H_6 , the rate constants at 298 K are quite similar. Wallington and Kurylo [23] have previously suggested that the enhanced reactivity of C-H bonds on the β -carbon atom of ketones compared to C-H bonds of similar strength in hydrocarbons may be due to stabilization of the transition states resulting from the interaction of the attacking OH radical with the carbonyl group. A similar effect may explain the enhanced reactivity shown by carboxylic acids with respect to reaction with OH radicals. The rate constant for reaction of OH radicals with $CF_3C(O)OH$ is about six times smaller than for the analogous reaction with CH₃C(O)OH [24]. Deactivation of the acidic hydrogen with respect to reaction with the OH radical, following fluorine substitution at the CH₃ group, is proposed to be largely due to destabilizing polar effects in the transition state. Both reactions are strongly exothermic, since D(H-OH) = 119 kcal mol⁻¹ [22], and it is expected that fluorine substitution will cause only a small change in the O-H bond strength in the acid. It seems unlikely therefore that changes in the overall enthalpy