Kinetics of the Reactions of Acetonitrile with Chlorine and Fluorine Atoms

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The rate coefficients for the reactions of chlorine and fluorine atoms with acetonitrile have been measured using relative and direct methods. In the case of chlorine atoms the rate coefficient k_1 was measured between 274 and 345 K using competitive chlorination and at 296 K using laser flash photolysis with atomic resonance fluorescence. The rate coefficient measured at ambient temperature (296 \pm 2 K) is (1.15 \pm 0.20) \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹, independent of pressure between 5 and 700 Torr (uncertainties are 2 standard deviations throughout). This result is a factor of 6 higher than the currently accepted value. The results from the three independent determinations reported here yield the Arrhenius expression $k_1 = (1.6 \pm 0.2) \times 10^{-11} \exp[(2140 \pm 200)/T$] cm³ molecule⁻¹ s⁻¹. Product studies show that the reaction of Cl atoms with CH₃CN proceeds predominantly, if not exclusively, by hydrogen abstraction at 296 K. The rate coefficient for the reaction of fluorine atoms with acetonitrile was measured using both the relative rate technique and pulse radiolysis with time-resolved ultraviolet absorption spectroscopy. The rate coefficient for the reaction of F atoms with CH₃-CN was found to be dependent on total pressure. The observed rate data could be fitted using the Troe expression with $F_c = 0.6$, $k_0 = (2.9 \pm 2.1) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹, and $k_{\infty} = (5.8 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, with a zero pressure intercept of $(0.9 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The kinetic data suggest that the reaction of F atoms with CH₃CN proceeds via two channels: a pressure-independent H atom abstraction mechanism and a pressure-dependent addition mechanism. Consistent with this hypothesis, two products were observed using pulsed radiolysis with detection by UV absorption spectroscopy. As part of the product studies, relative rate techniques were used to measure $k(Cl+CH_2ClCN) = (2.8 \pm 0.4) \times 10^{-14}$ and $k(F+CH_2FCN) = (3.6 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Introduction

Acetonitrile, CH₃CN, is emitted into the troposphere from a number of combustion processes, including biomass burning, internal combustion engines, and cigarette smoke.¹ It is also used widely as a solvent. Tropospheric concentrations of the order of 100 ppt have been reported, associated with a total source strength of 1.1 ± 0.5 Tg/yr.¹ Acetonitrile has a lifetime in the troposphere of approximately 0.5 yr,¹ leading to mixing ratios of 40 ppt in the lower stratosphere and falling to around 0.3 ppt at 45 km altitude.^{2–6} In the stratosphere, its large dipole moment and large proton affinity allow it to replace water in hydrated complexes of ions and to produce the so-called non-proton hydrates. Vertical profiles of acetonitrile and the associated ionic chemistry have been modeled by Brasseur and co-workers.^{7,8}

The reaction between chlorine atoms and acetonitrile (1) has been studied several times before.⁹⁻¹¹

$$Cl + CH_3CN \rightarrow HCl + CH_2CN \tag{1}$$

Olbregts et al.9 performed a competitive chlorination experiment

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at 370 and 413 K, using chloroform as the reference gas. Poulet et al.¹¹ measured absolute values of k_1 between 295 and 723 K using a discharge flow tube, with chlorine atoms in excess, and mass spectroscopic detection of acetonitrile. The results of Poulet et al. showed a curved Arrhenius plot, with effective activation energies of 6 kcal mol⁻¹ at 723 K and 3 kcal mol⁻¹ at 295 K. The value determined at room temperature was 9 \times 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹. Kurylo and Knable¹⁰ used flash photolysis with resonance fluorescence detection of chlorine atoms to derive an upper limit of 2×10^{-15} cm³ molecule⁻¹ s^{-1} at 298 K. Clearly, there is a large discrepancy in the measurements. The high temperature values of Olbregts et al. and Poulet et al. extrapolate back to values at room temperature similar to the upper limit of Kurylo, and this has been the accepted value since 1984.^{12,13} However, if the results of Poulet and co-workers¹¹ at 295 K are extrapolated down to stratospheric temperatures, a significant value of k_1 is expected.

The reaction of OH with acetonitrile appears to proceed by a complex mechanism, with both addition and abstraction channels taking place.¹⁴ If one assumes that the value of that rate coefficient at low pressure and in the absence of oxygen $(2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ corresponds to an abstraction

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reaction, the upper limit for the chlorine reaction seems anomalously low, since exothermic abstractions by chlorine atoms are typically a factor of 3-10 faster than the corresponding reactions of OH.^{12,13} Thus, we have reinvestigated the reaction of chlorine atoms with acetonitrile using the complementary approaches of flash photolysis with resonance fluorescence and the relative rate technique. The relative rate experiments were carried out in two separate chambers, with very good consistency, and one of the systems was used to measure the temperature dependence of k_1 . The results of the high-temperature relative rate study of Olbregts et al.⁹ have been reevaluated using new data on the reference reaction (Cl + CHCl₃) and are shown to be in excellent agreement with an extrapolation of the current data to higher temperature.

To complement our study of reaction 1 the rate coefficient k_2 for the reaction of F atoms with acetonitrile was measured both by use of the relative rate technique and by pulse radiolysis with detection of transient intermediates using ultraviolet optical absorption spectroscopy.

$$F + CH_3CN \rightarrow products$$
 (2)

Reaction 2 has been the subject of two previous studies, both of which were carried out at less than 2 Torr total pressure.^{15,16} We find k_2 to be pressure-dependent, with the values obtained at low pressure in good agreement with the earlier studies. The effects of the rate coefficients on calculated CH₃CN concentrations in the stratosphere are examined.

Experimental Section

Experiments were carried out in four different systems: (a) an environmental chamber at ambient temperature with FTIR detection at Ford Motor Company, (b) a temperature-controlled chamber with FTIR detection at NCAR, (c) a flash photolysis—resonance fluorescence experiment at ambient temperature at NCAR, and (d) a room temperature pulse radiolysis—UV absorption system at Risø National Laboratory. All have been described in detail elsewhere, and so only important details will be summarized here.

a. Ford FTIR-Smog Chamber System. The apparatus and experimental techniques employed at Ford have been described previously.¹⁷ The apparatus consists of a Mattson Instruments Inc. Sirius 100 FTIR spectrometer interfaced to a 140-L, 2-m-long evacuable Pyrex chamber (S/V = 0.14 cm^{-1}). The Pyrex chamber was surrounded by UV fluorescent lamps (GTE F40BLB) which were used to generate halogen atoms by the photolysis of molecular halogen.

$$\operatorname{Cl}_2(\operatorname{or} F_2) + h\nu \rightarrow 2\operatorname{Cl}(\operatorname{or} 2F)$$
 (3)

White-type multiple reflection optics were mounted in the reaction chamber to provide a total path length of 27 m for the IR analysis beam. The spectrometer was operated at a resolution of 0.25 cm^{-1} .

Reaction mixtures consisting of CH_3CN , a reference compound (CH_4 , CD_4 , or CF_3CCl_2H), and molecular halogen were admitted to the reaction chamber in N_2 , O_2 , or air diluent. In the presence of atomic chlorine, CH_3CN and the reference compound decay via reactions 1 and 4.

$$Cl + CH_3CN \rightarrow products$$
 (1)

$$Cl + reference \rightarrow products$$
 (4)

Provided that CH₃CN and the reference are lost solely by reactions 1 and 4 and that neither is re-formed in any process,

then

$$\ln\left(\frac{[CH_3CN]_{t_0}}{[CH_3CN]_t}\right) = \frac{k_1}{k_4} \ln\left(\frac{[reference]_{t_0}}{[reference]_t}\right)$$
(I)

where $[CH_3CN]_{t_0}$ and $[reference]_{t_0}$ are the concentrations of CH₃-CN and the reference compound at time t_0 and $[CH_3CN]_t$ and $[reference]_t$ are the corresponding concentrations at time t; k_1 and k_4 are the rate coefficients of reactions 1 and 4, respectively. An analogous equation holds for fluorine atoms.

The decay of CH₃CN and the reference were measured using their characteristic absorptions in the infrared over the following wavelength ranges (in cm⁻¹); CH₃CN, 1300–1600; CH₄, 1200– 1400; CD₄, 950–1050; CF₃CCl₂H, 1100–1200. Initial concentrations of the gas mixtures were 15–74 mTorr of CH₃CN, 0.2–0.5 Torr of Cl₂ or 0.3–0.5 Torr of F₂, and 11–90 mTorr of the reference compound (CH₄, CD₄, or CF₃CCl₂H), in 5–700 Torr total pressure of either N₂, O₂, or air diluent at 296 K. All reagents were purchased from commercial vendors at purities of >99% and used without further purification. Experiments were performed at room temperature, 296 ± 2 K.

b. NCAR Environmental Chamber. Relative rate measurements of k_1 were carried out as a function of temperature in a 48-L stainless steel chamber (S/V = 0.25 cm^{-1}).^{18,19} The chamber is surrounded by a jacket through which ethanol or water can be circulated to regulate the temperature. Photolysis was accomplished using light from a xenon arc lamp filtered by a glass filter (Corning 7-51). Measurements were made between 274 and 345 K. Infrared spectra were taken using a Bomem DA3.01 FTIR spectrometer, with a path length of 32.6 m. Spectra were taken by coadding 200 scans at a resolution of 1 cm⁻¹. Experiments were carried out using both N₂ and O2 as bulk gas. Acetonitrile was degassed before use and was added to the chamber by sweeping known pressures from a calibrated bulb using the appropriate carrier gas. Methane was taken from a cylinder of research grade gas without further purification.

c. NCAR Flash Photolysis–Resonance Fluorescence System. The rate coefficient for chlorine atoms with acetonitrile was measured using excimer laser flash photolysis of chlorine gas and resonance fluorescence detection of chlorine atoms.^{20,21} The reaction vessel consists of a 300-cm³ Pyrex cylinder with side arms for photolysis and resonance fluorescence detection. The reactive gases (Cl₂, CH₃CN) were flowed into the reaction vessel and photolyzed with an excimer laser at 308 nm (Questek Model 2440). A chlorine atom resonance lamp was directed at right angles to the laser beam, and resonance fluorescence was detected orthogonally to both beams using a solar-blind photomultiplier (Hamamatsu R1459). Acetonitrile was degassed by several freeze–pump–thaw cycles at liquid nitrogen temperature and made up into 4–5% mixtures in N₂ in a 5-L bulb.

d. Pulse Radiolysis–UV Absorption Experiment at Risø. The pulse radiolysis transient UV absorption spectrometer and the experimental procedure used are described in detail elsewhere.^{22,23} Fluorine atoms were generated by irradiation of SF₆/ CH₃CN gas mixtures in a 1-L stainless steel reaction cell with a 30-ns pulse of 2-MeV electrons from a Febetron 705B field emission accelerator. The radiolysis dose could be varied using steel attenuators. SF₆ was always in great excess:

$$SF_6 + e^- (2 \text{ MeV}) \rightarrow F + \text{ products}$$

Transient absorptions were followed by multipassing the output of a pulsed 150-W xenon arc lamp through the reaction cell using internal White cell optics. A total path length of 120

cm was used. A McPherson grating spectrometer, Hamamatsu R 955 photomultiplier, and Biomation 8100 wave form digitizer were used to isolate, detect, and record the light intensity at the desired wavelength. Ultraviolet absorption spectra could be recorded using a Princeton Applied Research OMA-II diode array equipped with an image intensifier (Type 1420-1024HQ) installed at the exit slit of the monochromator in place of the photomultiplier. Gas mixtures were prepared by adding one component at a time and measuring the corresponding partial pressure on a MKS Baratron-170 absolute membrane manometer with a resolution of 10^{-5} bar. Reagent concentrations used were as follows: SF₆, 1000 mbar; CH₃CN, 0–2 mbar. All experiments were performed at 296 K. SF₆ (99.9%) was obtained from Merck. All reagents were used as received.

Results

a. Relative Rate Studies of the Reactions of Cl and F Atoms with CH₃CN at 296 K. Initial experiments in which Cl_2 was photolyzed in the presence of acetonitrile showed formation of HCl, indicating that a reaction does indeed occur at room temperature. When N₂ was used as the bath gas, only a short chain decomposition was observed, consistent with the observations of Olbregts at higher temperature.⁹ This observation implies that the reaction of CH₂CN with Cl₂ (5) is very slow, as is also the case for other methyl radicals with electronegative substituent groups (e.g., CH₂F, CF₃, etc).²⁴

$$CH_2CN + Cl_2 \rightarrow CH_2CICN + Cl$$
 (5)

Other products were observed in nitrogen bath gas, corresponding to further substitution of hydrogen atoms by chlorine (see later). The products formed in air will be addressed in a separate publication.

The relative rate technique relies on the assumption that both CH₃CN and the reference compound are removed solely by reaction with halogen atoms. To verify this assumption, mixtures of the halogen (either chlorine or fluorine) with CH₃-CN and each of the references used were prepared and allowed to stand in the dark. In all cases, the reaction of the organic species with molecular halogen, in the absence of ultraviolet light, was of negligible importance (<2%) over the typical time periods used in this work. To test for possible photolysis, mixtures of CH₃CN and the reference compounds were prepared and irradiated for 2 min in the absence of added halogen. No photolysis (<2%) of any compound was observed.

The kinetics of reaction 1 were measured relative to reactions 6-8, and reaction 2 was measured relative to reactions 9 and 10.

 $Cl + CH_3CN \rightarrow products$ (1)

 $F + CH_3CN \rightarrow products$ (2)

$$Cl + CD_4 \rightarrow CD_3 + DCl$$
 (6)

$$Cl + CF_3CCl_2H \rightarrow CF_3CCl_2 + HCl$$
(7)

$$Cl + CH_4 \rightarrow CH_3 + HCl$$
 (8)

 $F + CD_4 \rightarrow CD_3 + DF \tag{9}$

$$F + CH_4 \rightarrow CH_3 + HF \tag{10}$$

The observed loss of CH_3CN versus CD_4 , CF_3CCl_2H , and CH_4 in the presence of Cl atoms, and that of CH_3CN versus CD_4 and CH_4 in the presence of F atoms, are shown in Figures 1–3.



Figure 1. Plot of the decay of CH₃CN versus those of CH₄, CF₃CCl₂H, and CD₄ in the presence of Cl atoms in the following diluents: 700 Torr of air (filled circles), 700 Torr of N₂ (open circles), 700 Torr of O₂ (open squares), 15 Torr of O₂ (open diamonds), and 5 Torr of N₂ (open inverse triangles) at 296 K.



Figure 2. Plot of the decay of CH_3CN versus those of CD_4 and CH_4 in the presence of F atoms at 700 Torr of air (filled circles) or N_2 (open circles) at 296 K.



Figure 3. Plots of the decay of CH_3CN versus CD_4 in the presence of F atoms at total pressures of 200 Torr (triangles), 30 Torr (circles), 10 Torr (inverse triangle), and 5 Torr (diamonds).

As shown in Figure 1, there was no discernible effect of total pressure over the range 5–700 Torr, or O₂ partial pressure over the range 15–700 Torr, on the kinetics of reaction of Cl atoms with CH₃CN. Linear least-squares analysis of the data in Figure 1 gives $k_1/k_6 = 1.85 \pm 0.10$, $k_1/k_7 = 0.85 \pm 0.05$, and $k_1/k_8 = 0.11 \pm 0.01$. The uncertainties quoted are 2 standard deviations. Using $k_6 = 6.1 \times 10^{-15}$, $^{25}k_7 = 1.2 \times 10^{-14}$, $^{25}and k_8 = 1.0 \times 10^{-13}$, 12,13 gives $k_1 = (1.13 \pm 0.06) \times 10^{-14}$, $(1.02 \pm 0.06) \times 10^{-14}$, and $(1.10 \pm 0.10) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, respectively. The results obtained using the different references

TABLE 1: Values of k_1 Measured in This Study

temperature (K)	method ^a	rate coefficient ^b $(10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$		
296	R-R	1.08 ± 0.12		
274	R-R	0.70 ± 0.15		
296	R-R	1.22 ± 0.15		
325	R-R	2.37 ± 0.30		
336	R-R	2.90 ± 0.45		
345	R-R	3.49 ± 0.30		
296	FP-RF	1.24 ± 0.20		

^{*a*} R-R, relative rate technique; FP-RF, flash photolysis with resonance fluorescence. ^{*b*} Uncertainties are 2 standard deviations plus a contribution to account for uncertainties in the reference reactions, etc.

TABLE 2: Measured Values of k_2/k_9 at 296 K

press. (Torr)	diluent	k_2/k_9^{a}	press. (Torr)	diluent	k_{2}/k_{9}^{a}
5	N_2	(0.48 ± 0.04)	100	air	(1.21 ± 0.10)
10	air	(0.62 ± 0.04)	200	N_2	(1.27 ± 0.07)
30	N_2	(0.94 ± 0.07)	700	air	(1.31 ± 0.06)

^a Uncertainties are 2 standard deviations.

show good internal consistency. Errors quoted thus far reflect statistical uncertainty. In addition, we estimate that there is an additional 10% systematic uncertainty associated with the values of the reference rate coefficients. We choose to quote a final value for k_1 that is an average of the determinations above with error limits that encompass the extremes of the determinations plus an additional uncertainty to account for uncertainties in the reference rate coefficients. Conventional error analysis techniques were used to propagate the uncertainties. Hence, $k_1 = (1.08 \pm 0.12) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This average value is given in the first line of Table 1.

Figure 2 shows the data obtained for reaction 2 at 700 Torr total pressure using both CH₄ and CD₄ as reference compounds. Linear least-squares analysis of the data in Figure 2 gives k_2/k_9 = 1.31 ± 0.06 and $k_2/k_{10} = 0.83 \pm 0.04$. The uncertainties quoted are 2 standard deviations. Using $k_9 = 4.7 \times 10^{-11} 26$ and $k_{10} = 6.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \frac{26}{26} \text{ gives } k_2 = (6.1 \pm 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ s}$ 0.3 × 10⁻¹¹ and (5.6 ± 0.3) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, respectively, at 700 Torr total pressure. The consistency between results obtained using the different references is gratifying. A series of experiments performed over the total pressure range 5-700 Torr of either N₂ or air diluent using CD₄ as reference revealed a substantial effect of total pressure on k_2 . Representative data are shown in Figure 3, and linear least squares analysis of the data in Figure 3 and analogous plots yielded the rate coefficient ratios given in Table 2. Calibration experiments were performed to ensure that the IR features of CD₄ and CH₃CN were linear under the experimental conditions employed. The data in Table 2 can be placed on an absolute basis using $k_9 = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.26}$

There are two previous measurements of k_2 , both at low total pressure. Smith et al.¹⁵ measured a value of $(1.3 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in Ar diluent at a total pressure of around 1 Torr, using HF chemiluminescence. Hoyermann and Seeba¹⁶ employed the discharge flow technique using He diluent at a pressure of 1.2 Torr and found $k_2 = (1.25 \pm 0.13) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. For the sake of comparison with the data measured here in N₂ diluent, we have assumed that the third body efficiency of He and Ar is 50% of that of N₂. Figure 4 shows a plot of the values for k_2 derived in this work as a function of total pressure together with the corrected values of Smith et al. and Hoyermann and Seeba. The solid line in Figure



Figure 4. Kinetic data for the reaction $F + CH_3CN$ from the present work (filled circles) and Smith et al.¹⁵ (open triangle) and Hoyermann and Seeba¹⁶ (open square) versus total pressure. The solid curve is a fit of the Troe expression to the data (see text for details).

4 is a three parameter fit of expression II to all the data.

$$k = k_{\text{abst}} + \frac{k_0 k_\infty [\mathbf{M}]}{k_0 [\mathbf{M}] + k_\infty} 0.6^{\{1 + [\log(k_0 [\mathbf{M}]/k_\infty)]^2\}^{-1}}$$
(II)

Expression II is the standard Troe expression which has been modified to include the possibility of a nonzero rate coefficient at zero total pressure (k_{abst}). Values of k_0 , k_{∞} , and k_{abst} were varied simultaneously to provide the best fit values of $k_0 = (2.9 \pm 2.1) \times 10^{-28}$ cm⁶ molecule⁻² s⁻¹, $k_{\infty} = (5.8 \pm 0.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and $k_{abst} = (0.9 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Quoted uncertainties are 2 standard deviations.

b. Relative Rate Studies of Reaction 1 as a Function of **Temperature.** The stainless steel chamber at NCAR was used to determine the temperature dependence of reaction 1 between 274 and 345 K. Conditions used were similar to those just described. Experiments were carried out using both N₂ and O₂ as bath gases. Methane was used as the reference gas for all the experiments. Although the rate coefficients for the two reactions differ by approximately a factor of 8.2 at room temperature, which is not ideal for a relative rate experiment, CH4 is the only one of the reference gases for which the temperature dependence is known with sufficient accuracy to be used as a reliable reference. The experiments were carried out at a resolution of 1 cm⁻¹ using 200 coadded scans. Since the spectra of methane and acetonitrile are both structured, calibration experiments were performed using standard additions of the two compounds to ensure that the spectra were linear at this resolution over the range of concentrations encountered.

At room temperature (296 K) the measured ratio was k_1/k_8 $= 0.122 \pm 0.010$ (2 standard deviations, precision only), leading to a rate coefficient of $(1.22 \pm 0.10) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} for reaction 1, using the latest recommendation for reaction 8.^{12,13} This result is in excellent agreement with that measured at Ford and described in the previous section. The ratio k_1/k_8 was found to increase with increasing temperature, indicating a larger activation energy for reaction 1 than for $Cl + CH_4$ over this temperature range. Experiments were carried out down to 274 K, but below this temperature the difference in the rate coefficients became too large to allow accurate determination of the ratio. Representative data from experiments at 274 and 345 K are shown in Figure 5. The kinetics appeared wellbehaved at all temperatures studied, and the determinations are summarized in Table 1. The results can be combined to yield the following Arrhenius expression for k_1 (where the uncertain-



Figure 5. Plots of the decay of CH_3CN versus that of CH_4 in the presence of Cl atoms at (a) 273 K and (b) 345 K.



Figure 6. Arrhenius plot for $Cl + CH_3CN$ measured in this study: open circles, relative rates measured at NCAR; open triangles, relative rates measured at Ford; filled circle, flash photolysis. Uncertainties are 2 standard deviations, precision only.

ties include possible systematic errors):

$$k_1 = (1.70 \pm 0.25) \times 10^{-11} \exp[-(2140 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The measurements of k_1 made in this study are summarized in Figure 6. The preexponential factor is reasonable for an abstraction reaction by Cl, while the activation energy is larger than that for Cl with either CH₄ or CH₃Cl, although the C–H bond is weaker. Knable and Kurylo rationalized the trends observed for substituted methanes in terms of the electron affinity or the dipole moment of the reagent. The current results are consistent with their hypothesis that the high activation energy for reaction 1 is associated with the extremely large dipole moment of acetonitrile.

c. Absolute Measurement of k_1 at 296 K. An absolute determination of k_1 was made at room temperature (296 K) by monitoring the time resolved resonance fluorescence from chlorine atoms in the presence of acetonitrile. As discussed by Kurylo and Knable,¹⁰ Cl atom fluorescence was reduced in the presence of acetonitrile, with the extent of attenuation consistent with the absorption cross sections near 135 nm given by Suto and Lee.²⁷ The experiments were thus carried out at fairly low acetonitrile concentrations, using 80 Torr of nitrogen as diluent to reduce the rate of loss of Cl atoms by diffusion to a value less than the loss by reaction with acetonitrile. The Cl₂ concentration was also kept as low as possible ($<2 \times 10^{14}$ molecule cm⁻³) in order to minimize regeneration of Cl atoms



20 40 60 80 [CH₃CN] (10¹⁴ molecule cm⁻³)

Figure 7. Second-order plot for $Cl + CH_3CN$ measured by resonance

by the reaction of CH₂CN with Cl₂.

fluorescence at 296 K.

(s_1

$$Cl_2 + CH_2CN \rightarrow CH_2ClCN + Cl$$
 (5)

Some experiments were also carried out in the presence of O_2 in an attempt to scavenge CH₂CN radicals. However, this was found to lead to an increase in the apparent rate coefficient. On closer inspection it was found that the fluorescence decays from the runs containing O_2 were curved downward, indicating that a reactive product was being formed. The most likely candidate is the cyanomethylperoxy radical NCCH₂O₂, which, by analogy with methylperoxy and ethylperoxy, would be expected to react rapidly with Cl,²⁸ competing with CH₃CN for Cl atoms.

 $O_2 + CH_2CN + M \rightarrow NCCH_2O_2 + M$ (11)

$$Cl + NCCH_2O_2 \rightarrow NCCH_2O + ClO$$
 (12)

Since the relative rate experiments suggested that the reaction of CH_2CN with Cl_2 is slow, experiments were carried out in the absence of O_2 , but with as low a Cl_2 concentration as possible so as to avoid regeneration of Cl atoms.

The data were fitted where possible using an unweighted, linear least-squares fit of ln(fluorescence) against time. In the case of the rapid decays, the necessity to use low [Cl₂] meant that the signal was soon lost in the noise, and so a commercial nonlinear least-squares fitting routine was used. When this routine was used to fit the slower decays, comparable firstorder rate coefficients were obtained by both methods (within 10% of each other). The first-order rate coefficients measured are plotted against acetonitrile in Figure 7. Due to the severe restrictions imposed by the attenuation of the signal and the requirement of using low [Cl₂], only a small range of acetonitrile concentrations could be used, $(1.0-8.5) \times 10^{15}$ molecule cm⁻³. Nevertheless, the rate coefficient is well-defined, with a value of $(1.24 \pm 0.10) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In view of the slowness of the reaction and the experimental difficulties involved, along with the possibility that some regeneration may have occurred, we choose to quote a somewhat larger overall uncertainty, i.e., $k_1 = (1.24 \pm 0.20) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} . This result is in good agreement with the two relative rate experiments presented earlier in this paper.

The purity of the acetonitrile was checked using FTIR spectroscopy to look for reactive impurities (specifically HCHO, CH₃OH, and CH₃CHO). Upper limits of a few percent were found for each. Although this impurity level is not low enough to preclude a contribution to the Cl atom reactivity, the excellent agreement with the relative rate experiments suggests that no reactive impurities were present.

100



Figure 8. Spectrum acquired 1 μ s after irradiation of a mixture containing 5 mbar of CH₃CN and 995 mbar of SF₆. The resolution was 0.5 nm, and the dwell time was 100 ns.



Figure 9. Absorption at 348 nm observed following the pulsed radiolysis (using 0.32 of maximum dose) of a mixture of 0.53 mbar of CH₃CN and 999 mbar of SF₆. The trace is the result of a single pulse with no signal averaging. The solid line is a least-squares fit of the expression $Abs(t) = (A_0 - A_{inf}) \exp(-k^{1st}t) + A_{inf}$ to the data, where Abs(t) is the absorbance as a function of time, and A_0 and A_{inf} are the absorbances at time t = 0 and infinity, respectively.

d. Pulse Radiolysis Study of Reaction 2. Following the pulse radiolysis of SF₆/CH₃CN mixtures, a rapid increase in UV absorption at several wavelengths between 280 and 350 nm was observed. Figure 8 shows the spectrum acquired $1 \,\mu s$ after radiolysis of a mixture of 5 mbar of CH₃CN and 995 mbar of SF₆. The absorption consisted of two sets of relatively narrow vibrational bands, with the strongest being at 348 nm. The disappearance kinetics of the bands suggested that two distinct species were absorbing. Control experiments were performed in which either 1 mbar of CH₃CN or 1000 mbar of SF₆ was subjected to pulse radiolysis; no significant transient absorption at 348 nm was detected (<0.01 absorbance units). Figure 9 shows typical data obtained following radiolysis of a mixture of 0.53 mbar of CH₃CN and 999 mbar of SF₆. The trace shown is a result of a single pulse with no signal averaging. The rise in absorption is presumably due to a direct product of reaction 2, and so the kinetics can be determined by monitoring the rate of appearance of this product. The smooth curve in Figure 9 is a first-order fit to the trace which yields a pseudo-first-order rate coefficient, $k^{1st} = (7.9 \pm 1.2) \times 10^5 \text{ s}^{-1}$. The observed values of k1st are plotted as a function of the CH3CN concentra-



Figure 10. Plot of *k*^{1st} versus [CH₃CN] for experiments conducted at 1000 mbar total pressure using monitoring wavelength of 348 nm.



Figure 11. Results of relative rate experiments involving CH₂ClCN and CH₂FCN. Circles are the decay of CH₂ClCN versus those of CH₃-CN (in air, filled symbols) and CH₄ (in N₂, open symbols) in the presence of Cl atoms. Triangles are the decay of CH₂FCN versus that of CD₄ in the presence of F atoms in N₂ diluent. All experiments were performed at 296 K and 700 Torr total pressure.

tion in Figure 10, where it can be seen that $k^{1\text{st}}$ values increased linearly with [CH₃CN]. Linear least-squares analysis of the data shown in Figure 10 gives $k_2 = (5.1 \pm 0.5) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 296 K and a total pressure of 1000 mbar of SF₆. The *y*-axis intercept of $(1.1 \pm 1.7) \times 10^5 \text{ s}^{-1}$ is not statistically significant. The results are in good agreement with the high pressure limiting rate coefficient obtained at Ford using the relative rate technique.

e. Mechanistic Study of the Reactions of Cl and F Atoms with CH_3CN . To provide information on the mechanism of reactions 1 and 2, experiments were performed at Ford Motor Co. in which CH_3CN/Cl_2 and CH_3CN/F_2 mixtures were subject to UV irradiation in 700 Torr of N_2 .

$$Cl + CH_3CN \rightarrow products$$
 (1)

$$F + CH_3CN \rightarrow products$$
 (2)

CH₂CN radicals formed via the H atom abstraction channel of reactions 1 and 2 are expected to react with molecular chlorine or molecular fluorine to give CH₂ClCN or CH₂FCN, and so the yields of CH₂ClCN and CH₂FCN provide insight into the relative importance of the H atom abstraction channels of reactions 1 and 2. As a preliminary exercise, experiments were performed using the relative rate technique to measure the rates of reactions 13 and 14. Results are shown in Figure 11.

$$Cl + CH_2ClCN \rightarrow products$$
 (13)



Figure 12. Formation of CH_2CICN following the UV irradiation of CH_3CN/Cl_2 mixtures in 700 Torr of N_2 . The filled symbols are observed data; the open symbols have been corrected for secondary reaction with Cl atoms.



Figure 13. Formation of CH_2FCN following the UV irradiation of CH_3CN/F_2 mixtures in 700 Torr of N_2 . The filled symbols are observed data; the open symbols have been corrected for secondary reaction with F atoms.

$$F + CH_2FCN \rightarrow products$$
 (14)

Linear least-squares analysis of the data in Figure 11 gives $k_{13}/k_1 = 3.00 \pm 0.12$, $k_{13}/k_8 = 0.34 \pm 0.03$, and $k_{14}/k_9 = 0.77 \pm 0.04$ (where the uncertainties are 2 standard deviations). The rate coefficient ratios $k_{13}/k_1 = 3.00 \pm 0.12$ and $k_{13}/k_8 = 0.34 \pm 0.03$ can be combined to yield a ratio $k_1/k_8 = 0.11 \pm 0.01$. This indirect result is indistinguishable from the value measured directly as discussed in a previous section. Using the reference rate coefficients $k_8 = 1.0 \times 10^{-13}$ and $k_9 = 4.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, we derive $k_{13} = (3.4 \pm 0.3) \times 10^{-14}$ and $k_{14} = (3.6 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

The observed yields of CH₂ClCN and CH₂FCN following irradiation of CH₃CN/Cl₂/N₂ and CH₃CN/F₂/N₂ mixtures are shown in Figures 12 and 13, respectively. The initial conditions used were as follows: $[CH_3CN] = 74-120 \text{ mTorr}, [Cl_2] = 1.4-$ 5.4 Torr, $[F_2] = 1.9 - 4.3$ Torr, in 700 Torr of N₂ diluent at 296 K. Corrections were computed for the secondary loss of CH₂-CICN by Cl atom attack, and CH2FCN by F atom attack, using the Acuchem chemical kinetic program²⁹ with $k_{13}/k_1 = 3.0$ and $k_{14}/k_2 = 0.77/1.31 = 0.59$. Observed and corrected data are given in Figures 12 and 13. There was no discernible effect of molecular halogen concentration over the ranges used. The solid lines in Figures 12 and 13 are linear fits to the data which give yields of $81 \pm 6\%$ and $9 \pm 1\%$ for CH₂ClCN and CH₂FCN, respectively. Errors quoted throughout are 2 standard deviations. It is not surprising that the yields of the monohalogenated products are not 100%. We know that the chain lengths are very short in these experiments, implying that termination reactions compete with the chain propagation reactions. Thus, considerable yields of the termination products such as NCCH₂-CH₂CN are to be expected.

After subtraction of CH₃CN and CH₂ClCN from the product spectra, residual IR features attributable to CHCl₂CN and CCl₃-CN were observed. For completeness, a relative rate study of the reactions of Cl atoms with each of these products was carried out. Rate coefficient ratios for dichloroacetonitrile relative to CHD₃ and CH₄ of 1.24 ± 0.11 and 0.27 ± 0.02 , respectively, were obtained. Using the available literature data for the reference reactions gives $k(Cl+CHCl_2CN) = (2.8 \pm 0.4) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. Quoted uncertainties are 2 standard deviations. Chlorine atoms were found to react slowly with trichloroacetonitrile, with a rate coefficient of the order of 10^{-15} cm³ molecule⁻¹ s⁻¹. However, the observed kinetic behavior was not straightforward, and a reliable rate coefficient could not be derived.

The yields of the products could all be modeled well using the rate coefficients derived above; radical-radical termination rate coefficients were fixed at 5×10^{-11} cm³ molecule⁻¹ s⁻¹ and rate coefficients for the reactions of the radicals with molecular chlorine between 10^{-15} and 10^{-14} cm³ molecule⁻¹ s⁻¹. Finally, after subtraction of all known product features from the infrared spectra, absorption bands due to one or more unidentified products were observed at 792, 945, 985, 1024, 1143, 1652, and 1774 cm⁻¹. The results of the product study presented here show that the major pathway for reaction of Cl atoms with acetonitrile is hydrogen atom abstraction, although the occurrence of a slow reaction of Cl with Cl₃CCN may indicate that a minor addition channel may occur. Poulet et al.¹¹ also found evidence for consecutive chlorination reactions at low pressures.

Discussion

The results of the experiments presented here demonstrate conclusively that a reaction between Cl atoms and acetonitrile occurs at ambient temperatures. The three independent experimental systems described here give indistinguishable results. We recommend a value for k_1 of $(1.15 \pm 0.20) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 296 K. The results can be combined to yield a temperature-dependent rate coefficient of $(1.6 \pm 0.2) \times 10^{-11}$ $\exp[-(2140 \pm 200)/T]$. This was derived by taking the activation energy from the temperature dependence study of k_1 and calculating a preexponential factor which reproduced the mean value at 296 K derived from the independent studies. This method guaranteed the most systematically consistent representation of the temperature dependence of the data. All measurements of k_1 to date are summarized in Figure 14, along with the line obtained as described above. The product study shows that reaction 1 proceeds predominantly, if not exclusively, by a direct abstraction reaction.

The two previous measurements at ambient temperature were in substantial disagreement with one another. Poulet et al.¹¹ measured 9×10^{-15} cm³ molecule⁻¹ s⁻¹, in good overall agreement with this determination, while Kurylo and Knable¹⁰ determined an upper limit of 2×10^{-15} cm³ molecule⁻¹ s⁻¹. The data obtained by Poulet and co-workers exhibited a curved Arrhenius plot, and the data obtained at lower temperatures have been discounted by most evaluations, since heterogeneous loss of acetonitrile was suspected. However, the data at 296 K are in agreement with those found here. There is no evidence in our data for the curvature in the temperature dependence observed by Poulet et al.¹¹

The competitive chlorination experiments of Olbregts et al.⁹ yielded values for k_1 at 370 and 413 K. They measured



Figure 14. Arrhenius plot showing all measurements of k_1 : filled triangles, this work; filled circles, Poulet et al.,¹¹ open triangles, Olbregts et al.,⁹ open square, upper limit of Kurylo and Knable;¹⁰ line, fit to data described in text.

production of CH₂ClCN versus CCl₄ in the competitive photochlorination of mixtures of CH₃CN and CHCl₃.

$$Cl + CHCl_3 \rightarrow HCl + CCl_3$$
 (15)

$$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl \tag{16}$$

Olbregts et al. evaluated the available data to reach their reference expression, based largely on the direct data of Clyne and Walker³⁰ and indirect data of Knox³¹ and others (discussed in ref 31). The data produced by Clyne and Walker are usually regarded as being too high, and current evaluations^{12,13} are based on the data of Knox. However, recent relative rate studies by Wallington³² and Beichert et al.³³ at room temperature gave a rate coefficient $k_{15} = 1.13 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is roughly 50% higher than the room temperature value derived from the data of Knox. In order to reevaluate the data of Olbregts et al., we have taken the room temperature value of k_{15} measured by Wallington, with the activation energy recommended in refs 12 and 13 (the mean of two determinations by Knox). The revised values for k_1 measured by Olbregts then become 4.6 \times 10⁻¹⁴ and 9.4 \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at 370 and 413 K, respectively. The revised data of Olbregts et al. are included in the Arrhenius plot (Figure 14) and are found to be in excellent agreement with the current data set.

In the stratosphere, the strong temperature dependence of k_1 means that it will not compete with the OH reaction, since OH/ Cl is typically about 20, and k_{OH}/k_{Cl} is calculated to be around 3–4 for all temperatures encountered in the atmosphere.¹² Nevertheless, the reaction will have a larger effect than previously thought, especially at higher altitudes, where CH₃-CN profiles may be more sensitive to reaction 1.

We have reported the first measurements of the pressure dependence of the rate coefficient for the reaction of fluorine atoms with acetonitrile. There is evidence from the FTIR product study that abstraction occurs at least part of the time, and the time-resolved UV experiments show the production of two absorbing species. The species OCN and NHCN, which are both isoelectronic with CH₂CN, are known to have banded spectra between 300 and 420 nm,^{34–36} and it would be expected that CH₂CN would also absorb in this region. Although CH₂-CN has been observed in interstellar space through its millimeter wave spectrum,^{37,38} its ultraviolet spectrum has not been positively identified. The spacings of the vibrational progressions in Figure 8 are 400 ± 50 cm⁻¹ for the bands below 350 nm and 980 \pm 20 cm⁻¹ for the bands below 300 nm. Jacox codeposited CH₃CN and excited argon atoms in a cryogenic

matrix and measured infrared and ultraviolet spectra of the products.³⁹ She observed the bands below 300 nm seen here but attributed them to CH₂CNH. It is unlikely that this molecule could be formed in the pulse radiolysis experiments, and we tentatively assign those bands to CH₂CN. The bands below 359 nm could be associated with a fluorine atom adduct, although the good correspondence between the rate coefficients measured by fluorine atom loss and by the relative rate method suggest that the ultimate fate of the adduct is reaction.

It is interesting that the reaction of fluorine atoms with acetonitrile involves an addition mechanism, while that of chlorine atoms appears to proceed entirely by abstraction. The reaction of chlorine atoms with alkenes and alkynes is thought to proceed by electrophilic addition. The strong carbon-nitrogen triple bond and high ionization potential of acetonitrile probably make this mechanism unfavorable. However, it is not clear why the addition of fluorine atoms is so rapid.

Although the reaction of F atoms with CH₃CN is very fast, with a rate coefficient of $(5.5 \pm 1.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 296 K and ambient pressure, the concentration of F atoms in the stratosphere is very small, of the order of 1 molecule cm⁻³,⁴⁰ and so reaction 2 will not impact the calculated profiles of CH₃CN.

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