

REACTION OF ACETONITRILE AND CHLORINE ATOMS

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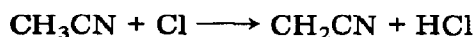
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Summary

Acetonitrile, an atmospheric trace gas of very low concentration, is believed to be primarily removed from the stratosphere by reaction with hydroxyl radicals. Another possible way for destruction of atmospheric acetonitrile, attack by chlorine atoms,

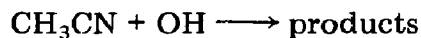


was investigated in this work. The corresponding rate constant was measured at 370 and 413 K using a competitive method. It was established that this reaction, with an activation energy of 6 kcal mol⁻¹ and a pre-exponential factor of 5×10^{10} l mol⁻¹ s⁻¹ (or 8×10^{-11} cm³ s⁻¹), is several orders of magnitude slower under atmospheric conditions than the reaction of acetonitrile with hydroxyl radicals.

1. Introduction

Observations of positive ions in the stratosphere [1, 2] by mass spectroscopy have shown the presence of cluster ions including a molecule X with a proton affinity higher than that of water and a mass of 41 a.m.u. [3]. It has been suggested that this X molecule might be acetonitrile [4]. Although acetonitrile has recently been detected in the troposphere [5], the atmospheric budget of this gas is not yet well established. Acetonitrile seems to be produced at ground level by industrial activity and is also released when bush and grass [5] are burnt. Its global production could therefore be connected with agricultural practices, especially in the tropical regions. This gas diffuses into the stratosphere where it is progressively destroyed by chemical reactions [6].

The main stratospheric loss of acetonitrile is attributed to the action of hydroxyl radicals



The rate constant of this reaction has been measured by several researchers [7 - 9] and values between 2×10^{-14} and $4.7 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, at room temperature, have been reported.

The possibility of a supplementary acetonitrile destruction reaction by chlorine atoms [6] may become significant at high altitudes if the corresponding reaction rate were equal to or larger than that of the $\text{CH}_3\text{Cl} + \text{Cl}$ reaction ($k \approx 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 298 K [10, 11]).

The purpose of this work is to determine the kinetics of the reaction of acetonitrile with chlorine atoms. This measurement can be achieved by a competitive method [12] using gas chromatography as an analytical tool. For a long-chain competitive photochlorination, the ratio of the rate constants for hydrogen abstraction by chlorine atoms for two compounds



and



is given by

$$\frac{k}{k'} = \frac{[\text{RCl}][\text{R}'\text{H}]_m}{[\text{R}'\text{Cl}][\text{RH}]_m} \quad (3)$$

whatever the chain-terminating steps are, provided that the R and R' radicals do not decompose but undergo chlorination in the steps



and



$[\text{RCl}]$ and $[\text{R}'\text{Cl}]$ are the concentrations of the chlorination products when the extent of reaction is a few per cent; $[\text{RH}]_m$ and $[\text{R}'\text{H}]_m$ are the mean values of the concentrations of the competing reactants during the reaction.

The rate constant of hydrogen abstraction from chloroform by chlorine atoms is well known [13 - 15]. Therefore, using this reactant as the competitor, the absolute value of the rate constant of hydrogen abstraction for another substrate can be determined.

2. Experimental details

2.1. Apparatus and procedure

The experiments were performed in a cylindrical Pyrex reactor of volume 140 ml irradiated by the 4358 Å line of a mercury lamp (Philora HP

125). The light intensity was estimated from the rate of photochlorination of pure chloroform, using the known values of the rate constants for this reaction [16]. The partial pressure of the reactants was measured with a mercury manometer, a Pyrex spoon gauge serving as the zero instrument. The chlorine consumption during the reaction was monitored with a logarithmic photometer [17] at about 3500 Å.

When the extent of reaction is a few per cent, samples of the reaction mixture were distilled through a trap at -95°C (acetone slush) to eliminate the non-reacted chlorine and the hydrogen chloride. The products condensable at -95°C were then trapped at -195°C in a small tube which was sealed off. This tube containing the reactants and their chlorinated products was introduced into the gas chromatograph (Intersmat 112 M; 4 m column; 30% Carbowax 1500 on Chromosorb PAW 60-80; 90°C) where it was crushed in the stream of the carrier gas hydrogen (flow rate, 120 ml min^{-1}). The relative sensitivity of the katharometer for the different reaction products was determined by injecting known mixtures. The reaction products were identified by their retention time on the chromatographic column.

2.2. Materials

Commercial tank chlorine (Solvay) was purified as described earlier [18]. Chloroform (Solvay) and acetonitrile (Merck) were used without further purification: their purity was better than 99.5% as controlled by gas chromatography. The carbon tetrachloride (Carlo Erba) and chloroacetonitrile (provided by the Laboratoire de Chimie Organique, Université Libre de Bruxelles) used for the chromatograph calibration were 99% pure.

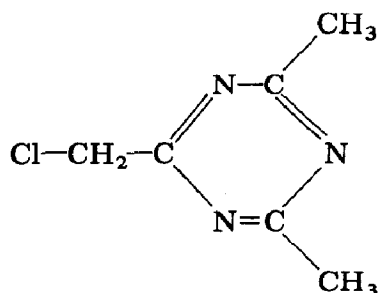
3. Results and discussion

3.1. Stoichiometry

A few preliminary experiments were performed on the chlorination of pure acetonitrile at 313 K to identify the reaction products. During the first stages of the reaction the major observed chlorination product was monochloroacetonitrile (identified by its retention time) following the stoichiometry



An analysis of the reaction products after irradiation for 24 h was also performed by gas chromatography coupled with mass spectrometry. The following products were observed and identified from their mass spectra: CH_3CN , CH_2ClCN , CHCl_2CN , CCl_3CN , $\text{C}_4\text{N}_2\text{Cl}_2$ (probably $\text{N}\equiv\text{C}-\text{CCl}=\text{CCl}-\text{C}\equiv\text{N}$), $\text{C}_4\text{HN}_2\text{Cl}$ (probably $\text{N}\equiv\text{C}-\text{CH}=\text{CCl}-\text{C}\equiv\text{N}$), $\text{C}_6\text{H}_8\text{N}_3\text{Cl}$, which probably has the structure



and $C_6H_7N_3Cl_2$, $C_6H_6N_3Cl_3$ and $C_6H_5N_3Cl_4$ with the same basic structural formula as $C_6H_8N_3Cl$ but with two chlorine atoms substituted on a methyl group, three chlorine atoms substituted on a methyl group and four chlorine atoms substituted on the methyl groups respectively.

The same kind of analysis for a mixture of chloroform, acetonitrile and chlorine that had been irradiated for a few hours indicated the presence of the same products and of chloroform, carbon tetrachloride, hexachloroethane and some minor products such as $CCl_2=CCl-C\equiv N$.

3.2. Quantum yield

At 313 K, with partial pressures of acetonitrile and chlorine of 70 Torr and 100 Torr respectively and an incident light intensity I_0 of 2.85×10^{-8} einstein $l^{-1} s^{-1}$, the initial quantum yield of the photochlorination of pure acetonitrile amounts to about two. This low quantum yield may be explained either by a very slow attack of the chlorine atom on acetonitrile in the chain-propagating step



or by a very fast chain-terminating step in which the chain carriers are destroyed more rapidly than they can react in the propagating steps. Which of these processes is responsible for the low observed quantum yield may be identified by a study of the competitive photochlorination of acetonitrile and chloroform. In such a competition, the chain carriers, and therefore the chain-terminating steps, are indeed common to both reactions. The photochlorination of chloroform is almost unaffected by the presence of acetonitrile, indicating no important inhibiting effect of the chain-terminating steps involving the radicals characteristic of the photochlorination of acetonitrile. It is thus clear that the low quantum yield observed for the photochlorination of acetonitrile is due to the low rate of reaction (7).

It also appears that the quantum yield of the photochlorination of acetonitrile increases rapidly with increasing temperature. It will thus be possible to determine the rate constant of reaction (7) by the method described above at temperatures of about 370 K and higher.

3.3. Competitive photochlorination of chloroform and acetonitrile

The competitive photochlorination of chloroform and acetonitrile has been studied at 370 and 413 K. The range of experimental conditions is

TABLE 1

Range of experimental conditions

T (K)	$I_0 \times 10^8$ (einstein $l^{-1} s^{-1}$)	P_{Cl_2} (Torr)	P_{CHCl_3} (Torr)	P_{CH_3CN} (Torr)	$-(dp_{Cl_2}/dt)_0$ (Torr min^{-1})
370	2.85	30 - 100	20 - 80	40 - 80	0.5 - 3.0
413	2.85	75	20 - 80	20 - 80	2.0 - 7.0

given in Table 1. Under these conditions, the total quantum yield for chlorine consumption ranges between 100 and 1000, whereas the quantum yield for acetonitrile consumption amounts to about 30 - 120.

Figure 1 shows that the ratio of the rates of photochlorination of acetonitrile and chloroform, *i.e.* the ratio of the observed amounts of chloroacetonitrile to carbon tetrachloride when the extent of reaction is a few per cent, is directly proportional to the ratio of the concentrations of the reacting acetonitrile and chloroform and does not depend on the chlorine concentration in agreement with eqn. (3).

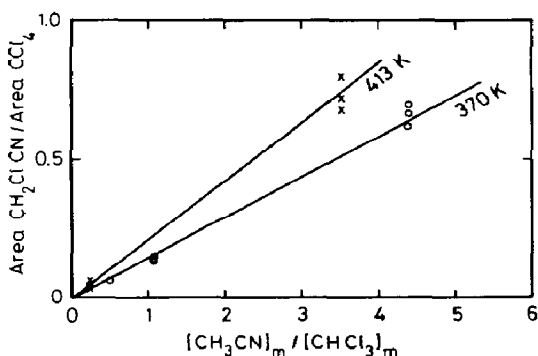


Fig. 1. Competitive photochlorination of acetonitrile and chloroform: ratio of the areas of the chromatographic peaks of chloroacetonitrile and carbon tetrachloride *vs.* ratio of the mean values of the acetonitrile and chloroform concentrations during the reaction at various chlorine pressures and constant incident light intensity.

It must be pointed out that the conversion was always kept low enough (less than 10% for chloroform and 1.5% for acetonitrile) so that the only observed chlorination product of acetonitrile was monochloroacetonitrile. From the slopes of the lines in Fig. 1, by taking into account the relative sensitivity of the katharometer for monochloroacetonitrile and carbon tetrachloride and the known value of the rate constant for hydrogen abstraction from chloroform [13 - 15]

$$\log_{10}\{k' (1 \text{ mol}^{-1} \text{ s}^{-1})\} = -\frac{3350}{4.58T} + 9.84 \quad (8)$$

the rate constant of hydrogen abstraction from acetonitrile (reaction (7)) is obtained:

$$k = 1.3 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (or } 2.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\text{)} \quad (9)$$

at 370 K and

$$k = 3.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (or } 5.1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\text{)} \quad (10)$$

at 413 K.

This yields the following Arrhenius parameters:

$$E = 6.0 \text{ kcal mol}^{-1} \quad (11)$$

and

$$\log_{10}\{A \text{ (l mol}^{-1} \text{ s}^{-1})\} = 10.7 \quad (12)$$

or

$$k \approx 8 \times 10^{-11} \exp\left(-\frac{3000}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad (13)$$

Taking into account the uncertainty in the value of k' and the most important sources of error in our experimental method (the reproducibility of the sampling and chromatographic analysis), we estimate that the pre-exponential factor should be correct to better than a factor of 2. The activation energy obtained from measurements at only two temperatures should not be in error by more than $0.5 \text{ kcal mol}^{-1}$. This latter point is supported by some data at 313 K. From two experiments at 313 K, applying the same method, even though the quantum yields are too low (the method applies only for long-chain reactions), we estimate a mean value of $k = 3.5 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (or $5.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$), while extrapolation of the higher temperature data (eqns. (11) and (12)) yields a value of $k = 3.2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (or $5.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$) at 313 K.

The Arrhenius parameters for the hydrogen abstraction by chlorine atoms have been determined previously for various chlorinated methanes and ethanes [15, 19]. It appears that the activation energy increases with the number of chlorine atoms substituting the attacked carbon: nevertheless this activation energy never exceeds $4.0 \text{ kcal mol}^{-1}$. From the present work it seems that the cyanide group has a still more important effect on the activation energy. As to the pre-exponential factor, it is of the same order of magnitude for acetonitrile as for other compounds with the same number of equivalent hydrogen atoms that can be abstracted.

3.4. Acetonitrile and chlorine atoms in the atmosphere

Extrapolating the data of Section 3.3 (eqns. (11) and (12)) at temperatures of interest in the atmosphere, we obtain

$$k = 2.9 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (or } 4.9 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}\text{)}$$

and

$$k = 7.9 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (or } 1.3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}\text{)}$$

at 250 K and 273 K respectively.

With the maximum chlorine atom concentration of 10^6 cm^{-3} measured at an altitude of 40 km in the stratosphere [20], the lifetime of acetonitrile against chlorine is about 65 years while the corresponding lifetime for the destruction by hydroxyl radicals is equal to 46 days when a hydroxyl concentration of 10^7 cm^{-3} is adopted. Calculations with a model described by Brasseur *et al.* [21] result in a maximum atomic chlorine concentration of $4 \times 10^5 \text{ cm}^{-3}$ at 45 km, which yields a lifetime of the order of 80 years for acetonitrile against chlorine. The action of chlorine on acetonitrile can thus be neglected in stratospheric studies.

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