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Kinetics of the Reaction of the Methyl Radical with Hydrogen Chloride in the Gas Phase

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The rate constants of a homogeneous gas phase reaction of hydrogen chloride with methyl radicals have been measured between 298 and 473 K. Methyl radicals were generated by flash photolysis of acetone, and determined by monitoring the UV absorption at 216 nm. The data can be fitted to the Arrhenius expression:

$$\log (k/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = (8.63 \pm 0.07) \exp[(1072 \pm 66)\ \text{K}/T]$$

Values for the rate constant of the reaction between methyl radicals and hydrogen chloride have been published previously by several authors.[1-5] These values were obtained by calculating the ratio of the rate constants of two competing reactions from the amounts of products, *i.e.*, reaction (1), and a reference reaction. The rate constant of reaction (1) could be calculated

$$CH_3 + HCl \rightarrow CH_4 + Cl \quad (1)$$

from the ratio since the rate constant of the reference reaction was known. However, there is some uncertainty in the rate constants obtained by such a product analysis, because of reactions of hot methyl radicals. A reaction of hot methyl radicals producing methane has been demonstrated[6] in flash photolysis experiments with acetone.

In this study the rate constant of reaction (1) was measured directly by monitoring the absorption of methyl radicals at 216 nm.

EXPERIMENTAL

Materials. Acetone was dried with anhydrous magnesium sulfate, distilled and degassed by the freeze-thaw method at liquid nitrogen temperature. Hydrogen chloride was degassed and purified by bulb to bulb distillation.

Methods. The gases were mixed in a storage bulb before their admission to the reaction cell. The initial acetone pressure was about 1 Torr, and that of hydrogen chloride was varied from 4 to 27 Torr (Table 1). The reaction tube was placed in a block furnace which could be heated and the temperature kept constant within 2 °C. The flash energies varied between 500 and 850 J. The decay of absorption of methyl radicals was displayed on an oscilloscope and the displays were photographed.

Calculations. In addition to reaction (1) a simultaneous combination reaction (2) of methyl radicals to ethane occurs:

$$2CH_3 \rightarrow C_2H_6 \quad (2)$$

The rate constant k_1 of reaction (1) was calculated by iteration using the least-squares method for the equation

$$k_1 t = \ln \frac{a}{a+(k_1/2k_2)} \frac{a-x+(k_1/2k_2)}{a-x}$$

The methyl radical concentration was calculated using the value[7] $\varepsilon = 1010\ \text{m}^2\ \text{mol}^{-1}$ for the molar absorptivity. A value of $k_2 = 2.70 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ for the rate constant of reaction (2) was measured previously.[7] The results are shown in Tables 1 and 2, and Figs. 1 and 2.

DISCUSSION

The rate constants and Arrhenius parameters found in this study are in good agreement with the values obtained[1-5] previously in the flash photolysis of acetone. The small amounts of

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Table 1. Rate constants of the reaction $CH_3 + HCl \rightarrow CH_4 + Cl$.

$\frac{T}{K}$	$\frac{P_{acet.}}{Torr}$	$\frac{P_{HCl}}{Torr}$	Number of experiments	$\frac{10^{-7}\,k}{dm^3\,mol^{-1}\,s^{-1}}$
298	0.85 – 1.7	7.3 – 27.4	25	1.19 ± 0.10
373	1.1 – 1.9	5.4 – 13.8	19	2.26 ± 0.20
423	1.3 – 2.0	5.7 – 13.5	24	3.30 ± 0.30
473	0.80 – 1.6	4.5 – 8.9	6	4.60 ± 0.30

Table 2. Kinetic parameters of the reaction $CH_3 + HCl \rightarrow CH_4 + Cl$.

$\frac{10^{-7}\,k}{dm^3\,mol^{-1}\,s^{-1}}$	$\log \frac{A}{dm^3\,mol^{-1}\,s^{-1}}$	$\frac{E}{kJ\,mol^{-1}}$	$\frac{T}{K}$	Ref.
1.19	8.63	8.9	298 – 473	This work
0.61 [a]	8.46	9.6	301 – 423	1
0.47 [b]	8.53	10.0	370 – 433	2
4.31 [c]			298	3
0.054 [d]	9.4	20.9	323 – 423	4
		10.5	298 – 473	5

[a] The result is based on product analysis of acetone photolysis using $k = 2.70 \times 10^{10}$ $dm^3\,mol^{-1}\,s^{-1}$ for reaction $2CH_3 \rightarrow C_2H_6$. [b] Based on product analysis of methyl iodide photolysis using $k = 1 \times 10^{10}$ $dm^3\,mol^{-1}\,s^{-1}$ for the reaction $CH_3 + I_2 \rightarrow CH_3I + I$. [c] Based on product analysis to obtain the equilibrium constant for reaction (1) and the rate constant $k = 5.6 \times 10^7$ $dm^3\,mol^{-1}\,s^{-1}$ for the reaction $CH_4 + Cl \rightarrow CH_3 + HCl$. [d] Based on product analysis of the photochlorination of methane.

products obtained,[6] indicate that acetyl and acetonyl radicals are present. The error in the rate constant of reaction (1) due to the reactions of methyl radicals with acetyl and acetonyl radicals is expected to be small, however, because the reactions occur only to a small extent, and because the value of the rate constant k_2 for the combination of methyl radicals, obtained from flash experiments with acetone, is in good agreement with values obtained by other methods.[7] In this work, experimental values were collected about 10 μs after the photolysis flash, which is long enough to thermalize methyl radicals.

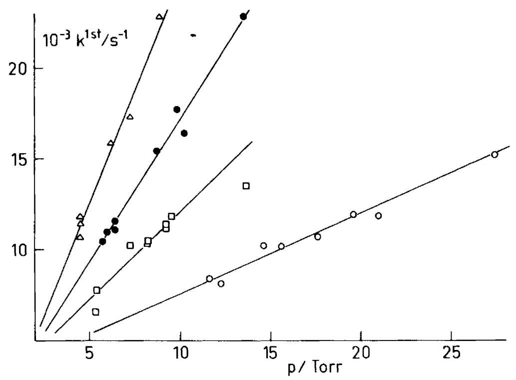

Fig. 1. First-order reaction constants for the reaction $CH_3 + HCl \rightarrow CH_4 + Cl$ *versus* HCl pressure. Symbols for different temperatures: 298 K, ○; 373 K, □; 423 K, ●: 473 K △.

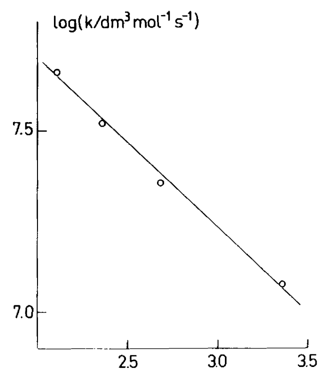

Fig. 2. Arrhenius plot for the reaction $CH_3 + HCl \rightarrow CH_4 + Cl$.

The chlorine atoms formed in reaction (1) may combine with methyl radicals:

$$CH_3+Cl+M \rightarrow CH_3Cl+M \quad (3)$$

In a previous work[3] no methyl chloride was detected even after extended reaction times and therefore reaction (3) is probably not important.

Chlorine atoms also combine to form chlorine molecules:

$$2Cl+M \rightarrow Cl_2+M \quad (4)$$

In a previous work,[3] however, no chlorine was observed. A value of $k_4=2.1\times10^8$ dm^6 mol^{-2} s^{-1} was reported[8] for reaction (4) when M was SF_6. If the same value is assumed here, where M = acetone, reactions (1) and (2) are about 10^5 times faster than reaction (4).

Chlorine atoms can also abstract hydrogen from acetone:

$$Cl+CH_3COCH_3 \rightarrow HCl+CH_2COCH_3 \quad (5)$$

The rate constant for reaction (5) is assumed to be equal to that of the hydrogen abstraction reaction of chlorine atoms with ethane,[9] $k_5=3.1\times10^{10}$ dm^3 mol^{-1} s^{-1} at 298 K. Since the value of this constant is about 500 times greater than the rate constant k_1, the chlorine atom concentration is expected to be small in our flash experiments. The acetonyl radicals react to form radical combination products:

$$2CH_3COCH_2 \rightarrow CH_3COCH_2CH_2COCH_3 \quad (6)$$

$$CH_3COCH_2+CH_3 \rightarrow CH_3COCH_2CH_3 \quad (7)$$

Small amounts of methyl ethyl ketone have been found[6] among the products of flash photolysis of acetone. Acetonyl radicals are formed in a secondary step and their concentration is small during the first part of the reaction. The presence of reaction (7) increases our value of the rate constant of reaction (1) but the error is estimated to be less than about 20 %.

The values of the activation energy and entropy of reaction (1) can be combined with the respective thermodynamic values of the species involved in reaction (1) and the values[10] of the activation energy $E=12.85$ kJ mol^{-1} and $A=1.11\times10^{10}$ dm^3 mol^{-1} s^{-1} of the reverse reaction (1) to give values of $\Delta H_f(CH_3)=142$ kJ mol^{-1} and $S°(CH_3)=192$ J mol^{-1} K^{-1}, both in good agreement with corresponding values published previously.[3,5]

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