Reactions of Chromium Atoms with Chloromethanes

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Abstract—The rate constants of the gas-phase reactions of the chromium atom with CCl₄, CHCl₃, and CH₂Cl₂ were measured behind shock waves at 800–1400 K. The results are presented in the Arrhenius form (the activation energy is given in kJ/mol): $k_{\text{CCl}_4} = 10^{14.32 \pm 0.36} \exp[-(2.0 \pm 7.5)/RT]$, $k_{\text{CHCl}_3} = 10^{14.72 \pm 0.21} \exp[-(18.5 \pm 4.0)/RT]$, and $k_{\text{CH}_2\text{Cl}_2} = 10^{14.33 \pm 0.16} \exp[-(24.1 \pm 3.1)/RT]$ cm³ mol⁻¹ s⁻¹.

INTRODUCTION

Gas-phase reactions of transition metal atoms are interesting for practical applications and for further development of the theory of chemical reactivity [1, 2]. Most of publications along these lines are considered with reactions of metal atoms with oxygen-containing molecules [3, 4]. However, the reactions of metal atoms with other oxidants are important for various technological and natural processes, in particular in the hightemperature treatment of industrial and domestic waste [5]. To our knowledge, the interaction of chromium atoms with chloromethanes was experimentally studied only for CCl_4 at room temperature [6].

In this work, the gas-phase reaction of chromium atoms with chloromethanes (carbon tetrachloride (CCl₄), chloroform (CHCl₃), and dichloromethane (CH₂Cl₂)) were studied. The thermal decomposition of chromium hexacarbonyl (Cr(CO)₆) was used as a source of chromium atoms. Measurements were carried out behind incident shock waves; the installation was described in [7].

EXPERIMENTAL

The temperature range of the measurements was selected so that the characteristic reaction time (~50 μ s) is significantly higher than the characteristic time of the decomposition of Cr(CO)₆ with the formation of Cr atoms and significantly shorter than the characteristic time of the decomposition of the chloromethanes. The experimentally measured rate constants for the decomposition of CCl₄, CHCl₃, and CH₂Cl₂ were taken from [8], [9], and [10], respectively.

The rate constants of the decomposition of chromium hexacarbonyl and the formation of Cr atoms were measured at 600–710 K and at a total density of 3.0×10^{-6} mol/cm³. A hollow cathode lamp was used as a light source of the Cr atomic spectrum. The light source for the measurements in the continuous spectrum was a DKsSh-150 high-pressure xenon lamp. The spectrum intervals were isolated using a DMR-4 double-pass monochromator. A FEU-39A photomultiplier was used as a light detector. The rate constant of chromium hexacarbonyl decomposition was measured from a decrease in absorption in the continuous spectrum at $\lambda = 228$ nm (this wavelength corresponds to the highest absorption coefficient of this compound [11]). The molar fraction of Cr(CO)₆ in Ar was 2.4 × 10⁻²%. The rate constant for the formation of chromium atoms was obtained by measuring the concentration of chromium atoms by means of resonance atomic absorption at $\lambda = 425.4$ nm. The fraction of Cr(CO)₆ in Ar in these experiments was 3.0×10^{-4} %.

RESULTS AND DISCUSSION

Figure 1 shows the Arrhenius plot for the rate constant of $Cr(CO)_6$ decomposition. As can be seen, the rate constants of hexacarbonyl decomposition and chromium atom yield are in good agreement. It should be noted that the rate of formation of chromium atoms is slightly lower than the rate of consumption of parent molecules. This can be explained assuming that intermediate steps of $Cr(CO)_6$ decomposition (sequential dissociation of carbonyl groups) contribute to the overall reaction time, although their rates are much higher than that of the first dissociation step. Also, a certain influence of secondary reactions is possible as found for the decomposition of iron pentacarbonyl [12]. An important conclusion for the present work is that, at a temperature higher than 800 K (lower-temperature boundary of the reactions of chromium atoms with chloromethanes), the yield of chromium atoms in the course of $Cr(CO)_6$ thermal decomposition may be considered an instantaneous process (i.e., its characteristic time is much shorter than the characteristic resolution time of the optical system).

The rate constants of reactions of chromium atoms with CCl₄, CHCl₃, and CH₂Cl₂ were determined via monitoring a decrease in the chromium atom concentration with time (measured at $\lambda = 425.4$ nm). The mixture compositions were 3.0×10^{-4} % Cr(CO)₆, 1.4×10^{-2} % CCl₄, 1.4×10^{-2} and 7.5×10^{-3} % CHCl₃, and 2.7×10^{-2} and 5.6×10^{-2} % CH₂Cl₂ in argon. Since the oxidants were in a large excess over the chromium atom, the kinetic curves were treated on the basis of the quasifirst-order kinetic equation. Figure 2 presents the experimental results.

The temperature dependences of the rate constants for the reactions of chromium atoms with CCl_4 , $CHCl_3$, and CH_2Cl_2 are given by the following expressions (the activation energies are given in kJ/mol)

$$k_{\rm CCl_4} = 10^{14.32 \pm 0.36} \tag{1}$$

$$\times \exp[-(2.0 \pm 7.5)/RT]$$
, cm³ mol⁻¹ s⁻¹,

$$k_{\text{CHCl}_3} = 10^{14.72 \pm 0.21}$$
 (2)

× exp[-(18.5 ± 4.0)/RT], cm³ mol⁻¹ s⁻¹,

$$k_{CH_2Cl_2} = 10^{14.33 \pm 0.16}$$
(3)

$$\times \exp[-(24.1 \pm 3.1)/RT]$$
, cm³ mol⁻¹ s⁻¹.

The random errors for the preexponential factors and activation energies were determined from standard linear regressions of the temperature dependences of the rate constants plotted in the Arrhenius coordinates at a confidence level of 95% [13].

The value of k_{CCl_4} extrapolated to room temperature is in close agreement with the experimental results at this temperature: $k_{CCl_4}(298) = 1.17 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [6]. Thus, over a wide temperature range, the value of k_{CCl_4} is close to the collision frequency factor.

Based on thermochemical data, we assume that the reactions of the chromium atom with chloromethanes involve the dissociation of one or two chlorine atoms from the parent molecule. However, a simultaneous dissociation of two chlorine atoms in a single reaction event may be associated with a complicated rearrangement which usually leads to low steric factors [14]. Since the preexponential factors of all of the reactions studied are characterized by a normal magnitude (or even slightly higher), the most probable pathway for all reactions is the dissociation of one chlorine atom.

The available thermochemical data on the detachment of the chlorine atom from studied chloromethanes [15] and on the dissociation of CrCl molecules [16] show that the reactions with the participation of CCl₄ and CHCl₃ are probably exothermic, and the heats of reactions are $\Delta H_{1,298} = -67 \pm 32$ kJ/mol and $\Delta H_{2,298} = -31 \pm 30$ kJ/mol, respectively. The sign of the heat for the



Fig. 1. Arrhenius plot of the rate constant for the decomposition of $Cr(CO)_6$ measured from (1) the parent molecule decay and (2) the Cr atom yield.



Fig. 2. Arrhenius plot of the rate constant for the reactions of Cr atoms with CCl₄(*I*), CHCl₃(*II*) and CH₂Cl₂(*III*). The mixtures contained (*I*) $3.0 \times 10^{-4}\%$ Cr(CO)₆ and $1.4 \times 10^{-2}\%$ CCl₄, (2) $7.5 \times 10^{-3}\%$ and (3) $1.4 \times 10^{-2}\%$ CHCl₃, and (4) $2.7 \times 10^{-2}\%$ and (5) $5.6 \times 10^{-2}\%$ CH₂Cl₂ in argon. Lines *I–III* are the least-squares approximations.

reaction of Cr atoms with CH₂Cl₂ cannot be determined because of a substantial error in the determination of the enthalpy of this reaction ($\Delta H_{3, 298} = -20 \pm (>25)$ kJ/mol). Therefore, a more detailed theoretical treatment of the reactions studied is complicated by the absence of accurate thermochemical data, primarily for the dissociation energy of the Cr–Cl bond.

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