J. Phys. Chem. A **1997,** *101,* 9341−9343

Shock Tube Study of the Reaction of H Atoms with $TiCl_4$

J. Herzler and P. Roth*

Institut für Verbrennung und Gasdynamik, Gerhard-Mercator-Universität Duisburg, 47048 Duisburg, Germany

Received: June 5, 1997; In Final Form: September 17, 1997[⊗]

The reaction of H atoms with $TiCl_4$ was studied behind reflected shock waves at temperatures between 1190 and 1500 K and pressures around 1.5 bar by applying atomic resonance absorption spectrometry for time-resolved measurements of H atoms at the L_α line. The thermal decomposition of ethyl iodide (C_2H_5I) served as the H atom source. By using a high excess of $TiCl_4$, the consumption of H could be modeled by pseudo first-order kinetics. For the reaction $TiCl_4 + H \rightarrow TiCl_3 + HCl$ a temperature-independent rate coefficient of $k_1 = 3.5 \pm 0.9 \times 10^{13}$ cm^3 mol^{-1} s^{-1} was found for the temperature range of the present experiments.

1. Introduction

$TiCl_4$ is the most commonly used precursor for the production of industrially very important products such as titania and TiN.[1,2] High-temperature gas-phase processes, like chemical vapor deposition (CVD), high-temperature reactors, and flames are often used for the production of these substances. Titania is synthesized on a large scale in flame reactors by the "chloride" process[3] using $TiCl_4$, oxygen, and hydrocarbons along with various additives as educts. The reaction of $TiCl_4$ + H is one of the important starting reactions during the oxidation of $TiCl_4$ in the flame. It is also part of the chain reactions by which $TiCl_4$ decomposes ($TiCl_4 + H \rightarrow TiCl_3 + HCl$, $TiCl_3 + H_2 \rightarrow TiCl_3H + H$) under lower temperatures CVD conditions.

For the further development of these high-temperature gas-phase production processes, the knowledge of the elementary kinetic steps is necessary. Despite the industrial relevance of the titanium compounds, there are no kinetic high-temperature data on reactions of $TiCl_4$.

In the present study the rate coefficient of the reaction

$$TiCl_4 + H \rightarrow TiCl_3 + HCl \qquad \text{(R1)}$$

was directly measured by using the shock tube as a high-temperature wave reactor, detecting H by atomic resonance absorption spectrometry (ARAS). The well-known two-step thermal decomposition of ethyl iodide (C_2H_5I)

$$C_2H_5I \rightarrow C_2H_5 + I$$

$$C_2H_5 \rightarrow C_2H_4 + H$$

was used to produce H atoms.[4] At temperatures $T \geq 1190$ K and low initial concentrations, the H formation is very fast (>97% within 30 μs) and no subsequent reactions of H, I, and C_2H_4 were observed so that ethyl iodide is a well-defined H atom source at these conditions.[5]

2. Experimental Section

The experiments were carried out in a stainless steel pressure driven shock tube with an internal diameter of 79 mm. It is divided by a thin aluminum diaphragm into a driver section of 3.5 m and a driven section of 5.7 m in length. The internal surface has been specially prepared for ultrahigh-vacuum (UHV) purposes. The driven section can be baked out and pumped down to pressures below 1×10^{-8} mbar by a turbo molecular pump. Gas mixtures were prepared manometrically in a stainless steel UHV storage cylinder, which also could be baked out and evacuated using a separate turbo molecular pumping unit. The residual gases in all UHV devices were analyzed by quadrupole mass-spectrometers, and were found to be practically free of hydrocarbons. More details of the setup are given elsewhere.[6,7] Argon used in the present study was of the highest commercially available purity (≥99.9999%). Ethyl iodide (≥99%) and titanium tetrachloride (≥99.9%), which are liquid at normal conditions, were injected and evaporated in separated stainless steel vessels.

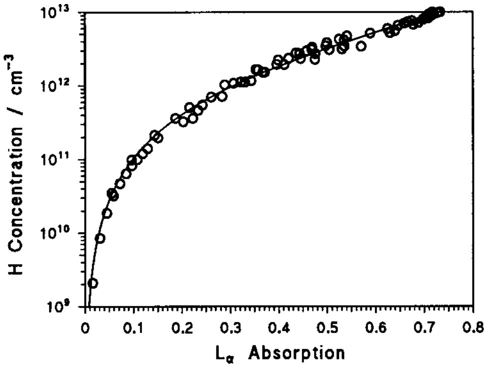

Figure 1. H atom calibration curve. Solid line: fit, $A_H = 1 - \exp(-7.9\ \text{cm} \times 1.17 \times 10^{-8}\ \text{cm}^{0.65} \times [H]^{0.55})$.

The shock tube is equipped with diagnostics for ARAS consisting of a microwave excited discharge lamp, the optical absorption path in the shock tube, a 1 m vuv monochromator, and a solar blind photomultiplier. The lamp was operated with a flowing gas mixture of 1% H_2 in He maintained at a pressure of about 5 mbar and a microwave power of about 50 W. The spectral shape of the L_α line ($\lambda = 121.6$ nm) emitted by the resonance lamp is not precisely known due to the influence of self-absorption and self-reversal in the lamp gas. Hence precise calibration measurements were made to relate measured absorption to the corresponding H atom concentration by using the reaction of O atoms with H_2 to produce H atoms.[8,9] This procedure is suitable because the thermal decomposition of H_2 is very slow at temperatures below 2100 K. The source of O atoms was the dissociation of N_2O, which is relatively fast. Therefore, a mixture of 1 ppm N_2O and 200 ppm H_2 is suitable to cover the temperature range from 1500 to 2100 K.[10]

The results of the calibration procedure shown in Figure 1 can be expressed by a modified Lambert−Beer law:

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S1089-5639(97)01841-0 CCC: $14.00

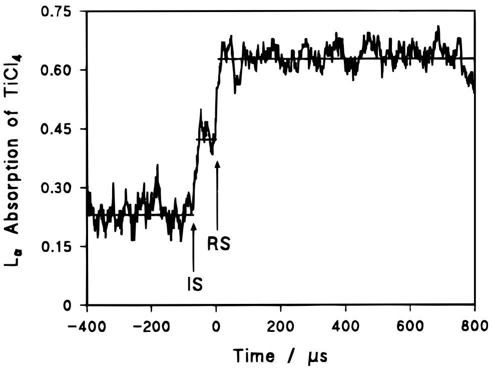

Figure 2. Typical example of L_α absorption of $TiCl_4$ in a shock tube experiment. Mixture: 235 ppm $TiCl_4$ in Ar. $T_5 = 1130$ K, $p_5 = 151$ kPa.

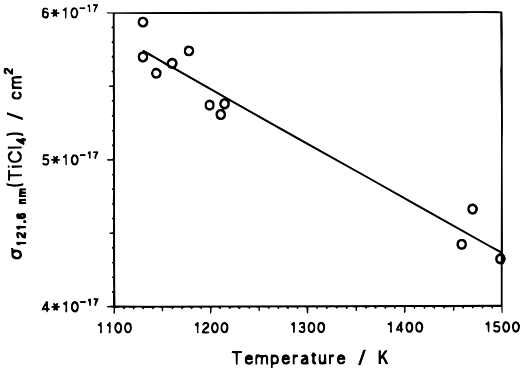

Figure 3. Measured absorption cross section of $TiCl_4$ at L_α in the temperature range 1130−1500 K.

$$A_H = 1 - \exp(-l\sigma_{L_\alpha}[H]^{0.55}) \qquad (1)$$

with l being the absorption path length. The absorption cross section was found to be $\sigma_{L_\alpha} = 1.17 \times 10^{-8}$ cm$^{0.65}$ and the concentration exponent of 0.55 was introduced to fit the Lambert−Beer expression of eq 1 to the calibration results. The slight temperature dependence of the calibration curve does not influence the first-order analysis of our data because we need only the concentration exponent which is temperature independent within the measurement uncertainty from 1200 to 2100 K.

3. Results and Discussion

For all the results presented in this paper, the absorption of the L_α radiation by the initial molecular reactant $TiCl_4$ was taken into account. In a first series of experiments the molecular absorption cross section σ_{L_α} was determined by performing experiments with mixtures containing 100−235 ppm $TiCl_4$ in Ar. A typical example of $TiCl_4$ absorption of L_α radiation is shown in Figure 2. The incident (IS) and reflected shock (RS) cause a steplike increase of the absorption to a level of about 63%. The results obtained from a total of 12 individual shock tube experiments are summarized in Figure 3. The temperature-dependent absorption cross section of $TiCl_4$ for L_α radiation can be approximated in the temperature range from 1120 to 1500 K by

$$\sigma_{L_\alpha}(TiCl_4) = 9.9 \times 10^{-17}\ \mathrm{cm}^{-2} - 3.7 \times 10^{-20}\ \mathrm{cm}^{-2}\,\mathrm{K}^{-1} \times T$$

The absorption cross section at room temperature is about $7.5 \pm 0.8 \times 10^{-17}$ cm^{-2}.

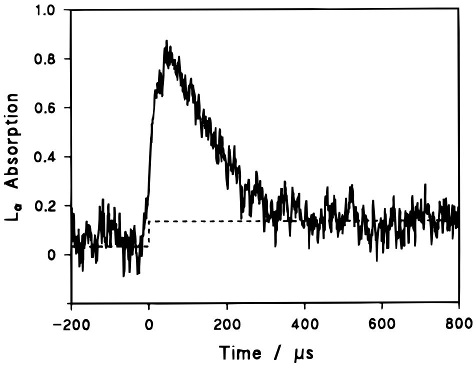

Figure 4. Typical example of L_α absorption obtained in a $TiCl_4/C_2H_5I/$Ar gas mixture behind a reflected shock wave. Mixture: 32.5 ppm $TiCl_4$ and 2 ppm C_2H_5I in Ar. $T_5 = 1191$ K, $p_5 = 166$ kPa.

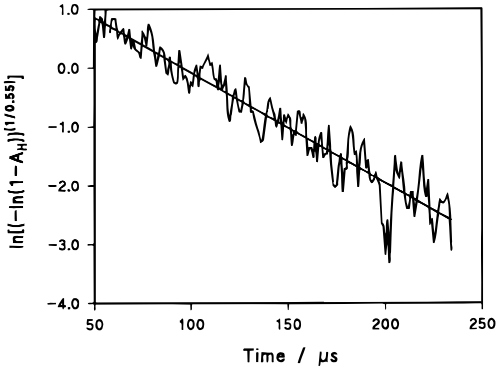

Figure 5. First-order plot deduced from the absorption signal given in Figure 4.

In mixtures containing C_2H_5I, the interference absorption of ethyl iodide and its molecular decomposition products were assumed to be negligible because of the very low concentration of these species in the present reaction systems. The temperature range of our $TiCl_4$ + H study was 1190 to 1500 K at pressures of about 1.5 bar. The lower limit was determined by the requirement of fast ethyl iodide decomposition, the upper limit by the stability of $TiCl_4$.[11,12] Mixtures of 15−40 ppm $TiCl_4$ and 2 ppm C_2H_5I in Ar were used. This high $TiCl_4$ excess reduces the importance of subsequent reactions so that the rate coefficients could be determined by a pseudo first-order analysis.

A typical example of an absorption profile is given in Figure 4. The signal is composed of two parts: the interference absorption of $TiCl_4$ (dashed line) and the absorption by H atoms. The measured absorption shows a fast increase at time zero and reaches a maximum at about 50 μs, followed by a fast decay to the interference absorption. All measured absorption profiles were transferred into first-order plots by applying the calibration relation of eq 1. For the example of Figure 4, this plot is given in Figure 5, where the value $\ln[(-\ln(1 - A_H))^{(1/0.55)}]$ is plotted against the reaction time. The slope is equal to the inverse time constant τ^{-1}.

$$\tau^{-1} = -\frac{d}{dt}\ln[(-\ln(1 - A_H))^{(1/0.55)}] \qquad (2)$$

where A_H is the absorption being related to H atoms. The rate coefficients of reaction R1 can directly be related to the measured time constants τ^{-1}:

$$k_1 = \tau^{-1}/[TiCl_4]_0 \qquad (3)$$

The individual k_1 values obtained from all experiments are summarized in the Arrhenius diagram of Figure 6. The rate

TABLE 1: Rate Coefficient Data for the Reactions of Chlorinated Compounds + H to HCl + Products

reaction	A ($cm^3\ mol^{-1}\ s^{-1}$)	E_a/R (K)	T-range (K)	authors
$TiCl_4 + H \rightarrow TiCl_3 + HCl$	3.5×10^{13}		1190−1500	this work
$SiCl_4 + H \rightarrow SiCl_3 + HCl$	1.4×10^{13}	4800	1530−1730	Catoire et al. [13]
$NCl_3 + H \rightarrow NCl_2 + HCl$	2.41×10^{12}		300	Exton et al. [14]
$PCl_3 + H \rightarrow PCl_2 + HCl$	1.45×10^{12}		298	Jourdain et al. [15]
$PCl_3 + H \rightarrow PCl_2 + HCl$	$0.05 \times k_{Cl_2+H}$		298	Sung et al. [16]
$BCl_3 + H \rightarrow BCl_2 + HCl$	1.02×10^{11}	1232	295−807	Jourdain et al. [17]
$CF_3Cl + H \rightarrow CF_3 + HCl$	1.70×10^{13}	4426	538−676	Bradley et al. [18]
$CH_2Cl_2 + H \rightarrow CH_2Cl + HCl$	1.08×10^{13}	3069	298−460	Combourieu et al. [19]
$CH_3Cl + H \rightarrow CH_3 + HCl$	5.01×10^{11}		998	Manion et al. [20]
$CH_3Cl + H \rightarrow CH_3 + HCl$	4.82×10^{8}		298	Jones, Ma [21]
$CH_3Cl + H \rightarrow CH_3 + HCl$	3.70×10^{13}	4680	500−800	Westenberg, DeHaas [22]
$CH_3Cl + H \rightarrow CH_3 + HCl$	1.10×10^{13}	2315	298−652	Aders et al. [23]

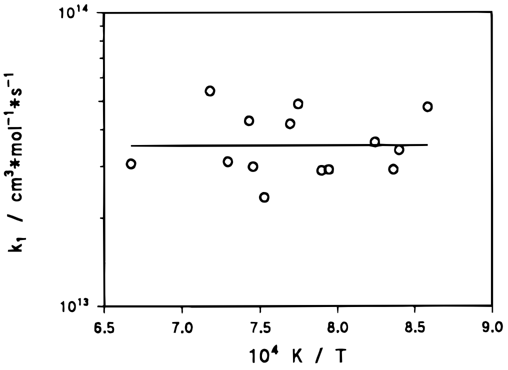

Figure 6. Arrhenius plot for the rate coefficient k_1.

coefficient is temperature-independent within the measurement uncertainty. The mean value is

$$k_1 = 3.5 \pm 0.9 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$$

where the uncertainty is given at the 1σ level.

A comparison of k_1 with literature values for this reaction is not possible because there are no data available. The only rate coefficients available for the reaction of fully chlorinated compounds with H and similar reactions of partially chlorinated organic molecules + H producing HCl are summarized in Table 1. It can be seen that an A factor of 3.5×10^{13}, which was determined in this work, is characteristic for this kind of reaction. All the reactions show only a small temperature dependence (assuming an A factor of $3 \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$, the activation energies of $NCl_3 + H$ and $PCl_3 + H$ are less than 2 kcal/mol) but our results are the only ones showing no activation energy.

References and Notes

(1) Akhtar, M. K.; Vemury, S.; Pratsinis, S. E. *AIChE J.* **1994**, *40*, 1183.

(2) Bouteville, A; Imhoff, L; Remy, J. C. *J. Electrochem. Soc.* **1996**, *143*, 3251.

(3) Clark, H. B. Titanium Dioxide Pigments. In *Pigments*; Myers, R. R., Long, J. S., Eds.; Marcel Dekker Inc.: New York, 1975; Part 1.

(4) Herzler, J.; Frank, P. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1333.

(5) Herzler, J. Ph.D. Thesis, Stuttgart, **1994**.

(6) Woiki, D.; Roth, P. *Shock Waves* **1994**, *4*, 95.

(7) Thielen, K.; Roth, P. *20th Symp. (Int.) on Comb.* **1984**, The Combustion Institute: Pittsburgh, PA, 685.

(8) Appel, D; Appelton, J. P. *15th Symp. (Int.) on Comb.* **1975**, The Combustion Institute: Pittsburgh, PA, 701.

(9) Just, Th. Atomic Resonance Absorption Sperctrometry in Shock Tubes. In *Shock Waves in Chemistry*; Lifshitz, A., Ed.; Marcel Dekker Inc.: New York, 1981.

(10) Frank, P.; Just, Th. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 181.

(11) Allendorf, M. D.; et al. *Electrochem. Soc. Proc.* **1995**, *95−4*, 393.

(12) Herzler, J. Unpublished results.

(13) Catoire, L.; Woiki, D.; Roth, P. *Int. J. Chem. Kinet.* **1997**, *29*, 469.

(14) Exton, D. B.; Gilbert, J. V.; Coombe, R. D. *J. Phys. Chem.* **1991**, *95*, 2692.

(15) Jourdain, J.-L.; Laverdet, G; Le Bras, G.; Combourieu, J. *J. Chim. Phys.* **1980**, *77*, 809.

(16) Sung, J. P.; Setser, D. W.; Heydtmann, H. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 3, 1272

(17) Jourdain, J.-L.; Laverdet, G.; Le Bras, G.; Combourieu, J. *J. Chim. Phys.* **1981**, *78*, 253.

(18) Bradley, J. N.; Whytock, D. A.; Zaleski, T. A. J. *Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2284.

(19) Combourieu, J.; Le Bras, G.; Paty, C. *14th Symp. (Int.) on Comb.* **1973**, The Combustion Institute: Pittsburgh, PA, 485.

(20) Manion, J. A.; Dijks, J. H. H.; Mulder, P.; Louw, R. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 434.

(21) Jones, W. E.; Ma, J. L. *Can. J. Chem.* **1986**, *64*, 2192.

(22) Westenberg, A. A.; Dehaas, N. *J. Chem. Phys.* **1975**, *62*, 3321.

(23) Aders, W.-K.; Pangritz, D.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem.* **1975**, *79*, 9, 90