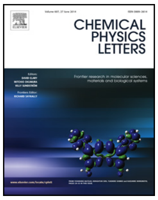
Chemical Physics Letters 624 (2015) 83–86

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



High-temperature kinetics of the reaction between chlorine atoms and hydrogen sulfide

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ARTICLE INFO

Article history:
Received 6 January 2015
In final form 6 February 2015
Available online 14 February 2015

ABSTRACT

The rate constant k_1 for $Cl + H_2S$ has been measured over 290–914 K using the laser flash photolysis/resonance fluorescence technique. Atomic chlorine was generated by pulsed 193 nm photolysis of CCl_4 and C_6H_5Cl and monitored by time-resolved resonance fluorescence at 130–140 nm. The data are summarized as $k_1 = (2.90 \pm 0.10) \times 10^{-11} \exp(2.38 \pm 0.11\ \mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{cm^3\,molecule^{-1}\,s^{-1}}$ where the uncertainties in the Arrhenius parameters are $\pm 2\sigma$. 95% confidence limits for k_1 are ±6%. These extended range measurements confirm a negative activation energy for the reaction.

1. Introduction

The reaction

$$Cl + H_2S \rightarrow SH + HCl \quad (1)$$

is of dynamic interest as a protypical heavy–light–heavy system of atoms [1]. Several studies have focused on the production of vibrationally excited products whose distribution may readily be monitored by infra-red techniques, and a population inversion between newly formed HCl($v = 0$) and HCl($v = 1$) allows laser action [2]. Reaction (1) may also be of significance in the atmosphere of Venus, where it could couple sulfur and chlorine chemistry, and possibly in the terrestrial atmosphere (such as volcanic plumes) and combustion systems as well.

Dill and Heydtmann generated Cl atoms in a discharge through Cl_2 at low pressures and detected infrared chemiluminescence (IRCL) from HCl in $v > 0$ [3]. Leone and co-workers used laser flash photolysis (LFP) of precursor molecules to generate atomic chlorine, and monitored the IRCL of the HCl product, attributed mainly to HCl in the $v = 1$ and $v = 2$ states [4,5]. Agrawalla and Setser were able to detect the weak emission from vibrationally excited SD produced via

$$Cl + D_2S \rightarrow SD + DCl \quad (2)$$

and deduced that approximately 3% of the reaction exoergicity led to SD vibrational excitation, with 7 ± 4% of the SD produced in $v = 1$ [6]. Hossenlopp et al. monitored the DCl distribution via time-resolved IR diode laser spectroscopy, and found the ratio for $v = 0{:}v = 1{:}v = 2$ to be 0.33:0.56:0.11 [7]. The most recent dynamics study by Chen et al. was based on time-resolved FTIR monitoring of reaction (1), and these workers obtained the ratio for $v = 0{:}v = 1{:}v = 2$ to be 0.41:0.52:0.07 [8]. These distributions are consistent with the general interpretation of heavy-light-heavy systems, where most of the energy release is expected to result in excitation of the new H—Cl bond [1].

There is uncertainty about the detailed mechanism of reaction (1). One possibility is direct abstraction, but an addition/elimination pathway has been discussed by several groups [5,9,10]. The *ab initio* work of Wilson and Hirst indicated the existence of a bound H_2S–Cl adduct, but not whether it could decompose to SH + HCl [11]. They also characterized a transition state (TS) for direct abstraction. Their transition state theory calculations for direct abstraction gave a room temperature rate constant an order of magnitude below that observed, which left open the possibility that addition/elimination dominates the kinetics. Resende et al. explored this possibility but obtained a rate constant about 15 times larger than experiment at room temperature [12]. Nicovich et al. commented that the available dynamics data "do not appear to allow clear differentiation between the two possible mechanisms" [10]. Subsequently, Chen et al. were unable to explain their measured rotational energy distributions in terms of a direct abstraction model, and speculated that an addition/elimination model might rationalize their observations [8].

Prior measurements of the rate constant k_1 for reaction (1) are listed in Table 1. It may be seen that at room temperature these span a factor of 3. In addition to some of the IR studies mentioned already, kinetic data have been obtained via the discharge-flow (DF) method combined with resonance fluorescence (RF) and

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http://dx.doi.org/10.1016/j.cplett.2015.02.011
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Table 1
Comparison of kinetic data for Cl + H_2S.

Experimental technique	$k_1(298\pm2K)$	$E_a\pm2\sigma$	T range
	10^{-11} cm^3 molecule^{-1} s^{-1}	kJ mol^{-1}	K
LFP-IRCL[a]	6.0 ± 1.2		
LFP-IRCL[b]	7.3 ± 0.9		
DF-RF[c]	4.0 ± 0.2		
DF-MBMS[d]	5.1 ± 1.4		
FP-RF[e]	6.3 ± 0.9	0[f]	211–353
RR[g]	10.5 ± 0.4	0[f]	232–359
LFP-RF[h]	7.4 ± 1.1	−1.73 ± 0.20	202–430
LFP-FTIR[i]	3.7 ± 1.5		
LFP-RF[j]	7.6 ± 0.5	−2.38 ± 0.11	290–914

[a] Ref. [4].
[b] Ref. [5].
[c] Ref. [13].
[d] Ref. [14].
[e] Ref. [9].
[f] No uncertainty reported.
[g] Ref. [15].
[h] Ref. [10].
[i] Ref. [8].
[j] Current work.

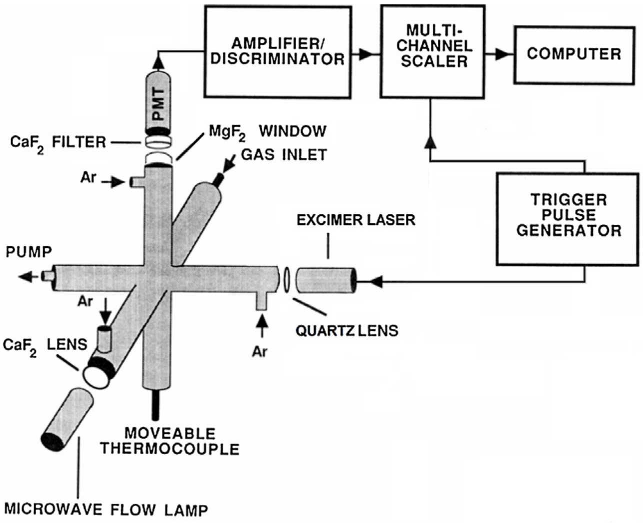

Figure 1. Schematic diagram of the apparatus used for laser flash photolysis/resonance fluorescence measurements.

molecular-beam mass spectrometry (MBMS) detection [13,14], via flashlamp photolysis (FP) or LFP combined with RF detection [9,10], and via relative rate (RR) measurements where radioactive ^{38}Cl was produced by irradiation of CF_3Cl [15]. As well as disagreements concerning the magnitude of k_1, there are disagreements concerning its temperature dependence, where zero or slightly negative activation energies (E_a) have been reported [9,10,15]. The NASA-JPL critical evaluation [16] is based on the kinetics studies of Nicovich et al. [10], who applied the LFP-RF technique over 200–430 K to both reactions (1) and (2).

The main aim of the present work is to extend the temperature range for k_1, to more closely determine its temperature dependence. Incidentally, our extension to beyond 900 K encompasses all high-temperature regions of the Venusian atmosphere including down to the surface.

2. Apparatus and methodology

2.1. Gas preparation and handling

Hydrogen sulfide (purity 99.5% Matheson Gas Products) and tetrachloromethane (purity ≥99.9%, Spectrum) were purified via several freeze–pump–thaw cycles and then mixed with a large excess of Argon (purity 99.9999%, Air Liquide) to a pressure of roughly 1300 mbar in Pyrex bulbs. Flows of the gas mixtures were combined after passage through mass flow controllers (MKS Instruments Types 1159A and 1159B), which were calibrated against a Teledyne Hastings–Raydist bubble meter (HBM-1A). Typical flow rates were up to about 0.3 μmol s^{-1} for H_2S, about 3 μmol s^{-1} for CCl_4, and (70–700) μmol s^{-1} for Ar. Pressures were measured with a capacitance manometer (MKS Instruments Type 622A).

2.2. Reactor and detection system

The reactor is a three-way stainless steel cross, as shown in Figure 1. The intersection region establishes a reaction zone of roughly 8 cm^3. The six side arms are each 11 cm long, as measured from the reaction zone boundaries, with an inner diameter of 2.2 cm. Nichrome resistance heating wire, electrically insulated with ceramic beads, is wrapped along the inner 7 cm portion of each side arm. The reactor is housed in thermal insulation, 20 cm on a side, made of 2.5 cm thick alumina boards (Zircar Products ZAL-50). The outermost 1.5 cm portions of each side arm extend past the insulation, and are water-cooled. Connections are made through standard ISO NW25 KF fittings.

Pulsed radiation from the laser enters the reactor at right angles to the continuous probe resonance radiation, and fluorescence is detected through a mutually perpendicular side arm. Two of the side arms are used for conducting the gas mixtures in and out of the reactor while another serves as a port for a thermocouple. The sheathed Type K thermocouple (chromel/alumel) is used to monitor the gas temperature inside the reaction zone, which is displayed on an Omega DP 285 readout. This thermocouple is not shielded against radiative heat exchange with the walls of the reactor, which can introduce radiation errors [17]. Separate experiments to derive empirical corrections have been outlined previously [18], and an uncertainty of ±2% for the corrected temperature was recommended. The thermocouple is removed from the reaction zone during kinetic measurements. A second sheathed thermocouple is placed outside the reactor for temperature control (Omega CN 3910 KC/S).

The resonance radiation is produced from a flow of about 0.3 mbar of a dilution of 0.1% of Cl_2 in Ar through a microwave discharge flow lamp operated at powers of 30–50 W. The intensity of the fluorescence is monitored by a solar-blind UV PMT (Hamamatsu R212) operated at 2490 V (Bertran Model 215 power supply). As can be seen from Figure 1, the PMT is connected to a computer-controlled multichannel scaler (EG&G Ortec ACE) via a preamplifier/discriminator (MIT Model F-100T) to count emitted photons as a function of time. Signals following 50–5000 laser pulses are accumulated and analyzed on a computer. The timing of the experiments is controlled by a digital delay/pulse generator (Stanford Research Systems, DG 535), which triggers the excimer laser (MPB PSX-100, beam cross section 7 mm × 8 mm) ahead of the multichannel scaler to allow measurement of the steady background signal that arises from scattered light from the resonance lamp.

As previously mentioned, the reagents are diluted in a large excess of argon, which thermalizes the radicals generated, increases the heat capacity of the gas mixture to maintain isothermal conditions during the reactions, and slows diffusion of the transient radicals to the reactor surfaces. The average time spent by the gases in the reaction zone is long compared to the time scale of the reaction (~1 ms), so that the reactor is kinetically equivalent to a static system.