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LA-UR-83-964

LA-UR--83-964

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TITLE: THE REACTION OF FLUORINE AND CHLORINE ATOMS WITH FORMALDEHYDE AND DEUTERO-FORMALDEHYDE

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SUBMITTED TO: Proceedings of Optics '83 meeting to be held at Los Alamos, April 11-15, 1983, Santa Fe, NM

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The reaction of fluorine and chlorine atoms with formaldehyde and deutero-formaldehyde*

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Introduction

As a result of recent work, gas-phase metathetical reactions of formaldehyde represent a particularly well-studied group of chemical reactions[1-8]. A wide variety of studies have been conducted including real-time[1,3-8] and relative-rate kinetics[9], product energy distributions[2,10,11] and theoretical calculations[12]. The interest prompting these studies is two-fold. First, the removal of reactive species, such as atomic chlorine, from the stratosphere via reaction with formaldehyde could have a tremendous impact on the ecological effects of anthropogenically released substances. Secondly, these reactions are generally quite fast and are of considerable interest from a dynamic point of view.

Other interest in formaldehyde chemistry concerns the microscopic details of its reactions. The reactions of chlorine and fluorine atoms with formaldehyde are highly exothermic (ΔH = - 15 and -49 kcal mole^{-1}, respectively) and the energy is released primarily as internal energy in the produce hydrogen halide.

$$Cl + H_2CO \longrightarrow HCl + HCO \qquad (1a)$$

$$F + H_2CO \longrightarrow HF + HCO \qquad (1b)$$

$$Cl + D_2C \longrightarrow DCl + DCO \qquad (1c)$$

$$F + D_2CO \longrightarrow DF + DCO \qquad (1d)$$

Detailed state distributions have been determined for the excited hydrogen halide formed in reactions (1)[2,10,11]. The results of these experiments can be summarized as follows: the highest observed HF energies coincide with the expected thermochemical limits (v = 4, J = 14) while the maximum population was found in v = 3; significant vibrational excitation was also found in the ν_1 mode of HCO; and vibrational distributions were found to yield linear surprisals using either three-body models or those incorporating HCO rotation, thereby permitting an estimate of the ground state population of the product that is initially formed.

We have undertaken a study of reactions (1a) - (1d) using infrared multiple photon dissociation (MPD) to produce fluorine atoms, and infrared chemiluminescence to monitor the rate of reaction. The rise in infrared luminescence with time due to reactions (1) is followed by a decay due to radiative and (predominantly) collisional deactivation:

$$H(D)X(v) + m \xrightarrow{k_2} H(D)X(v - n) + m \quad 1 < n < v \qquad (2)$$

where k_2 is a mole-fraction weighted rate constant. A deconvolution of the rising and falling portions allows independent determinations of the rate constant (1a - 1d), and (2). This technique was introduced by Flynn[13], Whittig[14], Houston[15], and their co-workers, and has been extensively used by Houston and Heidner et al[16]. The reactions can be carried out under "wall-less" conditions, using inert free radical precursors. Further, the use of infrared lasers as the photolytic source provides more chemical specificity than does conventional ultraviolet photolysis. There is usually less problem with simultaneous

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photolysis of the reactant molecule, and negligible likelihood of producing electronically excited fragments from the photolysis.

Experimental

The experimental technique has been described previously[16,17] Briefly, the fluorine atoms were produced via infrared multiphoton dissociation of a precursor molecule. The photolysis source was a grating tuned CO_2 TEA laser based on a Tachisto head. The output was restrained to be approximately circular by an intracavity iris, and consisted of a 45-ns spike (FWHM) containing ≥80% of the pulse intensity, followed by a low intensity tail of ~0.5 μs (determined with a photon drag detector). Repetition rates were typically 0.5 Hz, with pulse energies of ~0.8 J at λ = 10.591 μm, and ~0.2 J at λ = 9.201 μm. Shot to shot energy fluctuations were ± 5%.

A 200 mm AR-coated Ge lens was used to direct the beam into the photolysis cell, which was a Pyrex flow tube (2.5 cm ϕ × 10 cm) equipped with O-ring mounted NaCl entrance and exit windows, and epoxy mounted CaF_2 viewing windows. Flow rate and pressure were controlled by Teflon metering valves. Infrared fluroescence was viewed as right angles to the laser beam by focusing (6 cm CaF_2 lens) it onto an InSb (SBRC) detector cooled to 77 K. Interference filters were used to increase S/N and to isolate the relevant signal. The detector signal was coupled to a matched preamp (SBRC) and fed into a Tektronix amplifier (7A18) for further amplification. This signal was then digitized by a waveform recorder (Biomation 805) and averaged on an interfaced Z-80A based microcomputer[18]. Overall response time of the system was < 500 ns. A schematic of the experimental apparatus is shown in Fig. 1.

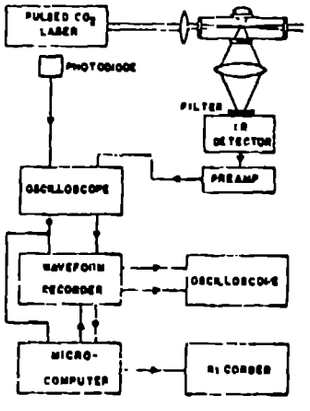

Figure 1. Schematic of the experimental apparatus.

Samples were prepared by freezing the halogen source (SF_6 or $CClF_3$) into an isolated cold finger of a 3 ℓ Pyrex bulb which had been conditioned prior to use. Formaldehyde and buffer gas (if any) were then added sequentially and the SF_6 was allowed to warm prior to mixing. The large volume to surface ratio of the bulbs, and the conditioning procedure—exposure to high formaldehyde pressures—insured that the amount of formaldehyde which polymerized on the surface was minimal. Derived rate constants were found to be independent of the time between sample mixing and the experimental determination, again indicating that formaldehyde polymerization was minimal. All gas handling was carried out on a grease free g lass vacuum line capable of vacuumn better than 5 × 10^{-6} T. Pressures were monitored by a Validyne differential pressure transducer in sample preparation and a Barocel capacitance manometer on the flow cell.

The monomeric formaldehyde was prepared from the isotopic paraformaldehyde (H_2CO-Aldrich, D_2CO-Merck, 98% D) by the method of Spence and Wild.[19] The formaldehyde monomer was then purified by vacuum distillation from 174 K to 77 K. Storage at 77 K prevented polymerization. N_2 and Ar (Matheson) were used without further purification. $CClF_3$ and SF_6 (PCR) were subjected to repetitive freeze-pump-thaw cycles.

Results

SF_6 and CCl_3F were the primary fluorine and chlorine atom sources, respectively. $CClF_3$ was used to simultaneously produce chlorine and fluorine atoms. The primary and secondary photolysis schemes are shown below:

$$SF_6 \xrightarrow{nh\nu} F + SF_5 \xrightarrow{mh\nu} F + SF_4 \qquad \bar{\nu} = 944.2\ cm^{-1} \tag{3}$$

$$CCl_3F \xrightarrow{nh\nu} Cl + CCl_2F \xrightarrow{mh\nu} Cl + CClF \quad \bar{\nu} = 1081.1\ cm^{-1} \tag{4}$$

$$CClF_3 \xrightarrow{nh\nu} Cl + CF_3 \xrightarrow{mh\nu} F + CF_2 \qquad \bar{\nu} = 1086.8\ cm^{-1} \tag{5}$$

Previous results have shown that the halogen atoms produced in these processes to be of near thermal energy. Reactions 1a - 1d are thus carried out very near the ambient translational temperature (T 295 ± 5 K).

Pseudo-first-order conditions ($[F]_0$; $[Cl] \ll [H_2CO]$; $[D_2CO]$) were maintained throughout all experiments. For SF_6 it is estimated that < 1% dissociation occurred within the focal volume of the CO_2 laser[17]. The amount of dissociation for the freon precursors is expected to be less. In all cases $[H_2CO]/[X]_0 > 15$, thus, satisfying the criterion for pseudo-first-order behavior.

The rise and fall of the infrared emission signal from the excited hydrogen halide can be shown to follow:

$$I(t) = \frac{ck_r'}{k_r' - k_2'} \left[\exp(-k_2't) - \exp(-k_r't)\right] \quad , \tag{6}$$

where $k_r' = k[H_2CO]$ and k is the bimolecular rate constant of the reaction being studied. The rising and decaying rates for the hydrogen halide fluorescence can be obtained by fitting Eq. (6) to the experimental fluorescence traces using standard methods.

The experimental data is shown in Figs. 2 - 5 for, respectively: Cl + H_2CO, F + H_2CO, Cl + D_2CO, and F + D_2CO. The data is displayed as k_r' vs $H(D)_2CO$ concentrations so the slope yields the bimolecular rate constant. Absolute rate constants measured in this study are shown in Table 1, along with previous determinations of those and related (X + $H(D)_2CO$) rate constants.

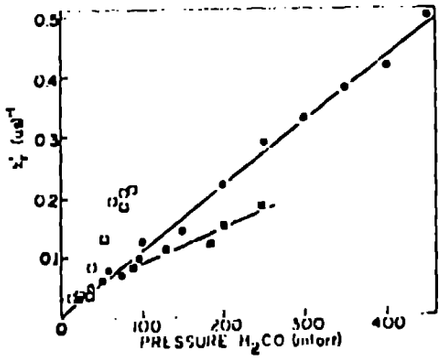

Figure 2. Plot of k_r' vs H_2CO pressure for the reaction Cl + H_2CO; o indicate CCl_3F as precursor; ▪ indicate $CClF_3$ as precursor and □ indicates static cell with CCl_3F as precursor.

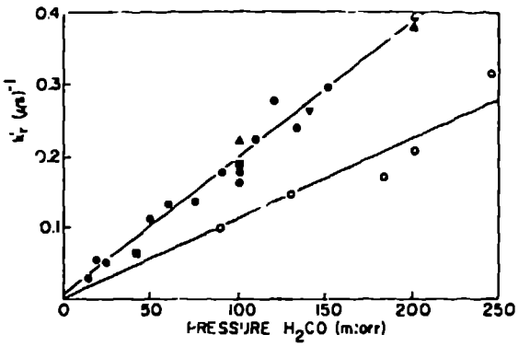

Figure 3. Plot of k_r' vs H_2CO pressure for the reaction F + H_2CO; open symbols indicate SF_6 and $CClF_3$ precursor, respectively. Circles indicate no buffer gas, ▼ - 5 torr N_2, ▲ - 5 torr Ar and □ - 10 torr Ar.

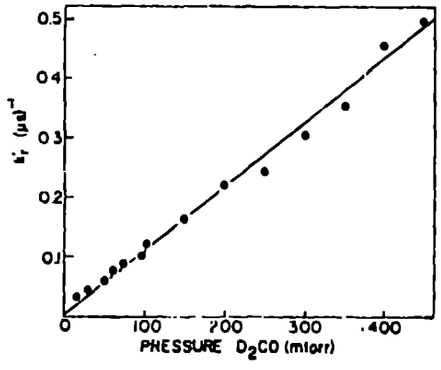

Figure 4. k_r' vs D_2CO for the reaction Cl + D_2CO.

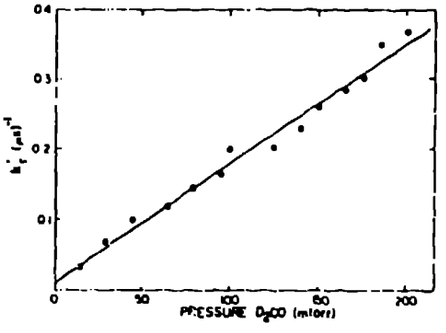

Figure. 5. k_r' vs D_2CO for the reaction F + D_2CO.

Discussion

Earlier experiments by this group[1] involving reaction 1 resulted in a larger rate constant than was deduced in the current study. This discrepancy is most likely due to differences in the experimental procedure of the two experiments. The original study utilized a simple static photolysis cell fitted with a single viewing window. In the latter experiments, a flow cell was used with a back reflecting mirror for more efficient collection of the emission. Improvements in the laser produced much higher intensities within the focal volume of the beam in the latter experiments, thus achieving higher signal-to-noise ratios.

In addition, use of the static photolysis cell in the earlier experiments may have introduced secondary reactions. Buildup of product species, in particular HClCO, could lead to an overall faster rate of chlorine atom removal. The rate of hydrogen abstraction from HClCO is expected to be faster than from H_2CO due to the weaker C-H bond; the electronegative chlorine draws electron density away from the bond. This trend is seen[20] in the hydrogen abstraction by chlorine atoms with CH_4 and CHCl where k_{CH_3Cl}/k_{CH_4} = 5 at 298 K.

HClCO can be formed by the reaction of HCO with the precursor, CCl_3F. HClCO has been observed in the study of reaction (1a) where molecular chlorine was used as the atom source[9]. However, HClCO could not be detected by infrared spectroscopy in the present experiments due to the low concentrations ($[HClCO] < [H_2CO]_0$) which would be formed and short lifetime (<1 hour).

The data for both the static and flow cell experiments are shown in Fig. 2. At low H_2CO pressures (≤ 40 mtorr) the data are in agreement but at higher H_2CO pressures, and presumably higher CHlCO concentrations during the experiment, severe disagreement is observed. Therefore the flow cell data are to be preferred over the static cell data.

A point of greater interest is the variation of a measured rate constant with photolysis frequency. The rate constants obtained for the various halogen atom/formaldehyde reactions by the IRMPD/TRIRC technique and other methods are given in Table I. The difference between the photolysis frequency employed to dissociate the appropriate atom precursor and the nearest vibrational absorption feature of formaldehyde (H_2CO; D_2CO)[21] is also given. It is evident that for laser lines corresponding to near resonances (presumably indicating a high degree of vibrational excitation in formaldehyde) there is a marked decrease in the derived rate constant relative to off-resonant experiments. This decrease is particularly evident in the reaction of F + H_2CO where 944.2 cm^{-1} excitation is far off resonance and produces a rate constant of 5.79×10^{-11} cm^3 $molecule^{-1}s^{-1}$ while 1086.8 cm^{-1} excitation is only 7 cm^{-1} off resonance and yields a rate constant of 3.8×10^{-11} cm^3 $molecule^{-1}s^{-1}$. The 7 cm^{-1} is easily compensated by laser power broadening[22], or the "red shift" effect which is likely if infrared multiphoton absorption is occurring. The decrease in rate constant with increasing reactant vibrational excitation can be explained qualitatively in terms of simple arguments concerning the nature of the reactive potential surface. A feature of attractive potential energy surfaces is their ability to effectively channel relative translational energy into the reaction coordinate. That is, if the barrier to reaction is along the approach coordinate, vibrational motion is roughly perpendicular to the reaction coordinate and, therefore, vibrational energy may trap reactants in the potential well prior to the transition state thereby inhibiting the reaction.

Table I. Absolute rate constants obtained for the reaction of halogen atoms with formaldehyde at T=295±5K

Reaction	Halogen Atom Source	Detection Method	$\Delta\bar{\nu}(cm^{-1})$[a]	$k(10^{-11}$ cm^3 $molecule^{-1}s^{-1})$	Reference
Cl + H_2CO	uv photolysis of Cl_2	FTIR	--	7.8	9
	flash photolysis of Cl_2	Cl resonance fluorescence	--	7.48 ± 0.50	3
	flash photolysis of Cl_2	Cl resonance fluorescence	--	7.18 ± 0.61	4
	IRMPD of CCl_3F	TRIRC	12	3.29 ± 0.15[b]	this work
	IRMPD of $CClF_3$	TRIRC	7	1.70 ± 0.37[b]	this work
Cl + D_2CO	uv photolysis of Cl_2	FTIR	--	6	9
	IRMPD of CCl_3F	TRIRC	23	3.26 ± 0.19[b]	this work
F + H_2CO	microwave discharge in F_2	EPR	--	6.6 ± 1.1	5
	IRMPD of SF_6	TRIRC	83	5.79 ± 0.56	this work
	IRMPD of $CClF_3$	TRIRC	7	3.8 ± 1.2[b]	this work
F + D_2CO	IRMPD of SF_6	TRIRC	14	5.22 ± 0.37[b]	this work
Br + H_2CO	microwave discharge in Br_2	EPR	--	0.16 ± 0.03	5

[a] $\Delta\bar{\nu}$ = formaldehyde absorption - laser line. Formaldehyde absorptions are from reference 26.

[b] These rate constants may not represent thermal reaction; see text for explanation.

It is likely that with 1081.1 and 1086.6 cm^{-1} excitation for both H_2CO and DCO and 944.2 cm^{-1} excitation for D_2CO there is a significant amount of vibrational energy deposited in the formaldehyde. The effects of intense CO_2 laser radiation on H_2CO and D_2CO have been studied and show absorption when the laser line is near resonant (~20 cm^{-1}) with formaldehyde transition[22]. The effect of vibrational excitation in the case of H_2CO at 944.2 cm^{-1} photolysis is insignificant and the derived value is reported as the rate constant at 295 ± 5 K. The remaining rate constants were all obtained with some degree of excess vibrational energy in the reactant formaldehyde. Therefore, these values should not be regarded as thermal rate constants.

It may be possible to employ this technique even though formaldehyde is a weak absorber in this spectral region. If a sufficient quantity of buffer gas were used such that the vibrational deactivation of formaldehyde was faster than the reaction of interest then the measured rate should be unperturbed. However, one must be judicious in choosing a suitable buffer gas. While it must efficiently deactivate vibrationally excited formaldehyde, it should not deactivate either the precursor molecule or the fluorescing hydrogen halide.

The study of the effect of internal energy of reactants on reaction rate is an expanding field. Recent articles[24] and a review[25] indicate the current interest in this aspect of chemical dynamics. Perhaps the use of laser excitation to produce nonthermal energy distributions in reactants will lead to a deeper understanding in this area of chemical kinetics.

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