BEAM-GAS CHEMILUMINESCENT REACTIONS OF Cu(²D) WITH Cl₂, Br₂, and I₂

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Received 21 January 1980, in final form 20 February 1980

Chemiluminescent reactions involving copper and halogen molecules are shown to result from the bimolecular reaction of metastable $Cu(^2D)$ with Cl_2 , Br_2 , and I_2 under single-collision conditions. The collision-energy dependence of the reactions is described by a hard-sphere model with zero threshold energy. Cross sections for these reactions are compared with that for chemiluminescent reaction of $Cu(^2S)$ with F_2 .

1. Introduction

The chemiluminescent (CL) emission from reactions of copper with the halogen molecules has been studied under multiple-collision and single-collision conditions [1-4]. The chemiluminescent reaction with fluorine has been shown in a molecular beam study to proceed by reaction of the ground state of the copper atom to populate directly several excited states of CuF [4]. Thus any reaction of F₂ with Cu excited states will likely be overshadowed by the chemiluminescence resulting from reaction with the much more abundant Cu ground state.

Chemiluminescence from reaction of Cu with Cl_2 and Br_2 in a heat pipe oven was reported by Capelle et al. [1], and spectra resulting from the reactions of Cu with Cl_2 and Br_2 were presented by Rosenwaks [2]. Both spectra were taken in the pressure region of 10 Torr so that energy transfer may be important for the excitation of the electronic states. The photon yields from the reactions of Cu with Cl_2 and Br_2 were seen to be very low, $\ll 0.1\%$, when compared with that of the $Cu + F_2$ reaction, approximately 0.3%.

Results from molecular beam experiments are presented here on the beam-gas and beam-spray reaction of copper atoms and halogen molecules. We show that the electronically excited states of CuX (X=Cl, Br, I) anse from reaction of metastable Cu (^{2}D) rather than Cu_2 with the halogen molecule. Time-of-flight experiments are presented which yield information on the energy dependence of the cross section for formation of the electronically excited states of CuX.

2. Experimental

The molecular beam and light detection systems have been described previously [5,6]. For the copper beam source, a tantalum oven with an alumina crucible was heated by a tungsten mesh radiator. For the spectral scans of Cu + X_2 , temperatures of 1770–1840 K were used. Cl₂ was used directly from a cylinder (Matheson, purity 99.5%), and leaked into the collision chamber via a needle valve. Br₂ and I₂ were leaked into the chamber from a thermostatted flask maintained at 298 and 350 K, respectively. Air was removed by pumping on the flask in a dry ice—acetone bath. The halogens were trapped on a liquid-nitrogen-cooled surface between the diffusion pump and the mechanical pump. Absolute collision-chamber pressures were determined with a capacitance manometer.

The CL spectra from beam-gas reactions were taken using pulse counting techniques as described previously [5], and the data were automatically entered into a programmable calculator for time normalization and subtraction of the background. Later, the data were corrected for the spectral response of the detection system. The CuCl CL spectrum was taken at 1.0 nm spectral

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bandwidth, and the CuBr and CuI spectra at 1.5 nm spectral bandwidth. X_2 pressures were in the range 2.5-3.5 × 10⁻⁴ Torr, which was expected to give negligible secondary collision effects on the spectra.

The time-of-flight apparatus incorporated a minor modification to the previously described apparatus to allow a longer flight path for the metal beam. Directly in front of the oven cooling jacket, a time-of-flight (TOF) initiation wheel with 6 equally spaced 2 mm slots was used to provide metal beam pulses. The wheel was located at a distance of 11.7 cm from the collision center, and rotated at 300 Hz by an asynchronous motor to give pulses of beam particles of duration $15 \,\mu s$ fwhm. The chemiluminescent signal at the collision center was viewed at a distance of 8.9 cm by a photomultiplier tube (EMI 9816B) with a 520.0 nm cut-off filter in front to minimize detection of oven light. The signal from the photomultiplier was amplified by a current amplifier (Keithley 427) which served as the input to a 100 channel signal enhancement instrument (Honeywell SAI-42) used with a delay of $5 \mu s$ per channel. The initiation pulse for the instrument was provided by means of a photomultiplier tube positioned inside the chamber so as to view the light from the oven through the slots in the TOF wheel. The experiment was run until sufficient signal/noise was achieved (typically $\frac{1}{2}$ -2 h). The TOF spectrum in the signal enhancer was then transferred to the programmable calculator for plotting and storage.

For the time-of-flight experiments, the copper oven was operated at a temperature of 1800 K, yielding a copper pressure of 0.3 Torr. Under our experimental conditions, the Knudsen number for the copper oven orifice was calculated to be approximately 3, making the beam close to effusive. We have also run other TOF scans of the Cu + Br₂ reaction at other metal beam pressures in the range 0.2-0.5 Torr which are identical to the 0.3 Torr result within experimental uncertainties. If the metal atom beam velocity distnbutton deviated significantly from the ideal maxwellian form, then we would have expected a major change in shape of the TOF spectrum as the pressure was altered. For these experiments, a 0.8 × 3.1 mm slit for the halogen at 298 K was positioned 1.25 cm from the collision center. The pressure behind this slit was monitored during the experiments and maintained in the range 0.6 - 0.8 Torr for X = Cl, Br and 0.2 - 0.6 Torr for I_2 . Thus corresponds to an effective scattering gas pressure

of 2.0–2.6 \times 10⁻⁴ Torr for Cl₂ and Br₂ and 0.6–2.0 \times 10⁻⁴ Torr for I₂.

3. Variation of signal with reactant pressures

The CL signal at a peak in the spectrum was measured as a function of X_2 pressure. For X_2 pressures less than 1.0×10^{-4} Torr, the signal increased linearly with X_2 pressure. These results are consistent with a reaction first order in X_2 with negligible attenuation of the Cu beam in the 4.6 cm of travel before the collision center.

The CL signal from the reaction was also studied as a function of the Cu oven temperature to determine the metal beam reactant. The beam exists in several energetically excited states, the Cu($^{2}D_{5/2}$) at 11203 cm⁻¹, Cu($^{2}D_{3/2}$) at 13245 cm⁻¹ [7] and the ground state of the dimer. The relative abundances of these species are Cu($^{2}D_{5/2}$) 4.2 × 10⁻⁴, Cu($^{2}D_{3/2}$) 2.8 × 10⁻⁴, and Cu₂ 1.5 × 10⁻² [8]. Fig. 1 displays a loganthmic plot of T_{Cu} times the CL intensity versus T_{Cu}^{-1} ,



Fig. 1. Logarithmic plots of T_{Cu} times CL intensity versus T_{Cu}^{-1} for Cl₂ (squares), Br₂ (triangles), and I₂ (circles) reactions. The smooth curves are predictions based upon reaction of Cu(²S), ---, Cu(²D_{5/2}), ----; and Cu₂, ----.

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which should be approximately linear with slope related to the enthalpy of vaporization of the metal and the activation energy for the CL reaction [9]. Fig. 1 displays the expected temperature dependence of this plot if ground-state $Cu(^{2}S)$, metastable $Cu(^{2}D_{5/2})$, or groundstate Cu₂ is exclusively the reactant with no activation energy. It is seen that the experimental points lie close to the temperature dependence expected for reaction of the Cu metastable or Cu₂ species. Deviations at the high temperature ends of the graphs may be due to beam attenuation. Reaction of Cu_2 to give CL via $Cu_2 + X_2$ \rightarrow CuX + CuX is energetically allowed [10,11], and thus we cannot say whether $Cu(^2D)$ or Cu_2 is the reactant species based on the CL spectra alone. The TOF spectra presented below serve to rule out reaction of Cu₂ based on its longer flight time to the collision center. If ground-state $Cu(^2S)$ were the reactant then an activation energy of 28 kcal/mole is indicated in all three cases. Such a high value can be ruled out on the basis of the TOF spectra. Thus, we can conclude that the CL is due to bimolecular reaction of the halogen with $Cu(^{2}D)$ rather than one of the other species in the beam.

4. CL spectra

The CL spectra for the reactions of Cu(²D) and X₂ (X = Cl, Br, I) are presented in fig. 2. In the Cl₂ reaction, the prominent peaks in the spectrum are due to the $|\Delta v| \leq 3$ sequences of the A.B,C--X transitions previously characterized by others under high resolution [10]. Some of the transitions with v' = 0, 1, and 2 for the D state are also apparent, and v' = 0 and 1 for the *E* state. For the Cu + Br₂ reaction, the major peaks in the spectrum are due to the CuBr A--X sequences, while the minor peaks are due to the B--X $\Delta v = -1, 0, 1, 2$ sequences. In the case of Cu + I₂, we observe the A,B,D--X transitions. No extensive simulations of the spectra have been performed because of the low resolution of the spectral scans, and the lack of rotational constants for many of the states involved.

One may be tempted to extract lower bounds on CuX bond strengths from the highest vibrational states which are apparent in the spectra in fig 2. We have found, though, by simulation of the CuCl D and E state spectrum, using a prior form for energy disposal and averaging over the reactant energy, that the highest state expected is not well defined due to the spread of



Fig 2 CL spectra corrected for detector response for the reaction with (a) Cl_2 , (b) Br_2 , and (c) I_2 .

initial translational energy and uncertainty as to the relative importance of $Cu(^{2}D_{5/2})$ and $Cu(^{2}D_{3/2})$. On the basis of the average energy available to the reactants and previous determinations of bond strengths [10], formation of CuCl states as high as D, v'= 2, and CuBr states as high as B, v'= 1, are expected if $Cu(^{2}D_{5/2})$ is the reactant. Thus, these CuCl, CuBr bond strengths are consistent with our spectra. For CuI there is much greater uncertainty in the bond strength. Gaydon's [11] recommended value of 16 100 cm⁻¹ predicts no chemiluminescence. However, a value of 24 200 cm⁻¹ based on a linear Birge–Sponer extrapolation [11] is consistent with our experiments in predicting states as high as D, v'=3.

5. TOF spectra

The TOF spectra for the CL products from copper reaction with Cl_2 and Br_2 are presented in fig. 3. Peaks at short delay times are due to oven light, and serve to establish the zero point for the time scale. The cross section for formation of the excited CuCl or CuBr prodVolume 71, number 3



Fig. 3. TOF spectra for the reactions with (a) Cl₂ and (b) Br₂. The smooth curves are predictions based upon hard-sphere interaction with $E_0 = 0$, ----; hard-sphere interactions with $E_0 = 0.2$ kcal/mol, $-\cdot -\cdot$; and long-range r^{-6} potential, ---.

uct from the dimer reaction can be estimated as less than 0.003 times the $Cu(^{2}D)$ cross section on the basis of the known dimer population and the failure to observe a peak at the flight time for the dimer in the **TOF** spectrum.

The TOF spectra can also be used to gain some information about the translational energy dependence of the cross sections for forming CL products. Because of several experimental broadening effects on the TOF spectra, we chose to simulate the TOF spectra using variable forms for the cross section, rather than to attempt to extract the cross section directly. In the simulations, averaging was carried out over the TOF pulse shape, the velocity distribution of the halogen beam, and the response function of the amplifier. Averaging effects due to uncertainty in the detection site were negligible. Comparison is made in fig. 3 with simulations based on two forms of the cross section σ as a function of collision energy E:

(1) hard-sphere interaction with a threshold energy E_0 , $\sigma = C(1 - E_0/E)$; and

(2) long-range r^{-6} potential governing the centrifugal barrier location, $\sigma = CE^{-1/3}$.

The first form with $E_0 = 0$ gave the best fit for the Cl₂ and Br₂. Fig. 3 shows the sensitivity of the TOF distributions to E_0 by comparing the cases $E_0 = 0$ and $E_0 = 0.2$ kcal/mole. The latter gives curves which are much too sharp. The $E^{-1/3}$ form for σ , on the other hand, gives curves which are too broad. A more complicated form for the cross section [12] involving both a threshold and a fall off with E for large E could also be fit to the experimental points, but no significant improvement over the best fits shown in fig. 3 was attained. We have also measured TOF spectra for the CL reactions with F₂ and I₂ and found the results, though somewhat noisier, to be consistent with reaction of monomeric Cu with negligible threshold energy.

6. Relative cross sections for CL reactions

Relative cross sections for total production of CL. products were obtained for the Cu + X₂ reactions for X = F, Cl, Br and I by comparing light emission observed with the PM tube located in the collision chamber. The relative number of photons emitted was obtained by correcting the emission for the varying response of the PM tube (S-20) over the CL spectra shown in fig. 2 and ref. [4]. Product states with radiative lifetimes $> 10^{-4}$ s, such as the a $^{3}\Sigma$ state of CuF, should not be considered as included in these relative cross sections since they will most likely exit the region viewed before radiating. Results for the cross sections, which are corrected for the relative number densities of the species which give the CL, are given in table 1, based on reaction of $Cu(^2S)$ in the case of the F_2 reaction and reaction of $Cu(^2D_{5/2})$ for the other three halogens. Uncertainties due to calibration errors are estimated at $\pm 50\%$.

Table 1			
Relative cross	sections fo	r reaction	of Cu + X ₂

Reactants	Relative cross section	Average collision energy (kcal/mol)	
$Cu(^{2}S_{1/2}) + F_{2}$	1.0	2.54	
$Cu(^2D_{5/2}) + Cl_2$	7.6	3.25	
$Cu(^2D_{5/2}) + Br_2$	17.3	4.08	
$Cu(^2D_{5/2}) + I_2$	0.6	4.47	

7. Discussion

Examination of the CL spectra reveals that at the resolution used individual band heads are not observed. It will not be possible to resolve the bands without much better resolution because of the closeness of the vibrational origins within many of the sequences, and the high CuX rotational excitation. Preliminary attempts to simulate the shapes of the sequences observed in the CuCl spectrum reveal that energy disposal into vibrational and electronic modes does not differ dramatically from expectations based on the simple prior model for energy partitioning [13]. This model previously gave acceptable fits to the observed CuF vibrational-energy distributions [4]. Further spectral simulation efforts must await the availability of rotational constants for many of the excited states observed.

The larger cross sections for reaction of excited Cu with Cl₂ and Br₂ than for the reaction of ground-state Cu with F_2 can be explained on the basis of adiabatic correlations of reactant surfaces with excited product surfaces. No such correlations exist for the $Cu(^{2}S) + F_{2}$ case [4] forcing the system to switch adiabatic surfaces numerous times in order to give CL reaction. $Cu(^{2}D)$ + X₂ surfaces on the other hand, do correlate adiabatically with some excited product surfaces, regardless whether the system is considered in C_s or $C_{\infty v}$ symmetry, thus obviating the need for surface changes in some cases. Further experiments giving the initial collisionenergy dependence of cross sections for forming particular product states will be useful for clarifying the importance of surface changes. Experiments are also planned to distinguish the reactivity of the $Cu(^2D_{3/2})$ and $Cu(^2D_{5/2})$ states by pumping one state out of the beam with laser excitation.

Acknowledgement

Support of the National Science Foundation is gratefully acknowledged. We would like to thank Dr. K. Liu for assistance with some of the experiments.

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