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Spectroscopic studies of the products of reactions of yttrium and scandium atoms with halogen molecules. I. The origin of chemiluminescence^{a)}

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Observations of laser induced fluorescence from the products of the reactions of yttrium and scandium atoms with halogen molecules have shown that chemiluminescence does not originate from electronically excited metal monohalide molecules, as previously suggested, but instead arises from electronically excited dihalide molecules, MX^{*}₂. Production of the metal dihalides appears to require the formation of vibrationally excited metal monohalides, MX^{*}₁, in a precursor reaction. Radiative lifetime measurements for chemiluminescent bands are presented.

I. INTRODUCTION

Recent studies have been reported of the chemiluminescence produced in reactions between yttrium and scandium atoms and halogen molecules.¹ In contrast to the chemiluminescences observed from other metal atom-oxidizer combinations which originate from band systems with wavelengths ranging extensively throughout the visible spectrum,² the chemiluminescences associated with these reactions are selectively confined to relatively narrow (100-200 Å) wavelength intervals in the blue spectral region.¹ In the Sc/F_2 and Y/Cl_2 systems the photon yield associated with this selective emission feature was reported to be relatively high, exceeding a few percent of the total reaction probability.¹ The origin of these chemiluminescences has been ascribed to electronic transitions in electronically excited yttrium or scandium monohalide molecules MX* formed in the reactions¹

$$M + X_2 - MX^* + X , \qquad (1)$$

where M = Sc or Y, and X = F, Cl, or Br, although the observed selective chemiluminescent features do not correspond to any presently known band systems in these molecules. Indeed, the absence of emission from the several known band systems in these molecules, energetically accessible via Reactions (1), is in remarkable contrast to prior expectations of the chemiluminescence associated with a statistical distribution of energy among the product states of Reactions (1).

In the studies reported here it has been found that the chemiluminescences do not originate from yttrium or scandium monohalides formed from Reactions (1), but instead arise from electronically excited dihalide molecules MX_2^* formed in a subsequent chemical reaction. A likely candidate for this reaction is

$$MX^{\dagger} + X_2 - MX_2^{*} + X , \qquad (2)$$

where MX^{\dagger} denotes vibrationally hot molecules formed in the reaction between M and X_2 .

Laser induced fluorescence (LIF) methods have been used here for measurements of the radiative lifetimes associated with the chemiluminescent electronic band systems in YCl₂, YBr₂, YClBr, and YI₂ molecules. LIF techniques have also been employed to obtain excitation spectra and radiative lifetimes for several new band systems in the yttrium and scandium monohalides. Spectroscopic constants and Franck-Condon factors are summarized for the observed band systems in the following paper,³ hereafter referred to as II.

II. EXPERIMENTAL APPARATUS

The experimental apparatus was designed to provide a convenient means for the vaporization of yttrium or scandium and a reaction zone for the observations of chemiluminescence and laser induced fluorescence from products of reactions between yttrium or scandium and halogen molecules (F2, Cl2, Br2, I2). Detailed descriptions of apparatus and techniques appear in Refs. 4 and 5. An effusive flow of yttrium or scandium vapor was provided by the oven system shown in Fig. 1. A commercially available electrically heated graphite oven (Astro Industries, model 1000-2560-PP) was modified to accomplish the experimental objectives. A major change was the installation of an oven liner to separate the interior hot zone from the surrounding graphite heat shields and heating elements. This cylindrical liner was made of either pure tantalum or a 90% tantalum/ 10% tungsten alloy of 1.5 mm thickness. The liner served to protect the graphite oven components from the effects of the yttrium, scandium, and halogen gases. The liner also provided for the containment of the effusive flow of either yttrium or scandium from a ~2250 °K tantalum crucible without contamination from degassing of the graphite oven components. This inner liner was connected directly to the reaction chamber as illustrated in Fig. 1. The liner had an inside diameter of 3.8 cm and a length of 28 cm. A background pressure of less than 10⁻⁵ Torr at operating temperature was readily achieved within the reaction chamber and oven liner. The surrounding graphite oven was purged with helium and maintained at a pressure of about 0.10 Torr by means of a separate oven pumping system. Measurements of the pressure within the reaction chamber were made with an ionization gauge (for pressures below 10⁻³ Torr), or a thermocouple gauge (for pressures above 10⁻³ Torr). Temperature estimates of the tantalum liner were made with an optical pyrometer sighted through the oven view port shown in Fig. 1. Typically, the oven

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was run at about 2000 °K for scandium and 2250 °K for yttrium. These temperatures provided vapor pressures of about 0.7 Torr within the tantalum crucible.⁶

The reaction chamber was a water cooled stainless steel tube, 14 cm long with a 12 cm inside diameter. The chamber was fitted with four view ports. Two ports provided access for the optical axis of a dye laser used to excite LIF; a third port at right angles to these was used for viewing fluorescence and chemiluminescence; the fourth port was used for occasional monitoring of the reaction flame intensity and provided access for injection of the halogen gases into the reaction zone. Collimating tubes of 18 cm length with internal apertures were installed on both laser ports to minimize laser scattering. Additional measures to reduce scattered light included the use of an internally threaded beam stop on the laser exit port and use of a stainless steel cone to define the optical cone for collection of the LIF. All view ports were purged with small flows of helium to prevent fogging by condensed particles. The optical layout is shown schematically in Fig. 2.

Three types of injectors were used for introduction of the halogen gases to the reaction chamber. The first of these, used primarily for preliminary studies of the $Y + Cl_2$ reaction system, consisted of a single watercooled copper tube of 0.023 cm i.d. The tube was pointed downstream with its exit 0.28 cm below the optical axis. A better injector which gave a more uniform density of halogen gas in the reaction chamber consisted of ten 0.04 cm diameter holes, equally spaced around the inner circumference of a ring flange of 7.5 cm i.d. located at the bottom of the reaction chamber, 3 cm below the optical axis. For studies of the reactions with iodine a third injector was built because the water



FIG. 2. Experimental arrangement employed for recording LIF excitation spectra.

cooling of the first two types caused clogging to occur. It consisted of a single uncooled stainless steel tube pointed downstream with its exit 0.7 cm below the optical axis. The iodine reservoir was maintained at 100 $^{\circ}$ C to provide an iodine vapor pressure of 65 Torr. The iodine metering valve and connecting lines were heated to prevent condensation.

The flow pumping system for the reaction chamber consisted of a 425 liter/min roughing pump, a 10 cm oil diffusion pump, and a liquid-nitrogen-cooled activated charcoal cryotrap.⁷

Laser excited fluorescence was viewed at right angles to the laser beam as indicated in Fig. 2. The conical light baffle, collimating apertures, and beam stop were effective in eliminating nearly all of the scattered laser light and background oven radiation from the field of view of the fluorescence detecting RCA 7265 photomultiplier. The fluorescence PMT signal was preamplified by a Tektronix 7A16A 225 MHz amplifier. The signal was then fed to a Biomation 8100 transient digitizer. The digitized output was sent to a Decgraphic GT-40 minicomputer for further processing. A second PMT, exposed to a portion of the dye laser beam, served as a trigger source for the transient recorder and occasionally as a monitor of the dye laser amplitude to provide normalization of the fluorescence intensity. With the use of thirteen different dyes, laser induced fluorescence could be excited over the wavelength interval from 3600-6500 Å. Fluorescence excitation spectra obtained by continuous scans of the dye laser wavelength had a spectral resolution of 0.05-0.10 nm.

The N₂ laser and dye laser were of our own construction. The N₂ laser delivered 1-1.5 mJ pulses of 8 nsec duration at a repetition rate of 15 Hz. The dye laser followed the standard Hansch design⁸ and consisted of the dye cell, a $20 \times$ expanding telescope, blazed grating, and output coupler. Scanning of the grating was accomplished by mounting the grating and dye laser on the base of a surplus scanning monochromator. The output of the dye laser could be set to any desired wavelength to within ± 0.05 nm. Typical dye laser output energies were 10^{-4} J.

A. Laser induced fluorescence detection

A schematic diagram of the apparatus used for the LIF experiments is shown in Fig. 2. Two types of signal processing were employed. Measurements of radiative lifetimes were performed by tuning the dye laser to a fixed wavelength corresponding to a given rare-earth halide transition of interest. The GT-40 minicomputer performed signal averaging over a time interval selected to include about four decay time constants. The averaging was done over as many laser pulses as was necessary to achieve a sufficiently high signal-to-noise ratio for accurate lifetime determinations.

A different method of signal averaging was used when the dye laser was continuously scanned to produce laser excitation spectra. After each laser pulse the digitized fluorescence signal was integrated over a selected time interval (typically 100-150 nsec) to give a total fluorescence signal. Each succeeding result was added to the previous signal until a set number of pulses (generally 45) had occurred. The final summed signal was then stored as part of a data array, and the process was initiated again. With a typical laser scan rate of 5 Å/ min and a repetition rate of 15 Hz, each summed data point represented 0.25 Å; thus, there would be 180 laser pulses per Å of dye laser scan. The final data



FIG. 3. Experimental arrangement employed for observations of chemiluminescence.

array could contain up to 1024 such data points corresponding to a laser scanning interval of 256 Å. The completed digitized scans were stored on floppy discs for further normalization to correct for the wavelength dependence of the dye laser output, for the wavelengthdependent response of the fluorescence detection system. and, in some cases, to subtract out residual scattered laser light appearing with the signal. These data then provided the input for graphical video displays and hard copies obtained with a data plotter. The software developed for the GT-40 minicomputer permitted pulseby-pulse normalization of the fluorescence intensity by the laser output intensity as the laser was scanned. In practice, this proved to be unnecessary and offered no advantage over the usual method employed which was to normalize the fluorescence output of a given run by the separately recorded wavelength-dependent laser output for that run.

B. Chemiluminescence recording

The apparatus of Fig. 3 was used for observations of chemiluminescence from the reaction zone. A lens with an f/5 entrance cone was used to focus chemiluminescence on the entrance slit of a 0.3 m McPherson model 218 monochromator. The output of an RCA 7265 PMT mounted on the monochromator exit slit was fed to a PAR model 126 lock-in amplifier with a model 116 differential preamplifier. The chemiluminescence was chopped at 1.2 kHz; a minature light bulb and photodiode built into the chopper housing provided a reference signal for the lock-in amplifier. The monochromator entrance slits were typically set at 260 μ m, and a grating blazed at 3000 Å with 1200 lines/mm was employed. Scan speeds of 20 to 50 Å/min were used. Chemiluminescence spectra were usually taken with use of 1:30 halogen-helium gas mixtures which gave very steady and reproducible flame intensities.

The chemiluminescence data presented in Sec. III are uncorrected for phototube response.

C. Reagents

Yttrium (99.9% pure) and scandium (99% pure) metals were obtained from Alfa Ventron. The metals were obtained in ingot form with samples ranging from 10 to 50 g in weight. The larger ingots were cut down to 10 g in size in an argon-filled glove box. The scandium was shipped in mineral oil which was removed prior to cutting by cleaning with trichloroethylene and acetone. Care was taken at all stages of handling and oven loading to prevent exposure of the samples to the atmosphere. The sources and stated purities of the halogen gases used were as follows: Cl_2 , Matheson Co., 99.965%; F_2 (5% mixture in helium), Air Products, 98%; Br_2 , E.M. Laboratories, 99.999%; I_2 , Fisher Scientific, 99.995%.

III. EXPERIMENTAL RESULTS

A. Chemiluminescence for yttrium-halogen reaction systems

The strong chemiluminescence from the $Y + Cl_2$ flame reported by Gole and co-workers¹ was easily observable in the apparatus of Figs. 1 and 3. Proper adjustment of the Cl₂ flow rate led to a blue flame, easily observable above the Cl₂ injector and surrounding region of the reaction chamber. Under these conditions the pressure in the reaction chamber was about 10⁻⁴ Torr. Figure 4 shows a comparison between the chemiluminescence we observe and that reported by Gole *et al.*¹ The chemiluminescence profiles are identical for both sets of measurements, except that the present data are shifted 25 Å toward the blue with respect to the previous data. As reported by Gole *et al.*, ¹ there appear to be no other emissions in the visible spectral region.

The smooth symmetrical shape of the narrow featureless band system of Fig. 4 is remarkable. Such a profile cannot be simulated from any known band systems of YCl. Since it seemed likely, contrary to the assertions of Gole *et al.*,¹ that this chemiluminescence does not arise from electronically excited YCl, a series of experiments was performed to identify the chemiluminescent emitter.

The intensity of the chemiluminescence of Fig. 4 was strongly dependent on Cl_2 flow rate. This dependence is shown by the data of Fig. 5 obtained by recording the chemiluminescence intensity as the flow rate of a 1:30 mixture of Cl_2 and helium was progressively increased. The data of Fig. 5 exhibit an initially supralinear growth in chemiluminescence intensity with Cl_2 pressure. This feature suggests that processes that are of higher than



first order in Cl_2 concentration are important in the chemiluminescence mechanism. One such possibility would be the reactions

$$Y + Cl_2 \stackrel{\mathcal{R}_1}{\to} YCl + Cl , \qquad (3)$$

$$YCl + Cl_{2} \xrightarrow{k_{2}} YCl_{2} + Cl , \qquad (4)$$

 $YCl_2 + Cl_2 \xrightarrow{k_3} YCl_3 + Cl , \qquad (5)$

$$YCl + Cl_2 \xrightarrow{R_4} YCl_2^* + Cl , \qquad (6)$$

$$\operatorname{YCl}_{2}^{*} \xrightarrow{R_{5}} \operatorname{YCl}_{2} + h\nu \quad . \tag{7}$$

The chemiluminescent emission of step (7) arises from electronically excited YCl_2 formed in Reaction (6).

Gole *et al.* have proposed that a second order dependence on Cl_2 concentration could be caused by collisionally induced emission from a long lived metastable state.^{1(a)} Such a mechanism would imply a pressure dependence for the apparent radiative lifetime associated with the chemiluminescence. We have found, however, in experiments described further in the following, that the radiative lifetime is pressure independent and too short to support the "collision induced emission" hypothesis.

The radiative lifetime of the emitter responsible for the chemiluminescence of Fig. 4 was measurable with the laser induced fluorescence apparatus of Fig. 2. In preparation for those measurements the Cl₂ flow rate (with no admixed helium) was adjusted to give a maximum chemiluminescence intensity (cf. Fig. 5). The dye laser was then scanned through the region from 3700 to 4100 Å and the laser induced fluorescence superimposed on the background chemiluminescence was averaged and recorded. Figure 6 shows the intensity variation with wavelength of the laser induced fluorescence; also shown in Fig. 6 is the distribution of background chemiluminescence of Fig. 4. The wavelength interval spanned by the laser induced fluorescence corresponds approximately to that of the chemiluminescence. The good agreement between intensity distributions shown in Fig. 6 suggests that the same molecular bands are likely to be responsible for both the fluorescence and the chemiluminescence.

A series of measurements of the decay of the laser induced fluorescence was made with the dye laser tuned to wavelengths in the region from 3880 to 3930 Å, where the chemiluminescence is strongest. No dependence of the fluorescence decay rate on either the wavelength or the Cl₂ pressure was observable. Pressures for the Cl₂



FIG. 5. Variation in chemiluminescence intensity from the Y/ Cl_2 reaction system with Cl_2 pressure. The open circles are the experimental data; the solid curve is the variation predicted with the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.

covered the range of values (cf. Fig. 5) which produced an observable chemiluminescence. The temporal decay of this laser induced fluorescence near 3900 Å is shown in Fig. 7. A simple exponential decay with a time constant of 450 ± 10 nsec was observed.

A simple experiment was performed to identify the chemiluminescent emitter of Fig. 4.⁹ Figure 8 shows the spectral profile of the chemiluminescence from the Y/Br_2 reaction system. The chemiluminescence for this system is somewhat narrower and shifted to the red of



FIG. 7. Semilogarithmic plot of the decay of LIF from the chemiluminescent emitter (YCl_2^*) of the Y/Cl_2 reaction system.

the Y/Cl_2 chemiluminescence. The spectral profiles of the Y/Br_2 and Y/Cl_2 reaction systems do not overlap strongly; it seemed feasible to look for chemiluminescence from the mixed halide YClBr which should exhibit a peak at a wavelength between the peaks for the Y/Br_2 and Y/Cl_2 systems. For these experiments separate flows of Br_2 and of a helium + Cl_2 mixture were introduced to the reaction chamber. Since the flows were introduced separately, there was no opportunity for the formation of CIBr molecules before the reaction of Y with Cl_2 or Br_2 . Figures 9(a), 9(b), and 9(c) show chemiluminescence profiles for the reaction of Y atoms with mixtures of Br_2 and Cl_2 which do indeed show a well defined third chemiluminescent band system located between the Y/Br_2 and Y/Cl_2 chemiluminescence features. The only possible explanation for the existence of the three separate chemiluminescent band systems of Figs. 9(a), 9(b), and 9(c) is that the three emitters are YCl₂, YClBr, and YBr₂.



FIG. 6. Laser induced fluorescence from the Y/Cl_2 reaction system in the 3900 Å region. The solid triangles show the spectral distribution of chemiluminescence presented in Fig. 4.

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FIG. 8. Chemiluminescence from the Y/Br₂ reaction system.

Radiative lifetime data analogous to those of Fig. 7 were obtained from LIF measurements on the YClBr and YBr₂ band systems. The radiative lifetimes were 240 ± 24 and 160 ± 16 nsec for the YClBr and YBr₂ band systems, respectively.

Additional experiments were performed on the Y/Cl_2 reaction system which lend support to the kinetic mechanism constituted by Reactions (3) to (7).

In addition to the relatively weak LIF associated with YCl₂, strong LIF signals were observable from yttrium atomic lines and from YCl band systems. Thus, it was possible to use the LIF signals to determine the dependences of the concentrations of Y, YCl, and YCl₂ on the concentration of Cl₂. These dependences are qualitatively described with the kinetic mechanism of Reactions (3) to (7). Figures 10-12 show the variations in the concentrations of Y, YCl, and YCl₂, respectively, on Cl₂ partial pressure. These data were obtained by monitoring the LIF signals as the pressure of a 1:30 mixture of Cl₂ with helium was systematically increased. Relationships are given in the Appendix which permit the calculation of the solid curves shown with the experimental data of Figs. 5 and 10-12. These curves are calculated with assumed values for the relative magnitudes of the rate constants k_1 , k_2 , k_3 , and k_4 . The assumed ratios of rate constants were $k_1: k_2: k_3 = 1:2.3:1.4$. The value of k_4 was taken to be negligibly small compared with k_2 . Our measured value for the radiative lifetime of the YCl₂ chemiluminescence (450 nsec) provides a determination of k_5 .

The decline in yttrium atom concentration with Cl_2 pressure is determined by the magnitude of k_1 . The ratio of k_2 to k_1 is determined by the rise and fall of YCl concentration with increasing Cl_2 pressure. The relative magnitude of k_3 is fixed by the dependence of YCl₂ concentration on Cl_2 pressure. Figure 13 shows the dependence of the concentration of YCl₃ on Cl_2 pressure predicted with the rate constants used for the computed curves of Figs. 5 and 10–12. No LIF signals were observed which could have originated from YCl₃. The computed curves of Figs. 5 and 10-12 would not be expected to give a good quantitative fit to the experimental data because of the necessarily oversimplified model adopted in the absence of complete knowledge of the flow and mixing characteristics of the reaction chamber. Nevertheless, the simple kinetic scheme of Reactions (3) to (7) apparently gives a good qualitative explanation for the behavior exhibited by the data of Figs. 5 and 10-12.

Figures 14 and 15 show the chemiluminescence spectra observed from the Y/F_2 and Y/I_2 reaction systems. The chemiluminescent emitters in these systems are presumably YF_2 and YI_2 in analogy with the Y/CI_2 and Y/Br_2 systems. Attempts to measure a readiative lifetime for the YF_2 chemiluminescence bands were unsuccessful because the LIF signal was very weak for these bands. The radiative lifetime measured for the Y/I_2 chemiluminescence band system was 260 nsec. The chemiluminescence of Fig. 14 for the Y/F_2 system is identical to that previously reported by Gole and coworkers¹; no previous data exist for the Y/I_2 system.

B. Chemiluminescence for scandium-halogen reaction systems

Observations of chemiluminescence were made for the Sc/F_2 , Sc/Cl_2 , Sc/Br_2 , and Sc/I_2 systems in the same manner that data were taken for the yttrium-halogen reaction systems. Figure 16 gives chemiluminescence spectra for the Sc/F_2 reaction. A strong 400 Å FWHM peak appears at 3500 Å, but very little emission was seen throughout the remainder of the visible spectrum. Very similar data were previously reported by Gole et al.¹ The chemiluminescence profile obtained for the Sc/Cl₂ reaction system of Fig. 17 differs from profiles observed for the other yttrium and scandium halides because small contributions are clearly present from identifiable band systems associated with the monohalide. Use of the spectroscopic data of Shenyavskaya¹⁰ permitted identification of the $\Delta v = 5, 4, \dots, -3, -4, -5$ sequences of the D - X system and $\Delta v = 4$, 3, 2, and 1 sequences of

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the B-X system in ScCl. The majority of the chemiluminescence for the Sc/Cl₂ reaction system, however, ap pears to originate from polyatomic emission bands. A strong 400 Å FWHM peak was observed, centered near 3500 Å. Previous chemiluminescence data for the Sc/ Cl₂ reaction system have been reported.^{1(a)}

Chemiluminescence profiles for the Sc/Br_2 and Sc/I_2 systems are given in Figs. 18 and 19. These profiles

are characterized by two broad emission features which together encompass the visible spectral region. It must be noted that since the chemiluminescence data are uncorrected for photomultiplier response, the decline in intensity of the Sc/I₂ chemiluminescence beyond 6000 Å may be primarily caused by the reduced PMT response. The Sc/I₂ chemiluminescence is unique in that the blue spectral feature near 4000 Å is a minor component of the total chemiluminescence in contrast to the other yttrium



FIG. 10. Variation in the concentration of Y atoms with Cl_2 pressure. The open circles are the experimental data; the solid curve is the variation predicted with the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.



FIG. 11. Variation in the concentration of YCl molecules with Cl_2 pressure. The open circles are the experimental data; the solid curve is the variation predicted with the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.



FIG. 12. Variation in the concentration of YCl_2 molecules with Cl_2 pressure. The open circles are the experimental data; the solid curve is the variation predicted with the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.



FIG. 13. Predicted variation in YCl_3 concentration with Cl_2 pressure based on the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.



and scandium halides.

Attempts were made without success to excite enough LiF from the chemiluminescent band systems of the scandium halides to measure radiative lifetimes for the chemiluminescent emitters.

IV. DISCUSSION

The studies reported here have established that the chemiluminescences of the Y/Cl_2 and Y/Br_2 reaction systems originate from electronically excited YCl_2^* and YBr_2^* molecules instead of electronically excited YCl^* and YBr^* monohalide molecules as was previously thought. This conclusion is based on several observations:

(1) Chemiluminescence from mixtures of Cl_2 and Br_2 gases reacting with Y atoms exhibits a prominent third feature near 3975 Å in addition to the features found at 3920 and 4025 Å, respectively, in the Y/Cl₂ and Y/Br₂ reaction systems. If the chemiluminescence had originated from the monohalides via Reaction (1) as asserted by Gole *et al.*,¹ then the third chemiluminescent feature would not have appeared in the $(Cl_2 + Br_2)/Y$ reaction system. If the chemiluminescence had originated from the trihalides YX₃, there would have been spectral features present from YClBr₂^{*} and YBrCl₂^{*} in addition to those from YCl₃^{*} and YBr₃^{*}.

(2) Qualitative studies of the dependence of LIF from Y, YCl, and from the chemiluminescent emitter (YCl_2) on Cl_2 pressure for the Y/Cl₂ reaction system show that the chemiluminescent emitter cannot be either YCl₃ or YCl. The observed and predicted dependence of the





FIG. 16. Chemiluminescence from the Sc/F_2 reaction system.

LIF from YCl on Cl_2 pressure is measurably different from the dependence observed and predicted for the chemiluminescent emitter. Moreover, the predicted dependence of the concentration of YCl₃ pressure is drastically different from that observed for the chemiluminescent emitter (i.e., the concetration of YCl₃ approaches a constant maximum value at high Cl_2 pressures).

(3) The measured radiative lifetime for the Y/Cl_2 chemiluminescent emitter is 450 nsec compared with measured radiative lifetimes for YCl bands of 21-36 nsec.

(4) The narrow featureless peak of the chemiluminescence spectral profile cannot be plausibly simulated from relatively simple YCl diatomic emission bands.

Although comparable studies to those described for the Y/Cl_2 and Y/Br_2 systems were not made for the other yttrium and scandium halide reaction systems, it seems quite likely that the singular spectral features noted in each of these reaction systems in the 3500-4300 Å spectral region originate from the electronically excited dihalides YX_2^* or ScX_2^* . Measured radiative lifetime values for the YCl_2 , YBr_2 , YClBr, and YI_2 chemiluminescent bands were 450, 160, 240, and 260 nsec, respectively.

Thermochemical considerations show that the kinetic model of Eqs. (3)-(7) can account for the observed chemiluminescence from YCI^{*} only if some of the molecules formed in the first step are highly vibrationally excited. Unfortunately, no direct measurements of bond energies for the yttrium halides are available. It is possible, however, to make estimates of bond energies for yttrium chlorides with methods that have given good results when applied to the scandium fluorides, for which direct measurements are available. Bond energy estimates and experimental values are summarized in Table I. Two types of bond energy estimates are given in Table I. The first of these is a Birge-Sponer extrapolation based on the spectroscopic data of Janney¹¹ with an empirical correction to account for the ionic character of the molecules following the method of Hildenbrand.¹² This type of estimate is expected to lead to underestimation of

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FIG. 17. Chemiluminescence from the Sc/Cl_2 reaction system.

bond energies. A second type of estimate has been given by Krasnov and Timoshinin,¹³ who used a potential function model with polarizable ions for calculation of bond energies. The estimates of Krasnov and Timoshinin are in good agreement with experimental data for the yttrium and scandium halides as is shown in Table I. Use of the estimated dissociation energies of Krasnov and Timoshinin and the known dissociation energy of Cl_2 (58 kcal/mole)¹⁴ leads to excergicities of 53 kcal for Reaction (3) and 61 kcal/mole for Reaction (4). These values would be increased by about 6 kcal/mole if it is assumed that all of the yttrium flow translational energy appears as energy release in the reaction products. The blue chemiluminescence from Y/Cl_2 has a short wavelength cutoff of 3825 Å which corresponds to an energy release of at least 75 kcal/mole. There is therefore an energy discrepancy of at least 75-67=8 kcal/mole for Reaction

TABLE I. Estimated bond energies (kcal/mole). Top row: potential function model^a; bottom row: experimental.^b

Halide	D _{MX}	D _{XM-X}	D _{X2M-X}	D _{MX3}
Y + C1	111(88)°	119	128	358
	• • •	• • •	•••	•••
Y+F	154(152)°	155	155	464
	143.6 ± 5	143.4 ± 7	166 ± 10	453
Sc + F	134(136) ^c	142	151	427
	140.8±3	140.3 ± 5	157 ± 7	438

^aK. S. Krasnov and V. S. Timoshinin, High Temp. 7, 333 (1969).

^bK. F. Zmbov and J. L. Margrave, J. Chem. Phys. 47, 3122 (1967).

^cCorrected Birge-Sponer extrapolation; D. L. Hildenbrand, in *Advances in High Temperature Chemistry*, edited by H. L. Eyring (Academic, New York, 1967), Vol. I. (6) which would require vibrational excitation of the YCl formed in Reaction (3) to vibrational levels of at least v = 8. Moreover, a maximum energy release of Reaction (3) of 59 kcal/mole is 16 kcal/mole too low to permit the direct formation of electronically excited YCl at wavelengths as short as 3825 Å.

The foregoing thermochemical estimates require that a substantial fraction of the energy release of Reaction (3) resides in vibrational excitation of the YCl bond. Black body radiation from the oven effectively prevents the direct observation of infrared emission from such vibrationally excited YCl molecules.

In summary, the results of this study suggest that the chemiluminescence observed from the Y/Cl_2 reaction system originates from electronically excited YCl_2^* formed in the reaction

$$YCl^{\intercal} + Cl_2 - YCl_2^{\intercal} + Cl , \qquad (8)$$

where YCl[†] denotes YCl vibrationally excited to levels of at least v = 8. Moreover, there is no present evidence that electronically excited YCl^{*} molecules are formed in Reaction (3). It appears likely that an analogous situation exists for reactions of the other yttrium- and



FIG. 18. Chemiluminescence from the Sc/Br_2 reaction system.

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scandium-halogen reaction systems. Only in the Sc/F_2 and Y/F_2 cases is there enough energy release available that no vibrational excitation of the monohalide is required in formation of the dihalide.

It should be noted that a reaction mechanism proposed for the formation of electronically excited BaCl^{*}₂, NaCl^{*}₂, NaF^{*}₂, CaF^{*}₂, CaCl^{*}₂, and CaBr^{*}₂¹⁵⁻¹⁸ would not require vibrationally excited monohalides as precursors to the formation of the electronically excited dihalide. This mechanism requires the stabilization of a longlived complex denoted by $(MX^*_2)^{\dagger}$ formed by the direct reaction of a metal atom M with the halogen molecule X_2 :

 $M + X_2 - (MX_2^*)^{\dagger} \text{ (formation)}, \qquad (9)$

 $(MX_2^*)^{\dagger} + Q \rightarrow MX_2^* + Q$ (stabilization), (10)

$$MX_2^* \rightarrow MX_2 + h\nu$$
 (radiation). (11)

This mechanism would not, however, lead to the formation of mixed halides such as the YClBr molecules observed to contribute to the chemiluminescence of Figs. 9(a), 9(b), and 9(c). It should also be noted that in further study¹⁹ of the Ba/Cl₂ reaction system, Wren has rejected the mechanism of Reactions (9)-(11) in favor of the two-step process involving formation of vibrationally excited monohalide molecules:

$$Ba + Cl_2 \rightarrow BaCl^{\dagger} + Cl , \qquad (12)$$

$$BaCl^{\dagger} + Cl_{2} - BaCl_{2}^{*} + Cl . \qquad (13)$$

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APPENDIX. KINETIC MODEL FOR THE $\rm Y+Cl_2$ REACTION SYSTEM

Differential rate equations for the processes defined in Eqs. (3) to (7) are

 $d[Y]/dt = -k_1[Y][Cl_2],$ (A1)

$$d[YC1]/dt = -k_{24}[YC1][C1_2] + k_1[Y][C1_2], \qquad (A2)$$

$$d[YCl_2]/dt = -k_3[YCl_2][Cl_2] + k_{24}[YCl][Cl_2], \qquad (A3)$$

$$d[\text{YCl}_2^*]/dt = k_4[\text{YCl}][\text{Cl}_2] - k_5[\text{YCl}_2^*], \qquad (A4)$$

$$d[\mathrm{YCl}_2]/dt = k_3[\mathrm{YCl}_2][\mathrm{Cl}_2] , \qquad (A5)$$

where $k_{24} = k_2 + k_4$ and the backward rates can be neglected under the present experimental conditions. The equations are integrated with the assumptions that at time t = 0 the Y atoms and Cl₂ molecules are uniformly mixed and that reaction proceeds until the time $t = \tau$ at which



FIG. 20. Variation in the concentrations of components of the Y/Cl_2 reaction system with Cl_2 pressure predicted with the kinetic model discussed in the Appendix. The ordinate scale gives the Cl_2 pressure in mTorr multiplied by the factor of 30.

LIF is observed. Moreover, it is assumed that since $[Y] \ll [Cl_2]$ in the present experiments, then the concentraction $[Cl_2]$ can be considered a constant; it is also assumed that $k_4 \ll k_2$. The initial conditions at t = 0 are

$$[Y] = [Y]_0$$
 and $[YC1] = [YC1_2] = [YC1_2^*] = [YC1_3] = 0$.

Solutions for the species concentrations with these approximations are

$$\begin{split} [Y] &= [Y]_{0} \exp(-k_{1}[Cl_{2}]\tau) , \end{split} \tag{A6} \\ [YCl] &= k_{1}[Y]_{0} [\exp(-k_{2}[Cl_{2}]\tau) - \exp(-k_{1}[Cl_{2}]\tau)] / (k_{1} - k_{2}) , \end{aligned} \tag{A7} \\ [YCl_{2}] &= k_{1} k_{2} [Y]_{0} \{ [\exp(-k_{3} [Cl_{2}]\tau) - \exp(-k_{2} [Cl_{2}]\tau)] / (k_{2} - k_{3}) - [\exp(-k_{3} [Cl_{2}]\tau) - \exp(-k_{1} [Cl_{2}]\tau)] / (k_{1} - k_{2}) , \end{aligned} \tag{A8} \\ [YCl_{8}^{*}] &= k_{1} k_{4} [Y]_{0} [Cl_{2}] \{ [\exp(-k_{5}\tau) - \exp(-k_{2} [Cl_{2}]\tau)] / (k_{2} [Cl_{2}] - k_{5}) - [\exp(-k_{5}\tau)] \end{split}$$

$$-\exp(-k_1[\operatorname{Cl}_2]\tau)]/(k_1[\operatorname{Cl}_2]-k_5))/(k_1-k_2), \qquad (A9)$$

$$[YCl_3] = [Y]_0 \{ 1 + [k_1 k_2 (k_2 - k_1) \exp(-k_3 [Cl_2] \tau) - k_1 k_3 (k_3 - k_1) \exp(-k_2 [Cl_2] \tau) + k_2 k_3 (k_2 - k_1) \exp(-k_1 [Cl_2] \tau)] / (k_1 - k_2) (k_1 - k_3) (k_2 - k_3) \} .$$
(A10)

The experimental data were fitted to Eqs. (A6)-(A9) using a least squares routine described by Bevington.²⁰ The relative rate constants giving a best fit to the experimental data were

$$k_1 \tau = (3.9 \pm 0.3) \times 10^3 \text{ Torr}^{-1}$$
,
 $k_2 \tau = (8.8 \pm 0.7) \times 10^3 \text{ Torr}^{-1}$,
 $k_3 \tau = (5.5 \pm 2) \times 10^3 \text{ Torr}^{-1}$,
 $k_3 \tau = 15 \pm 3$.

The fit was most sensitive to the choice of values for $k_1\tau$ and $k_2\tau$. Figure 20 shows a composite of the concentrations calculated with these parameters.

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