IF(A-X, B-X) CHEMILUMINESCENCE OF FLUORINE-IODIDE SYSTEMS IN A CROSSED MOLECULAR BEAM EXPERIMENT

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Very weak visible IF(A-X) and (B-X) chemiluminescence was observed in connection with the F + I₂, ICl, IBr reaction systems as studied in a single-stage molecular beam apparatus with two crossed effusive nozzles. In an earlier communication [1] we reported a first attempt at spectral resolution of the light emission associated with the F + I₂ system. There we attributed the spectrum to the reaction of F atoms with the trihalogen radical I₂F. The existence of this light-emitting reaction step had been verified in a molecular beam experiment by Kahler and Lee, yet without recording a spectrum of the emitter. In their experiment the trihalogen radicals, e.g. XIF (X=Cl, I), were formed by reactions of supersonically seeded F₂ above distinct translational threshold energies according to: F₂ + XI → XIF + F. It could be shown that this step including the subsequent reaction of F + XIF → XF + IF obeys bimolecular dynamics and hence proceeds as an elementary reaction [2]. We were able to extend our earlier work with a more sensitive detection system [3]. Hence at a collision energy of ~3.2 kJ mol⁻¹ it was possible to obtain a vibrational product state analysis of the IF(B) state. The chemiluminescence spectrum for the reaction F + I₂F is depicted in Fig. 1a.

Fig. 1b shows the corresponding IF(B) vibrational product state distribution. The population limit closely corresponds to the enthalpy according to ΔH° = -248.5 kJ mol⁻¹. The distribution is characterized by a "vibrational temperature" Tᵥ ~ 800 K. The latter observation is essentially identical with results of Whitehead et al. for a low-pressure I₂/F₂ flame [4], where the reaction mechanism of Lee et al. is also anticipated. In our experiment the above reaction sequence is most likely induced by the approximately 5% undissociated F₂ internally excited in the microwave discharge.

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FIGURE 1a. Chemiluminescence spectrum of the reaction F + I$_2$F as observed from a crossed molecular beam experiment of F(F$_2$) + I$_2$.

FIGURE 1b. The IF(B) vibrational product state distribution in agreement with results of Whitehead et al. for a low-pressure I$_2$/F$_2$ flame confirms the work of Kahler and Lee [2].
Much weaker chemiluminescence spectra were recorded from the systems F + ICl and IBr only at iodide flows approximately one order of magnitude higher (F_2 = 18 SCCM in all experiments; I_2 = 1.4; ICl = 17; IBr ~10 SCCM). Under these conditions a further increase in iodide flow or addition of Ar resulted in a strong nonlinear increase in chemiluminescence intensity without changing the spectral distribution, whereas at iodide flows of ~2 SCCM the overall chemiluminescence signal showed a linear flow dependence. The spectra for the F/ICl and F/IBr systems are shown in Fig. 2a.

FIGURE 2a. Chemiluminescence spectra for the F/ICl and F/IBr systems under enhanced flow conditions.
FIGURE 2b. The non-statistical IF(B) vibrational product state distributions are normalized with respect to the highest populated B state level. A different mechanism must be responsible for the IF(B) state excitation which may not depend on the XIF intermediate.

They are similar and significantly differ from the emission due to the F + I₂F reaction as shown in Fig. 1a. The population analysis for both systems resulted in more non-statistical distributions which are nearly identical within the error bars, as shown in Fig. 2b. If an interpretation in terms of the Kahler and Lee mechanism is again attempted here this leads to several contradictions. Firstly the different energetics of the two reaction systems should be reflected by the chemiluminescence spectra. Secondly, the threshold for the formation of CIIF is significantly higher than for I₂F (24.7 kJ mol⁻¹ compared with 17.6 kJ mol⁻¹) [2]. Thirdly, one would expect the formation of electronically excited FCl and FBr as anticipated by Kahler and Lee rather than excited IF [2]. Finally, the enthalpy for the reaction F + CIIF with ΔH₀° = -182.1 kJ mol⁻¹ is far from sufficient to populate the B state of IF where at least 226.7 kJ mol⁻¹ is required. (Although the stability of BrIIF is not exactly known, the argument also holds for the F + BrIIF reaction).

Hence for the F/ICl and F/IBr systems under given conditions there must be a different mechanism responsible for the IF(B) state excitation which may not depend on the XIF intermediate.
REFERENCES


