REACTIONS OF HCCl WITH NO_x

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INTRODUCTION

The combustion chemistry of chlorine containing compounds is of interest in both fossil-fuel combustion and hazardous waste incineration technology. Modeling these processes requires fundamental kinetic data on elementary radical-molecule reactions. We report here product channel measurements on reactions of HCCI with NO and NO_2 using eximer laser photolysis and infrared laser absorption spectroscopy.

METHODS

A vacuum system with a series of mirrors to bend the laser light, as in figure 1, was used to perform the reaction. A detector for the both the reaction and reference cells were attached to a oscilloscope which was connected to the computer in turn. The pressure of the reactant gasses was varied in order to find the optimal pressure ratio (Fig. 2). The various hypothesized reactions were as follows:

$$HCClBr_2 + h\nu(193\ nm) \rightarrow HCCl + 2\ Br$$

$$HCCl + NO_2 \rightarrow HCN + ClO_2$$

$$\rightarrow CO + HCl + NO$$

$$\rightarrow NCO + HClO$$

$$\rightarrow HCNO + ClO$$

Secondary Reactions

$$NCO + NO_2 \rightarrow N_2O + CO_2$$

$$\rightarrow 2NO + CO$$

$$HCClBr_2 + h\nu(193\ nm)\ HCCl + 2\ Br$$

$$HCCl + NO \rightarrow HCNO + Cl$$

$$\rightarrow HCl + NCO$$

$$\rightarrow HCN + ClO$$

$$\rightarrow HNCl + CO$$

Secondary Reactions

$$NCO + NO \rightarrow CO_2 + N_2$$

$$\rightarrow CO + N_2O$$

The products were detected by means of rotational infrared spectra. The reactants were excited by an eximer laser at 193 nm and the products were detected using a transient signal (Fig. 3) collected with the oscilloscope. The products detected were as follows:

For reaction with NO_2:

$$N_2O\ (00^00,\ J=22) + h\nu(2241.117\ cm^{-1}) \rightarrow N_2O\ (00^01,\ J=23)$$

For reaction with NO:

$$N_2O\ (00^00,\ J=4) + h\nu(2227.843\ cm^{-1}) \rightarrow N_2O\ (00^10,\ J=5)$$

$$CO_2\ (00^00,\ J=6) + h\nu(2354.434\ cm^{-1}) \rightarrow CO_2\ (00^01,\ J=7)$$

$$HCNO\ (0000^00^0,\ J=14) + h\nu(2184.608\ cm^{-1}) \rightarrow HCNO\ (0100^00^0,\ J=13)$$

RESULTS

In comparing the differences in the intensity of the resonance and off resonance transient signals the branching fraction (ϕ) of each reaction. The HCCl + NO_2 reaction produced the NCO with ϕ=0.0336. The HCCl + NO reaction produced NCO with ϕ=0.239 and HCNO with ϕ=0.70.

CONCLUSION

The reactions behaved very similarly, as predicted, with NO working better than NO_2. The NO reaction produced the predicted products in greater amounts. This was determined to be due to the fact that NO_2 absorbs light more readily. Therefore there were not as many radicals formed to react with the NO_2. HCNO was thought to be the primary product channel of the reactions and proved to be in the reaction with NO. It was assumed that this would be found true for the reaction with NO_2 as well.

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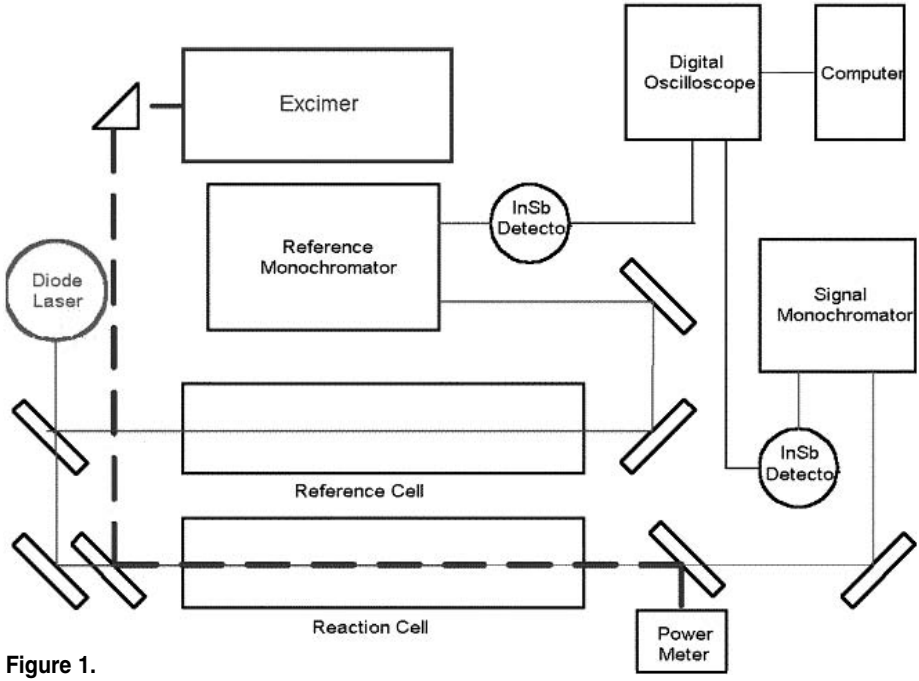

Figure 1.

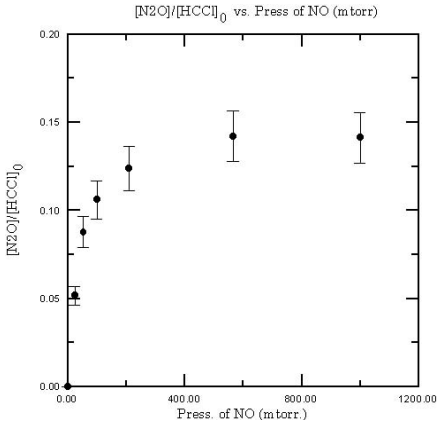

Figure 2.

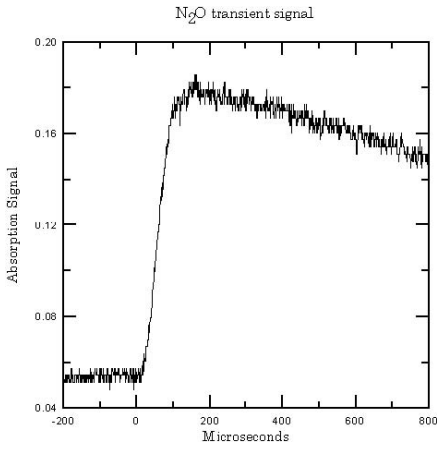

Figure 3.