ABSTRACT

Time profiles of ClN_3, $ClN_3(\nu_{asym})$, and NCl(a) were recorded under conditions where complete and incomplete loss of the parent ClN_3 occurred. Laser photolysis at 248 and 193 nm, flashlamp photolysis, and an electric discharge cavity were used to initiate dissociation. A new channel for the reaction of ClN_3 + NCl(a) was found which produces $ClN_3(\nu_{asym})$ with a rate of $1.4 \cdot 10^{-12}$ $cm^3/(molec \cdot s)$. The channel responsible for the decomposition of ClN_3 generates NCl(a) with unity yield.

The bimolecular rate of $ClN_3(\nu_{asym})$ + NCl(a) $\longrightarrow$ $2 \cdot NCl(a) + N_2(\nu)$ and radiative rate from $ClN_3(\nu_{asym})$ are $1.1 \cdot 10^{-11}$ and 2000 s^{-1} respectively. Rates for the reactions: $ClN_3(\nu_{asym}) + N_2(\nu) \longrightarrow ClN_3(2 \cdot \nu_{asym}) + N_2$, $ClN_3(2 \cdot \nu_{asym}) + N_2(\nu) \longrightarrow NCl(a) + N_2(\nu) + N_2$, and radiative rate of $ClN_3(2 \cdot \nu_{asym})$ are estimated to be $2 \cdot 10^{-13}$, $2 \cdot 10^{-13}$ $cm^3/(molec \cdot s)$, and 2000 s^{-1} respectively. A kinetic model incorporating the reactions of state-selected ClN_3, NCl, N_2, Cl, and N_3 is developed that gives reasonable agreement with experiment. The model incorporates chains carried by NCl(a), $N_2(\nu)$, and N_3. The NCl(a) chain dominates the decomposition of ClN_3 at low densities; the $N_2(\nu)$ chain becomes important at high $N_2(\nu)$ densities. The latter may be of significance for a chemical NCl-I laser system. The uncertainty in the products of NCl(a) self-quenching (either $2 \cdot Cl$ or Cl_2) limits our knowledge of the Cl atom density. The chain carried by Cl and N_3 was found to play a minor role in the decomposition even with NCl(a) self-quenching producing Cl atoms.