Kinetics of the Reactions of Atomic Chlorine with CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$

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Amines are thought to play an important role in secondary organic aerosol (SOA) formation in marine environments,[1] and atomic chlorine is a potentially important initiator of amine oxidation in such environments.[2] While one study of the dynamics and product branching ratio of the Cl + CH_3NH_2 reaction is reported in the literature,[3] there are no published kinetic data for any of the three title reactions. Using laser flash photolysis (LFP) studies of Cl kinetics in conjunction with supporting electronic structure calculations, we have investigated the kinetics of the three title reactions. In all experiments, atomic chlorine was generated by 248 nm LFP of phosgene (Cl_2CO). Dark reaction of amines with (presumably) HCl generated by hydrolysis of phosgene on the reactor walls was an experimental complication that had to be limited by careful choice of experimental conditions and dealt with in the data analysis. All three reactions studied are extremely fast, with measured 298 K rate coefficients ranging from 3.5 to 4.2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. Electronic structure calculations confirm that reaction proceeds via formation of pre-reactive complexes that dissociate to yield H-transfer products over barriers that lie below reactants in energy. Characteristic times for loss of marine boundary layer amines by reaction with Cl and OH[4-6] appear to be similar in magnitude.

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References

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