REACTIONS OF CHLORINE ATOMS WITH A SERIES OF AROMATIC HYDROCARBONS

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Aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), are present in urban and rural atmospheres. Reactions of PAHs with Cl atoms may occur in the marine boundary layer and in coastal regions. To assess the importance of these reactions and to investigate whether any unique chlorine-containing products are formed from these reactions, we have measured rate constants for the gas phase reactions of Cl atoms with toluene-d_8,1,3,5-trimethylbenzene (1,3,5-TMB), naphthalene, 1-methylnaphthalene-d_{10}, 1- and 2-methylnaphthalene (1- and 2-MN), 1- and 2-ethylnaphthalene (1- and 2-EN) and the dimethylnaphthalenes (DMNs) at 296 ± 2 K. A relative rate technique was used, and using our measured rate constant for the reaction of Cl atoms with 1,3,5-TMB of 2.42 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, the rate constants (in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}) are: naphthalene, £0.0091 ± 0.0003; 1-MN, 1.21 ± 0.16; 2-MN, 1.05 ± 0.13; 1-EN, 2.12 ± 0.35; 2-EN, 1.38 ± 0.27; 1,2-DMN, 3.61 ± 0.68; 1,3-DMN, 2.90 ± 0.22; 1,4-DMN, 2.93 ± 0.30; 1,5-DMN, 2.31 ± 0.19; 1,6-DMN, 2.15 ± 0.20; 1,7-DMN, 3.05 ± 0.34; 1,8-DMN, 3.07 ± 0.44; 2,3-DMN, 2.93 ± 0.49; 2,6-DMN, 2.34 ± 0.18; and 2,7-DMN, 2.00 ± 0.22, where the indicated errors are two standard deviations and do not include the uncertainty in the rate constant for 1,3,5-TMB.

The measured deuterium isotope effects for the toluene-d_8 and 1-methylnaphthalene-d_{10} reactions indicate that the reactions proceed by initial H- (or D-) atom abstraction. The products identified and quantified from the toluene and 1-methylnaphthalene reactions using gas chromatography and *in situ* direct air sampling atmospheric pressure ionization tandem mass spectrometry were benzaldehyde (84 ± 7% yield) and benzyl alcohol (11 ± 2% yield) from toluene and 1-naphthaldehyde (~36%, lower limit to yield) and 1-naphthyl alcohol (~12%, lower limit to yield) from 1-methylnaphthalene. These products confirm that H-atom abstraction is the dominant, if not sole, reaction pathway for the alkylbenzenes and alkylnaphthalenes, consistent with the 100-fold lower rate constant measured for naphthalene compared to the alkylnaphthalenes and with the measured deuterium isotope effects.