Reactions of Cl and Br With Selected VOCs: Kinetic Measurements and Theoretical Analysis

John Roscoe (1), Matthias Olzmann (2), Binod Giri (3), Núria González-García (4), John M. H. Lo (5), Robert Marriott (5), Mariusz Klobukowski (6), and W. James Frazee (7)

(1) Chemistry Department, Acadia University, Wolfville, Canada (john.roscoe@acadiau.ca), (2) Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Karlsruhe, Germany (matthias.olzmann@kit.edu), (3) Alberta Sulfur Research Ltd., Calgary, Canada (brgiri@ucalgary.ca), (4) Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, (5) Alberta Sulfur Research Ltd., Calgary, Canada , (6) Chemistry Department, University of Alberta, Edmonton, Canada, (7) Chemistry Department, Acadia University, Wolfville, Canada

Rate coefficients have been measured as a function of temperature and pressure for the reactions of Br and Cl with a series of ethers and for the reactions of Cl with toluene and the xylenes. The reactions investigated in this work are found to proceed by hydrogen abstraction. The reactions of Br have significant activation energies while the reactions of Cl revealed little or no T-dependence over our temperature range of approximately 280 K to 360 K. None of the measured rate coefficients exhibited a discernable pressure dependence over our pressure range of approximately 100 to 800 Torr. The reactions of Br with diethyl ether, tetrahydrofuran and tetrahydropyran have similar rate coefficients over our temperature range. The reactions of Br with dimethyl ether and 1,4-dioxane have rate coefficients that are of comparable magnitude and are more than an order of magnitude smaller than those of the other ethers. The rate coefficients of the reactions of Cl with the ethers and with toluene and the xylenes are of comparable magnitude and are several orders of magnitude larger than those for the reactions of Br.

The reaction paths for the reactions of Br with tetrahydrofuran, tetrahydropyran and 1,4-dioxane and the reaction of Cl with 1,4-dioxane were examined by calculating single-point energies of stationary points along the potential energy surfaces for these reactions. Rate coefficients for the reactions were calculated from statistical rate theory and equilibrium constants, if necessary, from statistical thermodynamics. The results suggest that all the reactions proceed with the initial formation of van der Waals adducts. Formation of the adducts takes place without a barrier and the reaction then proceeds by intramolecular hydrogen abstraction. The reaction is endothermic for the bromine atom reactions and exothermic for the chlorine atom reactions.

In the reaction of Br with 1,4-dioxane, no low-lying transition state could be found for the intramolecular hydrogen abstraction within the adduct formed by Br with the dominant chair conformer. Instead, a chair-to-boat isomerization of this adduct occurs as the rate-determining step followed by a hydrogen abstraction within the boat conformer. If this isomerization is taken into account, a temperature dependence of the rate coefficients in excellent agreement with experiment is obtained. The reaction of Br with tetrahydrofuran is different in that isomerisation is not required for reaction. The most stable adduct does not correlate with any transition state and is therefore not reactive. However, several other adducts were identified, the lower of which provides a reaction path which gives excellent agreement with the experimental rate coefficients. The reaction of Cl with 1,4-dioxane differs from the Br atom reactions in that a reaction path exists where all the stationary points lie below the energy of the reactants. Again, at first adduct formation takes place with the chair conformer without a barrier and the transition state for the intramolecular hydrogen abstraction lies 8.5 kJ/mol above this adduct. Since all the stationary points lie below the reactants, this is a chemical activation reaction path and the overall reaction can occur with negligible activation energy, because the barrierless association is the rate-determining step. The existence of a low energy reaction path for intramolecular hydrogen abstraction from the chair conformer means that the isomerisation step, required in the Br atom reaction, is not required in the Cl atom reaction. The calculated rate coefficients for the reaction of Cl with 1,4-dioxane are again in good agreement with the experimental results.