ESTIMATION METHOD FOR OH ABSTRACTION RATE CONSTANTS

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There are many compounds for which OH abstraction rate constants may be required, as, for example, to determine the atmospheric lifetimes. It is not economically feasible to determine them all experimentally. For that reason, empirical estimation methods are useful.

Two factors are important in the development of such methods. The first is the validity of the methodology which is used, and the second is the database on which the method is calibrated. If the calibration rate constants are accurate, the predictions are more reliable and the success of the methodology can be evaluated.

A technique developed specifically for the estimation of OH abstraction rate constants for halocarbons containing at least one H-atom will be demonstrated. The method is based on based on a matrix of approximately thirty-five calibration reactions. Success of the method depends on the fact that group effects on the rate constants are approximately constant among different halocarbons, provided that one normalizes for the number of reactive C-H bonds and makes a correction for multiple group effects which occur when more than one group is attached to a given carbon atom,

New rate constant data, obtained by the relative rate technique, will be presented for the compounds C_2H_5Cl, C_2H_5Br, C_2H_5F, CH_3CN, CO, CH_2C1_2, and $CHFCl_2$ (21). The current group contribution factors derived from the calibration reactions will be shown, and some general factors which appear to determine the group contributions will be discussed.

Relative rate measurements as a function of temperature provide accurate ratios of pre-exponential factors. The data show that the A-factors (per H-atom) for all OH abstractions which have been studied are similar in magnitude. However, there may be a small dependence on reaction rate. A clear dependence of this type for the case of Cl-atom abstractions will be shown.

In addition to calibration of the estimation technique, the database can be used to demonstrate correlations with Cl, Br and I atom abstractions from the same halocarbons. Close correlations of the rate constants with C-H bond energies are also observed, and possible anomalies or errors in the bond energies can be detected. Specific examples of the C-H bond energies in CH_3CN and cyclopropane will be discussed.

Preference: Oral presentation.