BEBO CALCULATIONS OF KINETIC ISOTOPE EFFECTS FOR METHYL RADICAL REACTIONS WITH ALKANES AND KETONES

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Kinetic isotope effects for hydrogen abstraction reactions of methyl radicals with methane, ethane, propane, acetone, butanone-2, pentanone-3 and biacetyl have been calculated using the BEBO method, considering recent values for the Pauling constant and the noble gas parameters. The results were compared with the experimental data.

INTRODUCTION

In previous papers we have reported the evaluation of the activation energies for methyl radical reactions with ketones /1/ and alkanes /2/ using the BEBO procedure of Johnston /3/. We present here the kinetic isotope effects for these reactions calculated with revised input parameters suggested by Gilliom /4/ and with more recent input data for acetone and butanone-2.
THEORY AND INPUT DATA

The kinetic isotope effect \( \frac{k_H}{k_D} \) is given by (3):

\[
\frac{k_H}{k_D} = \frac{\omega_i}{\omega_i} \frac{f^{R_s}_{b^*} f^{R_s}_{b^*}}{f^{R_s}_{b^*} f^{R_s}_{b^*}} \frac{1}{1 + \lambda} 
\]

(1)

where the \( \omega \) and \( f \) factors are defined by Johnston (3). In order to obtain these factors, the properties of the activated complexes were calculated by means of the BEBO method from the equation:

\[
V = D_{XH}(1 - np) - D_{HY}m^q + D_{XY}B(nm)^{P\beta} [1 + B(nm)^{P\beta}] 
\]

(2)

The \( B \) factor and the Morse parameter, \( \beta \), were calculated using the conventional procedure (3) with a Sato constant of 0.5. In our calculations, recent noble gas parameters and a Pauling constant of 0.028 nm were taken into account, as suggested by Gilliom (4). Assuming that the bond distances and force constants of the deuterated and undeuterated complexes are identical, the activated complex properties were evaluated using the formulas given by Johnston (3).

Bond dissociation energies used in the BEBO calculations are listed in Table 1. For the C-H and C-C bonds, the distances were taken to be 0.109 nm and 0.153 nm (4), respectively. Vibrational frequencies and force constants were taken from Shimanouchi (5) and other sources (1).

RESULTS AND DISCUSSION

The calculated activation energies, \( E_{BEBO} \), and the known experimental values, \( E_{exp} \), are summarized in Table 1 (\( T = 550 \) K). Calculated kinetic isotope effects and available experimental data for three selected temperatures are listed in Table 2.