EFFECT OF HIGH PRESSURE ON THE KINETIC ISOTOPE EFFECT IN THE ABSTRACTION OF HYDROGEN AND DEUTERIUM ATOMS BY THE CUMYLOXY RADICAL

V. M. Zhulin, T. V. Lipovich, and V. L. Antonovskii

UDC 541.12.034.2:541.127:541.515

The abstraction of a deuterium atom from the CD₃ group in deuterotoluenes is more accelerated by pressure than the abstraction of a hydrogen atom from the toluene methyl group, which is reflected in a decrease in the kinetic isotope effect k_H/k_D with increasing pressure. The value for $k_H/k_D = ([DMPC]/[AP])_H/([DMPC]/[AP])_D$ were determined by measurement of the amounts of dimethylphenylcarbinol (DMPC) and acetophenone (AP) formed upon the decomposition of 0.1 mole/liter dicumyl peroxide in C₆H₅CH₃, C₆H₅CD₃, and C₆D₅CD₃ at 399°K

p, MPa 0.1 20 200 500 700 $k_{\rm H}/k_{\rm D}$ 3.5 3.6 2.8 2.1 2.2

The difference in the volume effects for H and D abstraction is 4.1 cm^3 /mole.

These results are not in accord with our previous conclusions of greater acceleration of rapid hydrogen abstraction reactions by pressure [1]. This discrepancy may be attributed to the possibility that the reaction also proceeds by quantum-chemical tunnelling.

LITERATURE CITED

1. V. M. Zhulin, O. B. Rudakov, and G. A. Stashina, Izv. Akad. Nauk SSSR, Ser. Khim., 1205 (1985).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, p. 2831, December, 1985. Original article submitted August 5, 1983.