GENERATION AND REVERSIBLE DIMERIZATION OF THE PERFLUORO-TERT-HEXYL RADICAL

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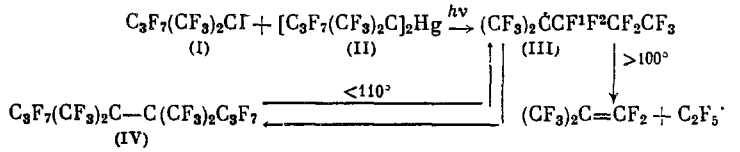
UDC 541.127:541.141.7:
547.254.9'161:541.515

The perfluoro-tert-hexyl radical (III) is generated in solution upon the combined UV photolysis of perfluoro-tert-hexyl iodide (I) and bis(perfluoro-tert-hexyl) mercury (II). Radical (III) is not formed by the separate photolysis of (I) and (II) under the same conditions. The EPR spectrum of (III) has the following coupling constants: $a_F(6F) = 18.4$, $a_F(F^1) = 18.1$, $a_F(F^2) = 26.8$, $a_F(2F) = 4.2$, $a_F(3F) = 1.6$ Oe.



The kinetics for the annihilation of (III) corresponds to its recombination with rate constant $k = 3.5 \cdot 10^5$ liters/mole·sec at 20°C. The addition of pyridine by analogy with our previous work [1] hinders the recombination, $k = 1 \cdot 10^4$ liters/mole·sec. The formation of dimeric product (IV) was established by ^{19}F NMR spectroscopy.

The kinetics for the annihilation of (III) is more complicated above 100°C. The first-order decomposition of (III) with $k = 1.5$ sec^{-1} to the unstable C_2F_5 radical and perfluoroisobutylene apparently occurs along with the second-order recombination. This scheme for the decomposition of (III) was postulated by Probst et al. [2] on the basis of the results for the thermolysis of (I).

The photolysis of a mixture of (I) and (II) at 40°C for 5 h leads to the accumulation of dimer (IV). A steady-state concentration (C_e) of radical (III) specific for a given temperature is determined by the reversible dissociation of (IV) above 110°C. The heat of dimerization of (III), $-\Delta H = 47 \pm 5$ kcal/mole, was determined from the temperature dependence of C_e.

LITERATURE CITED

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A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, p. 2426, October, 1988. Original article submitted April 18, 1988.

 0568-5230/88/3710-2188$12.50