Kinetic studies of the OH($X^2\Pi$) and O(^3P) initiated reactions with selected short chain iodoalkanes

Shaoliang Zhang,[1,2,3] Rafal S. Strekowski,[1,2,*] Anne Monod,[1,2] Sasho Gligorovski,[1,2] Henri Wortham,[1,2] Loïc Bosland,[2] and Cornelius Zetzsch[3]

[1] Aix-Marseille Univ., Laboratoire Chimie Environnement, 13331 Marseilles cedex 03, France
Tel: (+33) (0)4 13 55 10 40, Fax (+33) (0)4 13 55 10 60, E-mail: rafal.strekowski@univ-amu.fr
[2] CNRS, FRE 3416, 13331, Marseilles cedex 03, France
[3] Institut de Radioprotection et de Sûreté Nucléaire, DPAM / SEMIC / LETR, Cadarache, France
[4] Atmos. Chem. Research Lab, BAYCEER, University of Bayreuth, Dr.-Hans-Frisch-Str. 1-3, D-95448 Bayreuth, Germany

A Flash Photolysis–Resonance Fluorescence (FP-RF) technique was used to investigate the kinetics of the OH($X^2\Pi$) radical initiated reactions with selected iodoalkanes (RI), namely CH_3I, CH_2I_2, C_2H_5I, n-C_3H_7I, iso-C_3H_7I, CHI_3 and O(^3P) radical initiated reactions with selected RI, namely CHI_3 and C_2H_5I. The reactions of OH($X^2\Pi$) radicals with RI were studied over the temperature range 295 – 390 K and pressure around 200 Torr of He.[1-3] The reaction of the OH($X^2\Pi$) radical with CHI_3 was studied at T=298K only. The reactions of O(^3P) radical with CHI_3 and C_2H_5I were studied over the temperature range 296 – 373K in 14 Torr of He. The experiments involved time-resolved RF detection of OH ($A^2\Sigma^+ \rightarrow X^2\Pi$ transition at λ=308 nm) and of O(^3P) (λ=130.2, 130.5, and 130.6 nm) following FP of the H_2O/He, H_2O/RI/He, O_3/He and O_3/RI/He mixtures. The OH($X^2\Pi$) and O(^3P) radicals were produced by FP in the vacuum-UV at wavelengths λ>120 nm using a Xe flash lamp. Measured rate coefficients for the reactions of OH($X^2\Pi$) and O(^3P) radicals with RI are described by the following Arrhenius expressions (units are $cm^3 molecule^{-1} s^{-1}$):

$$k_{OH+CH_3I} = (4.1 \pm 2.2) \times 10^{-12} \exp[(-1240 \pm 200)K/T]$$

$$k_{OH+CH_2I_2} = (4.2 \pm 0.5) \times 10^{-11} \exp[(-670 \pm 20)K/T]$$

$$k_{OH+CHI_3} = (1.6 \pm 0.1) \times 10^{-11}$$

$$k_{OH+C_2H_5I} = (5.6 \pm 3.2) \times 10^{-12} \exp[(-830 \pm 90)K/T]$$

$$k_{OH+n-C_3H_7I} = (1.7 \pm 0.9) \times 10^{-11} \exp[(-780 \pm 90)K/T]$$

$$k_{OH+iso-C_3H_7I} = (7.6 \pm 3.7) \times 10^{-12} \exp[(-530 \pm 80)K/T]$$

$$k_{O+CHI_3} = (1.8 \pm 2.8) \times 10^{-12} \exp[(+430 \pm 260)K/T]$$

$$k_{O+C_2H_5I} = (2.0 \pm 1.4) \times 10^{-11} \exp[(+140 \pm 110)K/T]$$

The implications of the reported kinetic results for understanding the degradation mechanisms of iodoalkanes in case of a nuclear power plant accident are discussed. Further, the OH radical and O atom attacks on RI, namely OH-addition, H-atom and I-atom abstraction reaction channels, are discussed.

THURSDAY

References

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