P-107

SPIN TRAPPING OF INTERMEDIATE RADICALS IN THE SOLID STATE GAMMA RADIOLYSIS OF PERFLUOROPOLYETHERS

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Significant features of the mechanism of the solid state gamma radiolysis of perfluoropolyethers was elecidated by trapping of reactive radicals intermediates as spin adducts with 2-Methylnitrosopropane (MNP) or in solid matrices at low temperature. Polyethers with repeating units $-[(OCF_2CF_2)_x(OCF_2)_y]_n$ (A), yield radicals of type $ROCF_2\cdot$ and $ROCF_2CF_2\cdot$, which are identified from their nitroxyls derivatives

$ROCF_2-\underset{R}{N}=O$ 2a $(F)_\beta$ = 12.4 (G) a (N)= 11.5 (G)

$ROCF_2CF_2-\underset{R}{N}=O$ 2a $(F)_\beta$ = 21.8 (G) 2a $(F)_\gamma$ = 2.5 (G) a (N) = 11.2 (G)

Clear evidence for radical $ROCF_2\cdot$ was also obtained from its polycrystalline spectrum.

Polyethers of formula $-[(OCF_2CF(CF_3))_x-(OCF_2)_y-]_n$ (B), yield radicals $ROCF_2\dot{C}(CF_3)-$, as major product, togheter with minor amount of $ROCF_2\cdot$.

$RCF_2\underset{\underset{R-N-O}{|}}{C}(CF_3)OR'$ 4-5 $a(F)_\gamma$ = 2. (G)

$ROCF_2-\underset{R}{N}=O$ 2a $(F)_\beta$ = 22.8 (G) a (N)= 11.2 (G)

The polycrystalline ESR spectrum of the pure compound show the presence of $ROCF_2\cdot$ and $RO\dot{C}F(CF_3)-$ as major products whilst the tertiary radical is not observed. These observations suggest that prominent processes in the radiolysis of A are C-C and C-O bond homolysis followed by β scission of the resulting alkoxy radicals

$$-OCF_2CF_2-O-CF_2CF_2-O- \longrightarrow -OCF_2CF_2\cdot + -OCF_2CF_2O\cdot$$

$$-OCF_2CF_2O\cdot \longrightarrow -OCF_2\cdot + CF_2O-$$

$$-OCF_2CF_2O- \longrightarrow 2\ -OCF_2\cdot$$

The same type of reaction may be invoqued to rationalize the formation of $ROCF_2\cdot$ and $RO\dot{C}F(CF_3)$ in the radiolysis of B; however the identification of the tertiary radical implies either the partecipation of a dissociative elctron capture during the irradiation

a - $R-OCF_2CF(CF_3)OR' + e \longrightarrow R-OCF_2\dot{C}(CF_3)OR' + F^-$

or Fluorine abstraction by primay $ROCF_2\cdot$ species during the warm up above 77 K.

b - $ROCF_2\cdot + ROCF_2CF(CF_3)OR' \longrightarrow ROCF_3 + ROCF_2\dot{C}(CF_3)OR'$

A slow thermal reaction of MNP with polyethers, yielding nitroxyls, has been observed and it is actually being investigated.

1 C. Lagercrantz: J. Phys. Chem., 75, (1971) 3466.

2 E.G. Janzen in 'Free radicals in Biology' vol. IV, ed. W.A. Pryor Academic Press, 1980.