

P-107

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

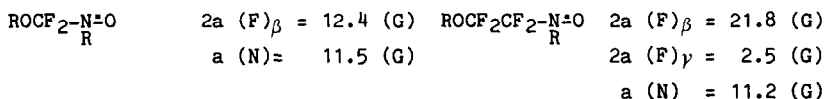
A. Faucitano*, A. Buttafava, F. Martinotti

Dipartimento di Chimica Generale dell'Università di Pavia (Italy)

G. Caporiccio and C. T. Viola

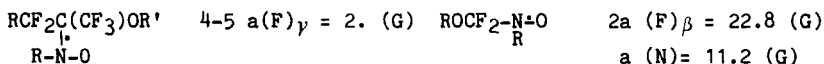
Montefluos-Linate, Milan (Italy)

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

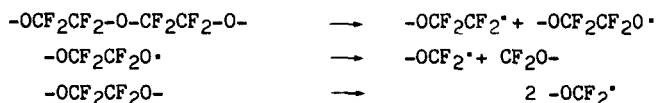


Clear evidence for radical $ROCF_2\cdot$ was also obtained from its polycrystalline spectrum.

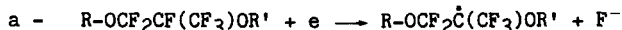
Polyethers of formula $-[(OCF_2CF(CF_3))_x(OCF_2)_y]_n$ (B), yield radicals $ROCF_2\dot{C}(CF_3)-$, as major product, together with minor amount of $ROCF_2\cdot$.



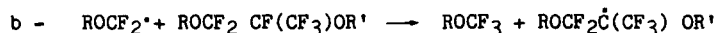
The polycrystalline ESR spectrum of the pure compound show the presence of $ROCF_2\cdot$ and $ROCF(CF_3)\cdot$ as major products whilst the tertiary radical is not observed. These observations suggest that prominent processes in the radiolysis of A are C-C and C-O bond homolysis followed by β scission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



The same type of reaction may be invoked to rationalize the formation of $ROCF_2\cdot$ and $ROCF(CF_3)\cdot$ in the radiolysis of B; however the identification of the tertiary radical implies either the participation of a dissociative electron capture during the irradiation



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



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.