

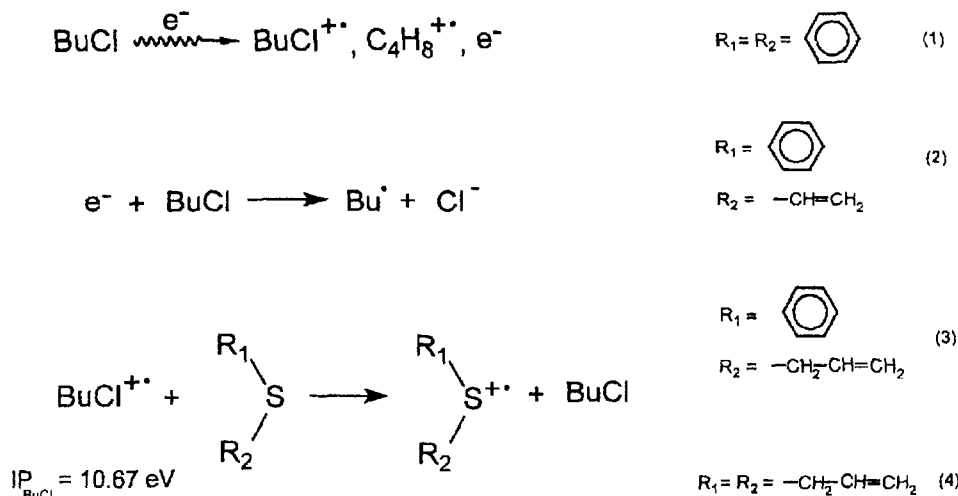
GENERATION OF RADICAL CATIONS FROM PHENYL, VINYL, AND ALLYL CONTAINING THIOETHERS IN ORGANIC SOLVENTS

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Radical cations derived from organic sulphides containing aromatic and unsaturated substituents have been the subject of recent studies [1-4] as they play an important role in a variety of chemical processes extending from those of industrial importance (or-

ganic synthesis) to the enzymatic oxidations in biological species. Although a certain amount of information on the nature of the transient species and kinetic parameters formed from the aryl-substituted sulphides are available, no similar studies have been performed for the sulphides with unsaturated substituents. Quantitative information on these systems would be of interest since the nature of the species is expected to be influenced by the degree of spin delocalization in the aromatic ring and the double bond. The last feature, as it has already been shown in aryl substituted sulphides, should affect the propensity of the radical cations to form dimers.



Scheme.

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Due to the high ionization potential of halocarbons the radical cations derived from organic sulphides are generated as a result of the charge transfer from the parental radical cations of the solvent (n-butyl chloride) to the solute (organic sulphides) (Scheme). The objective of the present study is to provide basic spectral and kinetic behaviour of the radical cations derived from the corresponding organic sulphides with the aromatic and the unsaturated substituents.

When diphenyl sulphide (1), phenylvinyl sulphide (2), and allylphenyl sulphide (3) were irradiated in N₂- and O₂-saturated n-butyl chloride three transient absorption bands were formed and assigned to the radical cation-type species (Chart). These radical cations exhibit very similar UV spectra, with the strong absorption bands between 320-350 nm and the weaker absorption bands between 490-510 nm. However, the location of the third strong absorption band (in the near IR

340, 500, and 760 nm (Fig.). In contrast to phenyl-containing sulphides irradiation of diallyl sulphide

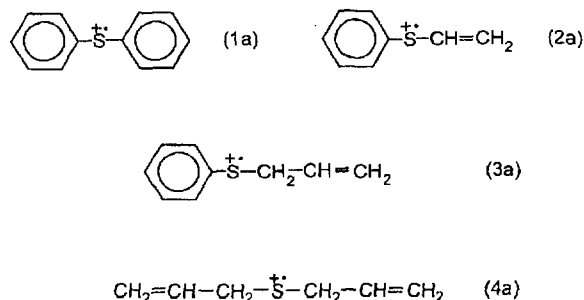


Chart.

(4) (in the same experimental conditions) led to the formation of only two strong transient absorption

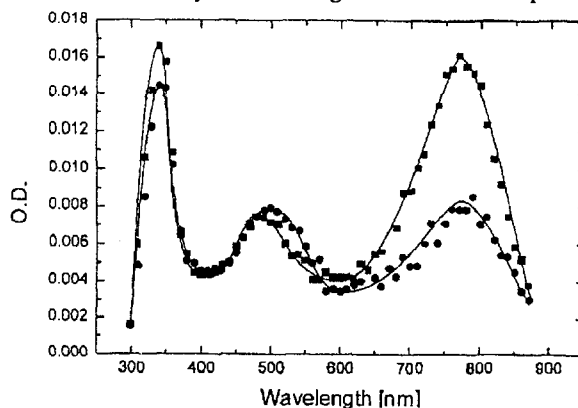


Fig. Transient absorption spectra recorded after pulse irradiation of an N₂-saturated n-butyl chloride solution containing 2 mM diphenyl sulphide (■) 50 ns and (●) 750 ns after the pulse (50 Gy).

bands with $\lambda_{\max}=360$ and 550 nm. The kinetic features at the absorption maxima were found different suggesting existence of two types of radical cation species.

Preliminary data with higher concentrations (up to 50 mM) of sulphides (1, 2, and 3) suggest the existence of dimer radical cations. Further experiments are in progress.

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References

- [1] Ioele M., Steenken S., Baciocchi E.: *J. Phys. Chem. A.*, **101**, 2979-2987 (1997).
- [2] Mohan H., Mittal J.P.: *J. Phys. Chem. A.*, **101**, 10012-10017 (1997).
- [3] Yokoi H., Hatta A., Ishiguro K., Sawaki Y.: *J. Am. Chem. Soc.*, **120**, 12728-12733 (1998).
- [4] Bauld N.L., Todd Aplin J., Yueh W., Loinaz A.: *J. Am. Chem. Soc.*, **119**, 11381-11389 (1997).

EPR STUDIES OF RADICALS INDUCED BY IONISING RADIATION IN FLUTAMIDE

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Flutamide (2-methyl-N-[4-nitro-3(trifluoromethyl)phenyl] propanamide, FA) is known as non-steroidal antiandrogen. We have estimated that it is moderate sensitive on ionising radiation [1], as comparing to other 15 drugs, and the population of paramagnetic species in FA determined 4 and 8 weeks following irradiation was average. We now report suggestions concerning a possible structure of the radicals generated in flutamide and the agents influenced on their formation and stabilisation.

All treatments and measurements were conducted at ambient temperature. Ionising radiation of a dose of 25 kGy induces in the polycrystalline powder of flutamide two kinds of radicals, which were identified by EPR spectroscopy. A peptide group is probably involved in production of the detected transients. A dominant singlet, partly saturated at microwave power of 20 mW and characterised by $g=2.0043$, was assigned to third order carbon centre radical (I), Scheme. Second component of EPR spectrum is anisotropic triplet of g factors equal $g_1=2.0081$, $g_2=2.0046$ and $g_3=2.0000$. It seems to be justified to interpret the signal as absorption exhibited by aryl radical (II) since the values of hyperfine splitting $A_1(2H_{ortho})=2.2\text{mT}$, $A_2(2H_{ortho})=1.6\text{mT}$, $A_3(2H_{ortho})=1.5\text{mT}$, $A_1(1H_{meta})=0.6\text{mT}$, $A_2(1H_{meta})=0.6\text{mT}$ and $A_3(1H_{meta})=0.6\text{mT}$ are near hfs postulated by Kasai for phenyl radical [2].

As the area under the absorption curve is proportional to the number of unpaired spins, the results of double integration of first derivative EPR signals were compared with those of standard (DPPH) and the number of free radicals per gram was determined. The sample was stored for 5 months at room temperature. Kinetics of radical decay during first 6 days upon irradiation is presented in Fig. The initial fast reduction of radical concentrations lasts no longer than 1 day. After this period of time, the amount of substance (I) slightly increases, probably due to reaction (iii), Scheme. This indicates that in the beginning formation of radical (I) from transient (II) is faster than its decay. However, after first a few days, population of σ aryl radical is becoming low and more molecules

of radical (I) decays than is formed following process (II)→(I). A total concentration of radicals measured directly after irradiation is 1.32×10^{17} spins/g

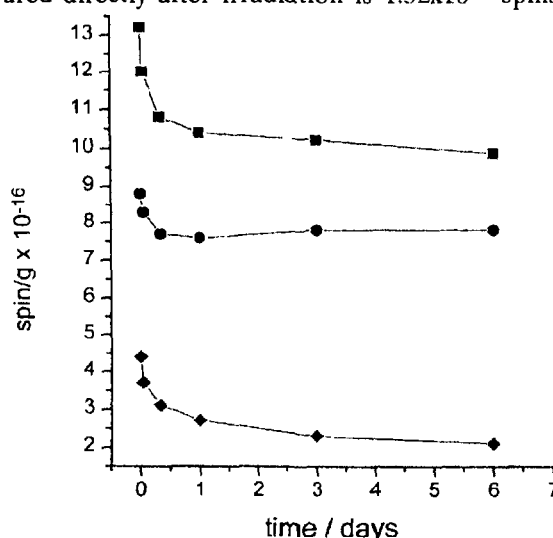
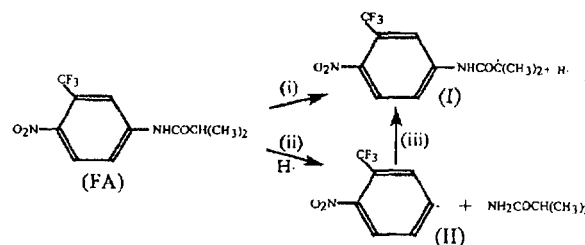


Fig. Kinetics of radical decay; (■) concentration of all radicals, (●) radical (I), (◆) radical (II), see Scheme.

and decreases of about 40% after 5 months of storage.

The population of radicals in flutamide results from the rate of radical conversion (II)→(I), stability of the later product and the efficiency of



Scheme.

microcrystalline matrices for trapping paramagnetic species.

References

- [1] Ambroź H.B., Kornacka E.M., Marciniak B., Ogrodowczyk M., Przybytniak G.K.: *Radiat. Phys. Chem.*, in press.
- [2] Kasai P.H., Hedaya E., Whipple E.B.: *J. Am. Chem. Soc.*, **91**, 4364-4368 (1969).



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