

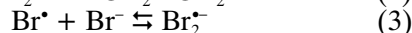
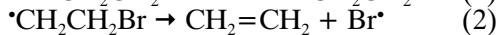
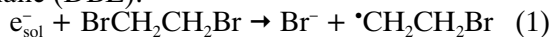
**PULSE RADIOLYSIS STUDY  
OF THE RADICAL REACTIONS IN IONIC LIQUIDS.  
INTERMEDIATE SPECTRA IN THE SYSTEM  $\text{Br}_2^{\cdot-}/\text{Br}^-/\text{SCN}^-$   
IN THE IONIC LIQUID METHYLTRIBUTYLAMMONIUM  
BIS[(TRIFLUOROMETHYL)SULFONYL]IMIDE**

Jan Grodkowski, Małgorzata Nyga, Jacek Mirkowski

Room temperature ionic liquids [1-3] are non-volatile and non-flammable and serve as good solvents for various reactions and have been proposed as solvents for green processing [3]. To understand the effect of these solvent on the chemical reactions, the rate constants of several elementary reactions in ionic liquids have been studied by the pulse radiolysis technique [4-8].

Fast kinetic measurements were carried out by pulse radiolysis using 10 ns, 10 MeV electron pulses from a LAE 10 linear electron accelerator [9] delivering the dose up to 20 Gy per pulse. The details of a computer controlled measuring system were described before [10]. 8 MB maximum memory for data recording covers a time range from single nanoseconds to milliseconds, depending on the oscilloscope settings, after every single electron pulse. Useful spectral range for the experiments with methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ( $\text{R}_4\text{NNTf}_2$ ) was from ~350 to ~800 nm.

In this study of the reactions of  $\text{Br}_2^{\cdot-}$ , anion radicals with thiocyanate anions in the ionic liquid  $\text{R}_4\text{NNTf}_2$  have been examined.  $\text{Br}_2^{\cdot-}$  in the  $\text{R}_4\text{NNTf}_2$  ionic liquid has been produced as before [9] via the reaction of solvated electrons with 1,2-dibromoethane (DBE):



The spectra following pulse irradiation of solution  $0.013 \text{ mol L}^{-1}$  DBE in  $\text{R}_4\text{NNTf}_2$  recorded at 80, 300 and 4000 ns after the pulse are presented in Fig.1. The data at 80 ns after the pulse correspond to the solvated electron. The spectrum – 4000 ns after the pulse is ascribed to  $\text{Br}_2^{\cdot-}$  anion radical. Its yield is equal to the reported value of the yield of the solvated electrons in  $\text{R}_4\text{NNTf}_2$   $G=0.7 \text{ mol J}^{-1}$  [7]. However, for higher concentrations of DBE,

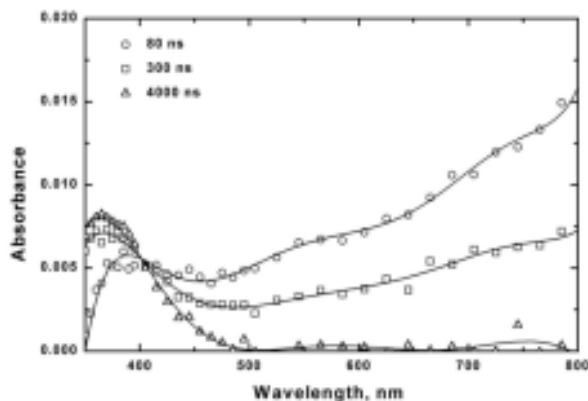
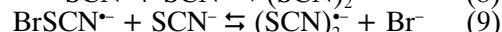
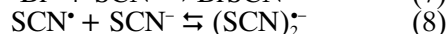
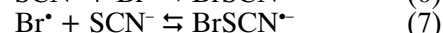
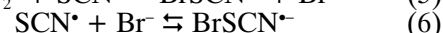
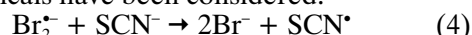


Fig.1. Transient optical spectra monitored by pulse radiolysis of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing  $0.013 \text{ mol L}^{-1}$  DBE. The spectra were taken 80 ns (○), 300 ns (□), and 4000 ns (△) after the pulse. Dose was 11 Gy.

the yield of  $\text{Br}_2^{\cdot-}$  is increased due to scavenging of dry electrons. The second order decay rate constant of the reaction (1) was calculated to be  $k_1=(1.2)\times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ .

After addition of  $\text{SCN}^-$  ions in the pulse irradiated solution, several reactions initiated by  $\text{Br}_2^{\cdot-}$  anion radicals have been considered:



From the intermediates listed above,  $\text{Br}_2^{\cdot-}$ ,  $\text{BrSCN}^{\cdot-}$  and  $(\text{SCN})_2^{\cdot-}$  are observed in  $\text{R}_4\text{NNTf}_2$ . Their contribution to the overall kinetics and the resulting spectra depends on the relative concentrations of  $\text{Br}^-$  and  $\text{SCN}^-$  ions. Their contribution to the overall kinetics and the resulting spectra is dependent on the relative concentrations of  $\text{Br}^-$  and  $\text{SCN}^-$  ions (Figs.2 and 3).

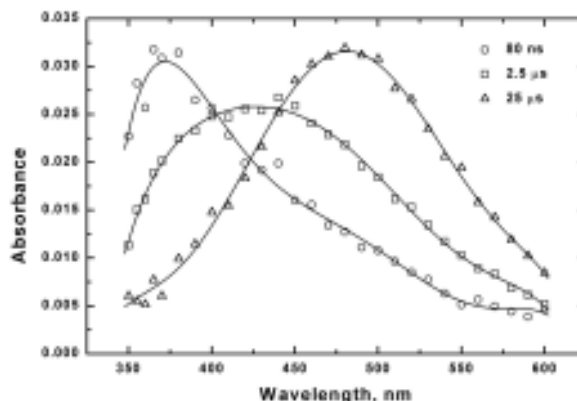


Fig.2. Transient optical spectra monitored by pulse radiolysis of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing  $0.19 \text{ mol L}^{-1}$  DBE and  $0.04 \text{ mol L}^{-1}$   $\text{SCN}^-$ . The spectra were taken 80 ns (○),  $2.5 \mu\text{s}$  (□), and  $25 \mu\text{s}$  (△) after the pulse. Dose was 18.5 Gy.

In the case when there is no  $\text{Br}^-$  added (Fig.2), spectra recorded at 80 ns,  $2.5 \mu\text{s}$  and  $25 \mu\text{s}$  after the pulse, only the last one corresponds to a single intermediate, namely  $(\text{SCN})_2^{\cdot-}$ . The others are a mixture of all the three components:  $\text{Br}_2^{\cdot-}$ ,  $\text{BrSCN}^{\cdot-}$  and  $(\text{SCN})_2^{\cdot-}$  with their relative proportions changing with progressing  $\text{Br}_2^{\cdot-}$  transformation into  $(\text{SCN})_2^{\cdot-}$ .

Pulse radiolysis of the solution containing  $0.18 \text{ mol L}^{-1}$  DBE,  $0.006 \text{ mol L}^{-1}$   $\text{SCN}^-$  and additional  $0.09 \text{ mol L}^{-1}$   $\text{Br}^-$  in  $\text{R}_4\text{NNTf}_2$  produces significantly different spectra. In the case presented in Fig.3 the participation of  $(\text{SCN})_2^{\cdot-}$  in the resulted spectra is negligible. This is probably the first direct observation of the spectrum of  $\text{BrSCN}^{\cdot-}$  anion radical; previous spectra were extracted from the composite results [11].

The rates of the  $\text{Br}_2^{\cdot-}$  anion radicals with thiocyanate are of the same order of magnitude as observed before for the reaction with chlorpromazine

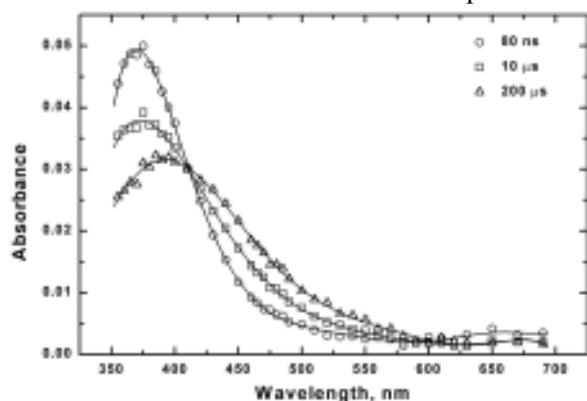


Fig.3. Transient optical spectra monitored by pulse radiolysis of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing  $0.19 \text{ mol L}^{-1}$  DBE,  $0.006 \text{ mol L}^{-1}$   $\text{SCN}^-$  and  $0.09 \text{ mol L}^{-1}$   $\text{Br}^-$ . The spectra were taken 80 ns (O), 10  $\mu\text{s}$  (□), and 200  $\mu\text{s}$  (Δ) after the pulse. Dose was 16.5 Gy.

in  $\text{R}_4\text{NNTf}_2$  [6]. It was suggested that the energy of solvation is the main factor which affects the driving force of  $\text{Br}_2^{\cdot-}$  reactions. In the present report, only the intermediates involved are discussed. The more complete description including evaluation of

the particular reactions rates and equilibria, will be done after completion of the experiments with a wider range of concentration of concerned species.

## References

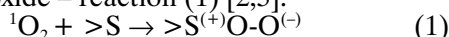
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## SINGLET OXYGEN-INDUCED DECARBOXYLATION OF CARBOXYL SUBSTITUTED THIOETHERS

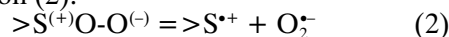
Monika Celuch, Dariusz Pogocki

Singlet oxygen ( $^1\text{O}_2$ ) could be generated in biological systems by a range of endogenous and exogenous processes (*e.g.* enzymatic and chemical reactions, UV or visible light in the presence of a sensitizer) [1]. Numerous data show that proteins are major targets for  $^1\text{O}_2$ , with damage occurring preferentially at aromatic and sulfur-containing amino acid residues (Trp, His, Tyr and Cys and Met) [1]. Reaction with each of these residues gives rise to further reactive species.

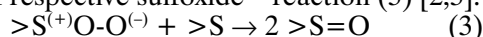
For example, reaction of  $^1\text{O}_2$  with thioether sulfur of methionine (Met) leads to the formation of peroxysulfoxide – reaction (1) [2,3]:



which is in equilibrium with superoxide radical-anion ( $\text{O}_2^{\cdot-}$ ) and respective sulfur-centered radical-cation – reaction (2):



Peroxy sulfoxide may react with the second molecule of thioether leading to the formation of two molecules of respective sulfoxide – reaction (3) [2,3]:



Reaction (3), then occurring intramolecularly in the peptides containing two or more Met residues, has the potential to be a convenient way to evaluate the flexibility of the polypeptide backbone. Since, double methionine sulfoxide (2MetS=O) arises in the process that requires direct contact of two backbone-separated side chains of Met [4,5]. Therefore, chromatographic quantification of 2MetS=O pro-

duced in the  $^1\text{O}_2$ -induced oxidation “coupled” with molecular modeling techniques may help to understand the structure dependent mechanism of free radicals related cytotoxicity of some proteins [6]. Among them are such “prominent” proteins as the human prion protein that contains nine Met residues [7].

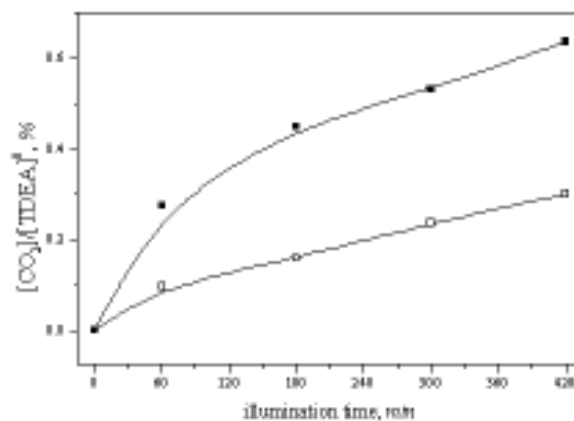


Fig.1. Efficiency of  $^1\text{O}_2$ -induced  $\text{CO}_2$  formation normalized to the initial concentration of thioether vs. time of illumination in solutions containing 50 mM TDEA, 22  $\mu\text{M}$  RB, (■) 1.045 or (□) 0.219 mM  $\text{O}_2$  at pH 6.

However, for quantitative use of reaction (3) in the field of peptide dynamics study, the deeper knowledge on the competitive processes is required. Therefore, we are involved in the research