

**Formation of  $\text{Br}_2^{\bullet-}$ ,  $\text{BrSCN}^{\bullet-}$  and  $(\text{SCN})_2^{\bullet-}$  intermediates in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide. Pulse radiolysis study**

Jan Grodkowski,  
Małgorzata Nyga,  
Jacek Mirkowski

**Abstract** The reactions of  $\text{Br}_2^{\bullet-}$  anion radicals with thiocyanate anions in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ( $\text{R}_4\text{NNTf}_2$ ) were studied by pulse radiolysis. Reaction of solvated electrons with  $\text{BrCH}_2\text{CH}_2\text{Br}$  (DBE),  $k = (1-2) \times 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , leads to the production of  $\text{Br}_2^{\bullet-}$  anion radicals. The intermediate absorption spectra following pulse radiolysis of DBE/ $\text{SCN}^-$ / $\text{Br}^-$  solutions in  $\text{R}_4\text{NNTf}_2$  correspond to  $\text{Br}_2^{\bullet-}$ ,  $\text{BrSCN}^{\bullet-}$  and  $(\text{SCN})_2^{\bullet-}$  anion radicals. The participation of these radicals in the spectra changes with progressing reactions and depends on the concentration  $\text{Br}^-$  and  $\text{SCN}^-$  in the solution.

**Key words** ionic liquids • pulse radiolysis •  $\text{Br}_2^{\bullet-}$  •  $\text{BrSCN}^{\bullet-}$  •  $(\text{SCN})_2^{\bullet-}$

### Introduction

Room-temperature ionic liquids (IL) are composed of ions and are liquid at ambient temperature. Their properties, negligible vapor pressure and non-flammability, made them very attractive alternatives to classical organic solvents. IL are very effective media for chemical catalysis and synthesis and they found other numerous applications including propositions for their use in some procedures in the nuclear industry. Due to potential environmental safety benefits IL have been anticipated as solvents for green processing [4, 15, 17, 18]. For radiation chemistry, the IL constitute a challenge as new objects to study in two aspects first, stability under ionizing radiation and second, a new medium for chemical reaction some of them unique, occurring in these solvents only. To understand the effect of IL on chemical processes, several elementary reactions in ionic liquids have been studied by the pulse radiolysis technique [2, 3, 6–9, 11, 19].

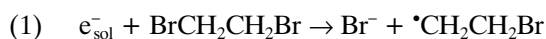
In a previous study, the reactions of  $\text{Br}_2^{\bullet-}$  anion radicals with chlorpromazine in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ( $\text{R}_4\text{NNTf}_2$ ) and several other solvents have been examined [6]. The process included only one step reaction. Contrary to that, the reaction of  $\text{Br}_2^{\bullet-}$  with  $\text{SCN}^-$ , studied in this paper, opens the possibility of the examination of several intermediates and equilibria involved, known from the data for aqueous solutions [1, 10, 12–14, 16]. That gives an opportunity to explore the influence of IL on more complex reaction systems. Besides, the radiolytic oxidation of  $\text{SCN}^-$  by  $\text{OH}^{\bullet}$  radical is the basis of pulse radiolysis dosimetry and, as such, is

J. Grodkowski✉, M. Nyga, J. Mirkowski  
Department of Radiation Chemistry and Technology,  
Institute of Nuclear Chemistry and Technology,  
16 Dorodna Str., 03-195 Warsaw, Poland,  
Tel.: +48 22-8112347, Fax: +48 22-8111532,  
E-mail: jangrod@orange.ichtj.waw.pl

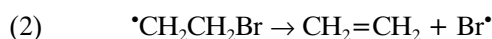
Received: 26 April 2005

frequently investigated [12]. In  $R_4NNTf_2$ , the  $Br_2^{\bullet-}$  has to be used as oxidizing species instead of  $OH^{\bullet}$ . The corresponding observations in the ionic liquids are expected to give a new data for the characterization of the influence of these media, extensively examined for various applications, on the chemical kinetics.

$Br_2^{\bullet-}$  in the  $R_4NNTf_2$  ionic liquid has been produced as before [6] via the reaction of solvated electrons with 1,2-dibromoethane (DBE):



followed by the fast decomposition:



and the subsequent reaction of  $Br_2^{\bullet-}$  formation:



### Experimental section

Methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide ( $R_4NNTf_2$ ) was prepared as described before [3]. All chemicals of the purest grade available (Aldrich) were used as supplied.

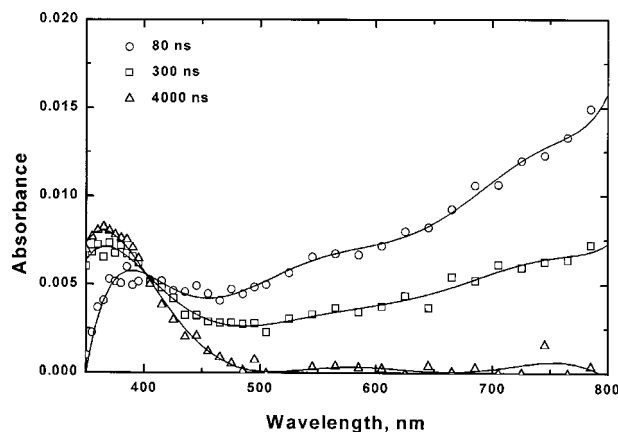
Tetraethylammonium bromide and tetrabutylammonium thiocyanate were used in the ionic liquid as a source of  $Br^-$  and  $SCN^-$  ions, respectively.

Fast kinetic measurements were carried out by pulse radiolysis using 10 ns, 10 MeV electron pulses from an LAE 10 linear electron accelerator [20] delivering the dose up to 20 Gy per pulse. The details of the computer controlled measuring system were described before [5]. Eight megabytes maximum memory for data recording covers the time range from single nanoseconds to milliseconds, depending on the oscilloscope settings, after every single electron pulse. Useful spectral range for the experiments with  $R_4NNTf_2$  was from  $\sim 350$  nm to  $\sim 800$  nm. The samples in the quartz cells, optical path 1 cm, were purged with argon and pulse irradiated by electron beam in the experimental setup. All the experiments were carried out at room temperature  $20 \pm 2^\circ C$ .

### Results and discussion

The representative spectra following pulse irradiation of  $0.013 \text{ mol}\cdot\text{L}^{-1}$  DBE solution in  $R_4NNTf_2$ , recorded at 80 ns, 300 ns and 4000 ns after the pulse, are presented in Fig. 1. The first spectrum (data at 80 ns after the pulse) corresponds to the solvated electron. The solvated electron in  $R_4NNTf_2$  has a very broad absorption band with a maximum at 1410 nm and extinction coefficient  $\epsilon = 2.2 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  [19]. The decay of solvated electron in argon saturated  $R_4NNTf_2$ , without DBE added, most probably in reactions with some impurities, could be fitted by a first order procedure with the rate constant of  $(2 \pm 1) \times 10^6 \text{ s}^{-1}$  which is close to the previous value of  $3.3 \times 10^6 \text{ s}^{-1}$  from reference [19].

The last spectrum (4  $\mu s$  after the pulse) in Fig. 1 is assigned to  $Br_2^{\bullet-}$  anion radical. The  $Br_2^{\bullet-}$  decay is very

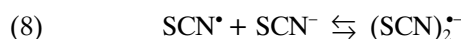
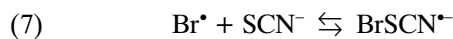
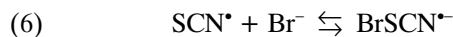


**Fig. 1.** Transient optical spectra monitored by pulse radiolysis of deoxygenated  $R_4NNTf_2$  containing  $0.013 \text{ mol}\cdot\text{L}^{-1}$  DBE. The spectra were taken 80 ns ( $\circ$ ), 300 ns ( $\square$ ), and 4  $\mu s$  ( $\triangle$ ) after the pulse. Dose 11 Gy.

slow and minor in tens of microseconds. Taking the extinction coefficient of  $Br_2^{\bullet-}$   $\epsilon_{360} = 9900 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  [15], and data from Fig. 1 (dose 11 Gy) the yield of  $Br_2^{\bullet-}$  was calculated as  $G = 0.7 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$ . However, for higher concentrations of DBE (up to  $0.19 \text{ mol}\cdot\text{L}^{-1}$ ) in the solution the yield of  $Br_2^{\bullet-}$  reaches value  $G = 1.6 \times 10^{-7} \text{ mol}\cdot\text{J}^{-1}$ . This could be explained by the fact that also dry electrons in  $R_4NNTf_2$  are captured by DBE, when it is added in a higher concentration. This effect was observed before in reactions of dry electrons with several solutes [19].

From the dependence of the solvated electrons decay rates on the concentration of DBE, the second order decay rate constant of the reaction (1) was calculated to be  $k_1 = (1-2) \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . This value is close to the diffusion-controlled rate limit in this medium [3].

After the addition of  $SCN^-$  ions to the solution, several reactions initiated by  $Br_2^{\bullet-}$  anion radicals can be expected [1, 10, 12–14, 16]. (To the scheme there were included only reactions corresponding to the observation time range of the present experiments.)



The above reactions are known from aqueous solutions, and some rate constants and equilibria involved have been characterized [1, 10, 12–14, 16].

From the intermediates listed above, in the actual experimental conditions,  $Br_2^{\bullet-}$ ,  $BrSCN^{\bullet-}$  and  $(SCN)_2^{\bullet-}$  are likely candidates to the observation in  $R_4NNTf_2$ , see Table 1. Their contribution to the overall kinetics and the resulting spectra will be dependent on the concentrations of  $Br^-$  and  $SCN^-$  ions, see Figs. 2 and 3.

**Table 1.** Characteristics of absorption spectra of intermediates in the  $\text{Br}_2^{\bullet-}/\text{SCN}^-$  system<sup>a</sup>

Species	$\lambda_{\text{max}}$ [nm]	Absorption coefficient [ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ]
$\text{Br}_2^{\bullet-}$	360	9900
$\text{SCN}^{\bullet}$	330	900
$\text{BrSCN}^{\bullet-}$	400	7300
$(\text{SCN})_2^{\bullet-}$	472	7580

<sup>a</sup> Aqueous solutions, data taken from Ref. [10].

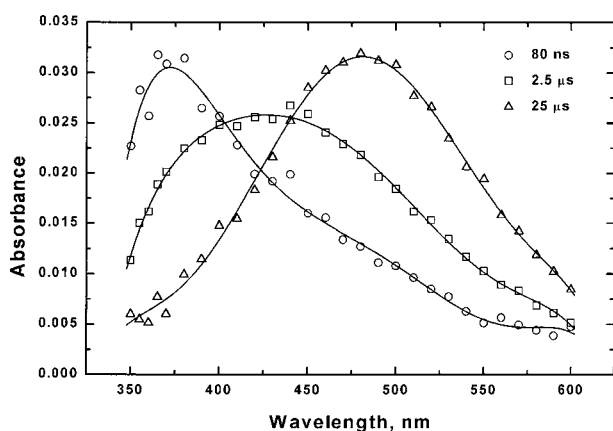
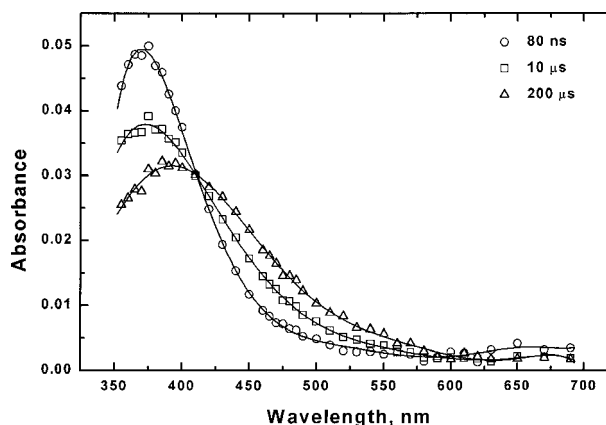
In Fig. 2, there are examples of spectra obtained in pulse irradiated solution of  $0.19 \text{ mol}\cdot\text{L}^{-1}$  BDE (such concentration of DBE reassures the fast formation of  $\text{Br}_2^{\bullet-}$ ) and  $0.04 \text{ mol}\cdot\text{L}^{-1}$   $\text{SCN}^-$  in  $\text{R}_4\text{NNTf}_2$ , when there is no  $\text{Br}^-$  added.

From the three spectra presented in Fig. 2: data at 80 ns, 2.5  $\mu\text{s}$  and 25  $\mu\text{s}$  after the pulse, only the last one represents a single component, namely  $(\text{SCN})_2^{\bullet-}$ . The others are mixture of the all three constituents:  $\text{Br}_2^{\bullet-}$ ,  $\text{BrSCN}^{\bullet-}$  and  $(\text{SCN})_2^{\bullet-}$  with relative proportions changing in a progress of the reactions, according to gradual transformation from  $\text{Br}_2^{\bullet-}$  to  $(\text{SCN})_2^{\bullet-}$ .

On condition when there is no  $\text{Br}^-$  added, experimental traces: decay measured at 350–360 nm and formation at  $\lambda > 480 \text{ nm}$ , can be fitted by first order kinetics with the rate constants dependent on  $\text{SCN}^-$  concentration.

This rate constant dependence on  $[\text{SCN}^-]$  gives the value of the experimental second order rate constant  $k = (5 \pm 1) \times 10^6 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ . This value characterizes only the time scale of the process and represents some estimates for comparison to the other  $\text{Br}_2^{\bullet-}$  reactions. To evaluate the participation of the particular reaction in the kinetics scheme, the data from solutions with various concentrations of  $\text{SCN}^-$  and  $\text{Br}^-$  ions have to be considered.

The next presented results are obtained in the system with  $\text{Br}^-$  added to the solutions. Pulse radiolysis of the  $\text{R}_4\text{NNTf}_2$  solution containing  $0.18 \text{ mol}\cdot\text{L}^{-1}$  DBE,  $0.006 \text{ mol}\cdot\text{L}^{-1}$   $\text{SCN}^-$  and additional  $0.09 \text{ mol}\cdot\text{L}^{-1}$   $\text{Br}^-$

**Fig. 2.** Transient optical spectra monitored by pulse radiolysis of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing  $0.19 \text{ mol}\cdot\text{L}^{-1}$  DBE and  $0.04 \text{ mol}\cdot\text{L}^{-1}$   $\text{SCN}^-$ . The spectra were taken 80 ns ( $\circ$ ), 2.5  $\mu\text{s}$  ( $\square$ ), and 25  $\mu\text{s}$  ( $\triangle$ ) after the pulse. Dose 18.5 Gy.**Fig. 3.** Transient optical spectra monitored by pulse radiolysis of deoxygenated  $\text{R}_4\text{NNTf}_2$  containing  $0.19 \text{ mol}\cdot\text{L}^{-1}$  DBE,  $0.006 \text{ mol}\cdot\text{L}^{-1}$   $\text{SCN}^-$  and  $0.09 \text{ mol}\cdot\text{L}^{-1}$   $\text{Br}^-$ . The spectra were taken 80 ns ( $\circ$ ), 10  $\mu\text{s}$  ( $\square$ ), and 200  $\mu\text{s}$  ( $\triangle$ ) after the pulse. Dose 16.5 Gy.

produces spectra significantly different from those reported above. The isosbestic point seen in the Fig. 3 indicates that there are only two individuals involved, with the negligible participation of  $(\text{SCN})_2^{\bullet-}$ .

Due to the excess of the  $\text{Br}^-$  concentration over the  $\text{SCN}^-$  the forward reactions (8) and (9) leading to the formation of  $(\text{SCN})_2^{\bullet-}$  are suppressed and the formation of  $\text{BrSCN}^{\bullet-}$  prevails. The  $\text{Br}_2^{\bullet-}$  anion radicals formed during the pulse and in tens of nanoseconds after (reactions ((1)–(3))) are gradually transformed into  $\text{BrSCN}^{\bullet-}$  anion radicals in  $\sim 200 \mu\text{s}$ ,  $k_{\text{exp}} = \sim 1 \times 10^5 \text{ s}^{-1}$ , and these after being formed remain stable in the time of observation.

The final spectrum is probably the first direct observation of the spectrum of  $\text{BrSCN}^{\bullet-}$  anion radical, previous spectra were extracted from the composite results [13]. However, some minor participation of  $\text{Br}_2^{\bullet-}$  in the final spectrum, due to the equilibria involved, cannot be a priori excluded. The final test will be deconvolution of the spectra obtained in the system with different  $[\text{Br}^-]/[\text{SCN}^-]$  ratios.

The rates of the reactions between  $\text{Br}_2^{\bullet-}$  anion radicals and thiocyanate are of the same order of magnitude as observed before for the reaction of  $\text{Br}_2^{\bullet-}$  with chlorpromazine in  $\text{R}_4\text{NNTf}_2$  [6]. It was suggested that the energy of  $\text{Br}^-$  solvations is the main factor which affects the driving force of  $\text{Br}_2^{\bullet-}$  reactions. In the present paper, 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 an enhanced range of concentrations of the concerned species. However, even the present results indicate that IL are very useful media for the observation and separation of some intermediates and could play a similar role as low temperature radiolysis in elucidation of reactions mechanisms.

**Acknowledgments** The authors like to express their thanks to the Foundation for Polish Science for the purchase of 9354AL digital oscilloscope.

## References

1. Behar D, Bevan PLT, Scholes G (1972) Pulse radiolysis of aqueous thiocyanate solutions. Nature of the intermediate transient species. *J Phys Chem* 76:1537–1542
2. Behar D, Gonzales C, Neta P (2001) Reaction kinetics in ionic liquids: Pulse radiolysis studies of 1-butyl-3-methylimidazolium salts. *J Phys Chem A* 105:7607–7614
3. Behar D, Neta P, Schultheisz C (2002) Reaction kinetics in ionic liquids as studied by pulse radiolysis: Redox reactions in the solvents methyltributylammonium bis(trifluoromethylsulfonyl)imide and N-butylpyridinium tetrafluoroborate. *J Phys Chem A* 106:3139–3147
4. Earle MJ, Seddon KR (2000) Ionic liquids. Green solvents for the future. *Pure Appl Chem* 72:1391–1398
5. Grodkowski J, Mirkowski J, Plusa M, Getoff N, Popov P (2004) Pulse radiolysis of diphenyl oxide. *Radiat Phys Chem* 69:379–386
6. Grodkowski J, Neta P (2002) Formation and reaction of  $\text{Br}_2^-$  radicals in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide and in other solvents. *J Phys Chem A* 106:11130–11134
7. Grodkowski J, Neta P (2002) Reaction kinetics in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide. Pulse radiolysis study of  $^{\bullet}\text{CF}_3$  radical reactions. *J Phys Chem A* 106:5468–5473
8. Grodkowski J, Neta P (2002) Reaction kinetics in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide. Pulse radiolysis study of 4-mercaptobenzoic acid. *J Phys Chem A* 106:9030–9035
9. Grodkowski J, Neta P, Wishart JF (2003) Pulse radiolysis study of the reactions of hydrogen atoms in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide. *J Phys Chem A* 107:9794–9799
10. Hug GL (1981) Optical spectra of nonmetallic inorganic transient species in aqueous solution. *Nat Stand Ref Data Ser NSRDS-NBS* 69
11. Marcinek A, Zielonka J, Gębicki J, Gordon CM, Dunkin IR (2001) Ionic liquids: novel media for characterization of radical ions. *J Phys Chem A* 105:9305–9309
12. Milosavljevic BH, LaVerne JA (2005) Pulse radiolysis of aqueous thiocyanate solution. *J Phys Chem A* 109:165–168
13. NDRL/NIST Solution Kinetics Database on the Web. <http://kinetics.nist.gov/solution/index.php>
14. Neta P, Huie RE, Ross AB (1988) Rate constants for reactions of inorganic radicals in aqueous solution. *J Phys Chem Ref Data* 17:1027–1284
15. Rogers RD, Seddon KR (eds) (2002) Ionic liquids: industrial application to green chemistry. *ACS Symp Ser* vol. 818
16. Schöneshöfer M, Henglein A (1969) Pulsradiolytische Untersuchung der Dissoziationsgleichgewichte des gemischten Radikal-Anion-Komplexes  $\text{BrSCN}^-$ . *Ber Bunsenges Phys Chem* 73:289–293
17. Wasserscheid P, Keim W (2000) Ionic liquids – new “solutions” for transition metal catalysis. *Angew Chem Int Ed* 39:3772–3789
18. Welton T (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem Rev* 99:2071–2083
19. Wishart JF, Neta P (2003) Spectrum and reactivity of the solvated electron in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide. *J Phys Chem B* 107:7261–7267
20. Zimek Z, Dźwigalski Z (1999) Linear electron accelerator. *Postępy Techniki Jądrowej* 42;2:9–17 (in Polish)