Stability of $[MeBu_3N][Tf_2N]$ under gamma irradiation

Émilie Bossé, Laurence Berthon, Nicole Zorz, Julie Monget, Claude Berthon,
Isabelle Bisel, Solène Legand, and Philippe Moisy*

CEA Marcoule, DCRP/SCPS, BP 17171, 30207 Bagnols sur Cèze Cedex, France
philippe.moisy@cea.fr

Abstract – *The stability of the ionic liquid $[MeBu_3N][Tf_2N]$, dry or after contact with water (where $[MeBu_3N]^+$ is the methyltributylammonium cation and $[Tf_2N]^-$ is the bistriflimide anion), was studied under ^{137}Cs gamma irradiation in argon and in air. In a quantitative study with an absorbed dose of 2 MGy this ionic liquid was highly stable regardless of the radiolysis conditions. The radiolytic disappearance yields determined by ESI-MS were -0.38 and -0.25 $\mu mol \cdot J^{-1}$ for the cation and anion, respectively. ESI-MS, NMR, and liquid chromatography coupled with ESI-MS identified a large number of degradation products in very small quantities for the same dose. The cation radicals were formed by the loss of a $Bu^{\bullet}$ group, the $Me^{\bullet}$ group, or two $H^{\bullet}$ atoms to form a double bond with the butyl chain. Radiolysis of the anion produced mainly $F^{\bullet}$ and $CF_3^{\bullet}$ radicals. The anion radicals recombined with the cation to form a wide range of secondary degradation products regardless of the radiolysis conditions.*

INTRODUCTION

Room-temperature ionic liquids (RTILs) possess physical and chemical properties that mitigate the drawbacks of conventional (flammable, highly volatile and toxic) solvents. These ionic liquids are thus potentially applicable in the nuclear fuel cycle and have increasingly become a subject of investigation. Ionic liquids also provide a much greater criticality safety margin than aqueous solvents (about 1000 $g \cdot L^{-1}$) [1]. However, for application as the solvent for actinide separation by liquid-liquid extraction [2-4] or supercritical CO_2 as an electrolyte [5,6], they must be resistant to very strong irradiation.

A few studies of radiolysis behavior have already been carried out, mainly on cations such as imidazolium. They do not lead to any significant decomposition of the organic compound; Allen et al. [7] showed that ionic liquids based on these cations are stable at 400 kGy regardless of the type of irradiation (α, β, γ). A recent study of $BuMeImTf_2N$ under γ irradiation at doses up to 1200 kGy showed the high stability of this ionic liquid [8]. A small fraction of products formed by recombination of the primary radiolysis products. The $BuMeIm^{+\bullet}$, $Bu^{\bullet}MeIm^+$, $MeIm^{+\bullet}$ radicals for the cation or $CF_3^{\bullet}$ and $F^{\bullet}$ for the anion form polymers and acidic species. Recombination of the anion or cation radicals with the main cation produces secondary species, for example, $BuMe(CF_3)Im^+$ and $MeIm^+Bu\text{-}Im^+BuMe$. Moreover, the presence of air or water does not modify the products. Allen et al. [7] and Berthon et al. [8] identified these degradation products using spectrometric techniques such as NMR and electrospray ionization mass spectrometry (ESI-MS).

Data are lacking on the stability of tetraalkylammonium-based ionic liquids. Nehar et al. [9-13] used this medium to observe the reactivity of the solvated electron—which is present for a longer time due to the low reactivity and high viscosity of tetraalkylammonium-based ionic liquids. Several published accounts demonstrate the high stability of these ionic liquids under β irradiation, although this high stability has never been quantified for any type of irradiation. Mass spectrometry can be used for quantification purposes; Alfassi et al. [14] developed a quantitative ESI-MS method to assess the concentration of an ionic liquid in solution using another cation and another anion as the internal reference.

The purpose of this work was to investigate the stability under γ irradiation of the ionic liquid methyltributylammonium bis-triflimide ($MeBu_3N^+$ and $(CF_3SO_2)_2N^-$, designated Tf_2N^-). The stability of this ionic liquid is demonstrated by quantitative analysis of the disappearance of the cation and anion, and by identification of the degradation products after γ irradiation at very high doses (between 0 and 2 MGy). The effect of water and atmosphere during radiolysis is also taken into account in this study.

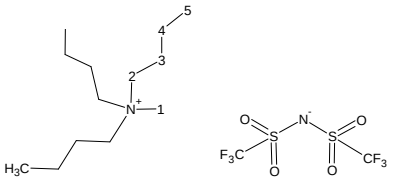

Fig. 1: Ionic liquid used: cation Methyltributylammonium $MeBu_3N^+$ and anion bis(trifluoromethylsulfonyl)imide Tf_2N^-

RESULTS

A/ Radiolytic yields

Two analytical techniques were used to quantify the radiolytic degradation of the RTIL Tf_2N^- anion: ^{19}F NMR and ESI-MS. The $MeBu_3N^+$ cation concentration during γ radiolysis was determined only by ESI-MS, as it is difficult to monitor by ^1H NMR due to the interference of radiolysis products with the signals for the initial compound.

The concentrations of the anion and cation varied in a linear manner with the radiation dose. The slope was used to determine the radiolytic disappearance yield for the cation $MeBu_3N^+$ and the anion Tf_2N^-. The yields were respectively -0.38 ± 0.04 and -0.25 ± 0.03 μmol·J^{-1}. These radiolytic yields are comparable, but the difference is sufficient to affirm that the cation is more sensitive to radiolysis than the anion [15]. Moreover, the low yields suggest a chain-reaction mechanism.

B/ Identification

Three techniques are used for the identification of degradation products: NMR, ESI-MS and liquid chromatography coupled ESI-MS. However, the results concerning the de gradation products of the ionic liquid $[MeBu_3N][Tf_2N]$ are difficult to interpret because of the small quantity and large number of degradation products formed.

Comparing the ^{19}F NMR spectra of the products formed from Tf_2N^- anion during degradation of [BuMeIm][Tf_2N] [8] and $[MeBu_3N][Tf_2N]$ shows that a few peaks—especially the main ones—correspond to the same chemical shifts. The groups formed after radiolysis of the anion do not appear to depend on the cation used and can be identified as $CF_3^•$ and $F^•$ groups. Other groups can also be identified depending on the bond rupture. The other radicals formed are thus $N(CF_3SO_2)SO_2^{-•}$, $NSO_2^{-•}$, and $NSO_2CF_3^{-•}$. Moreover, the primary radiolysis products of the cation $MeBu_3N^+$ are obtained by rupture of the weakest bonds. Depending on the bond energy, these radiolysis products are obtained mainly by rupture of the C-N bond or by rupture of the alkyl chains with nitrogen. With three butyl chains, the $MeBu_2N^+$ radical is obtained by the loss of one butyl chain. $Bu_3N^{+•}$ is another radical obtained by rupture of a methyl group with nitrogen. These two radicals are thus the primary radiolysis products. Furthermore, with the rupture of two C-H bonds, another primary radiolysis product is formed in small quantities with a double bond on one of the butyl chains.

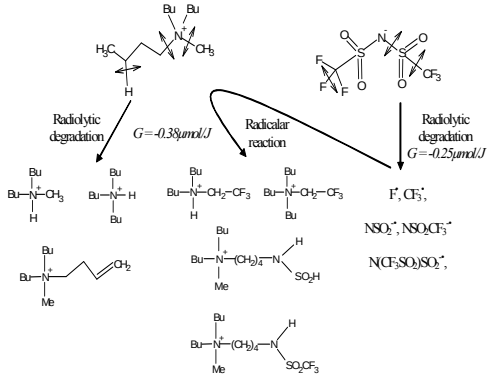

Fig. 2: Proposition of a degradation scheme of ionic liquid $[MeBu_3N][Tf_2N]$

In the light of these results, a reaction scheme (Figure 2) can be proposed for the degradation of $[MeBu_3N][Tf_2N]$. Figure 2 accounts for the difference in the radiolytic disappearance yield between the anion and cation. The anion degrades only under irradiation to form different radical products such as $F^•$ and $CF_3^•$, whereas the cation degrades in two modes: radiolytic degradation or reaction with the anion radicals. The combination of these two degradation modes of the $MeBu_3N^+$ cation, and especially the reactivity of the anion radicals on the alkyl chains of the cation, thus account for the lower stability of the cation compared with the Tf_2N^- anion. The secondary reactions of these radicals give stable radiolysis products at very low concentrations, and no significant difference was observed in the presence of air or water.

The radiolysis atmosphere and the quantity of water initially present in the ionic liquid $[MeBu_3N][Tf_2N]$ do not appear to affect the formation or reactivity of the anion and cation radicals, although the extremely small quantities of degradation products make it difficult to determine the possible new degradation products related to changes in the radiolysis conditions [15].

CONCLUSION

The ionic liquid $[MeBu_3N][Tf_2N]$ was examined in different atmospheres and at different water concentrations under irradiation up to 2 MGy. The radiolytic disappearance yields were determined for the cation and anion: 0.38 and 0.25 $\mu mol \cdot J^{-1}$, respectively. $[MeBu_3N][Tf_2N]$ is thus stable at high irradiation doses and its stability does not appear to be affected by the presence of water or air. The many degradation products obtained in small quantities arise mainly from recombination of the primary radiolysis products of the anion $CF_3^{\bullet}$ or $F^{\bullet}$ and of the cation.

REFERENCES

(1) Harmon, C. D.; Smith, W.; Costa, D. *Radiation Physics and Chemistry* **2001**, *60*, 157-159.

(2) Bartsch, R. A.; Chun, S.; Dzyuba, S. V. In *Ionic liquids: Industrial Applications to green chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818, 2002, pp 58-68.

(3) Dai, S.; Ju, Y. H.; Barnes, C. E. *Dalton Transactions* **1999**, 1201-1202.

(4) Visser, A. E.; Rogers, R. D. *J. of Solid State Chemistry* **2003**, *171*, 109-113.

(5) Oldham, W. J.; Costa, D. A.; Smith, W. H. In *Ionic liquids: industrial appplications to green chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818, 2002, pp 188-198.

(6) Thied, R. C.; Hatter, J. E.; Seddon, K. R.; Pitner, W. R., 18 august 1999; Vol. WO01/13379A1.

(7) Allen, D.; Baston, G.; Bradley, A. E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J. E.; Healey, J. F.; Hodgdon, B.; Lewin, R.; Lovell, K. V.; Newton, B.; Pitner, W. R.; Rooney, D. W.; Sanders, D.; Seddon, K. R.; Sims, H. E.; Thied, R. C. *Green Chemistry* **2002**, *4*, 152-158.

(8) Berthon, L.; Nikitenko, S. I.; Bisel, I.; Berthon, C.; Faucon, M.; Saucerotte, B.; Zorz, N.; Moisy, P. *Dalton Transactions* **2006**, 2526-2534.

(9) Behar, D.; Gonzalez, C.; Neta, P. *J. Phys. Chem. A* **2001**, *105*, 7607-7614.

(10) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, *106*, 3139-3147.

(11) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, *106*, 5468-5473.

(12) Wishart, J. F.; Funston, A. M.; Szreder, T. *Proceedings of the 14th symposium on Molten Salts* Honolulu, Hawaï 2004; The Electrochemical Society.

(13) Wishart, J. F.; Neta, P. *J. Phys. Chem. B* **2003**, *107*, 7261-7267.

(14) Alfassi, Z. B.; Huie, R. E.; Milman, B. L.; Neta, P. *Anal. Bioanal. Chem.* **2003**, *377*, 159-164.

(15) Bossé, E.; Berthon, L.; Zorz, N.; Berthon, C.; Bisel, I.; Legand, S.; Moisy, P. *Dalton Trans.* **2008,** 924-931.