

Formation of p-terphenyl excited states in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide: pulse radiolysis study

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Abstract Solutions of 80 mM benzophenone (BP) and up to 14 mM p-terphenyl (TP) in the ionic liquid methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide (R_4NNTf_2) have been investigated by nanosecond pulse radiolysis. The resulting transient absorption spectra of pulse-irradiated argon saturated solutions correspond to the formation of several intermediates derived from BP and TP: benzophenone radical anion $[(C_6H_5)_2CO]^{*-}$ (BP^{*-}) converted after $\sim 20 \mu s$ into ketyl radicals $(C_6H_5)_2C^*OH$ (BP^*H), a hydrogen adduct to the phenyl ring of benzophenone $C_6H_5COC_6H_6^*$, p-terphenyl triplet excited state $^3TP^*$, and traces of TP radical ions. $^3TP^*$ was formed in two steps, the first immediately during the pulse and the second in pseudo-first order process with a second order reaction rate constant calculated from TP concentration dependence: $k = \sim 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Keywords Benzophenone · p-terphenyl · Nanosecond pulse radiolysis

Introduction

Room temperature ionic liquids (ILs) are considered to be low volatility and combustion-resistant solvents. They serve as good media for various reactions and have been proposed as green solvents in many applications [1–9]. Their specific properties and promising experiments concerning the application of ILs to the nuclear industry [4, 10] raised the question of the radiation chemistry of ILs.

For radiation chemistry, the ILs constitute a challenge as a new object to study in two aspects, their stability under ionizing radiation and as a new medium for basic

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study of mechanism of chemical reactions, some of them unique, occurring only in these solvents.

To cope with problems of radiation chemistry in ILs, several elementary processes such as solvated and “dry” electrons reactions, charge and H transfer have been studied by the pulse radiolysis technique [11–26]. The radiation stability of ILs under ionizing radiation has also been studied in a few cases [27–30]. To the best of our knowledge, there has been no direct observation of excited state formation in irradiated ILs. However, there is a strong indication that excited state formation cannot be neglected in the radiolysis of ILs [29].

In the present study, the formation of excited states in methyltributylammonium bis[(trifluoromethyl)sulfonyl]imide (R_4NNTf_2) has been examined by the pulse radiolysis method. Benzophenone (BP) and p-terphenyl (TP) have been selected as sensors of excited state formation. Both molecules form singlet and triplet excited states with absorption spectra in convenient wavelength ranges for pulse radiolysis detection. Radiolysis of BP has already been studied in ILs solutions with emphasis on the formation of radical anions and radicals formation [13, 17]. Reactivity of $^3BP^*$ in ILs has also been observed in photolytic experiments [31, 32].

Photochemical activity of TP was particularly investigated in connection with CO_2 reduction [33]. In the presence of appropriate electron donors, the singlet excited state of $^1TP^*$ was converted to $TP^{\bullet-}$ radical anion, which has strong reducing properties. The yield of intersystem singlet–triplet crossing in the case of TP is not very high ($\phi \sim 0.05$ – 0.11) [34, 35] and to obtain the $^3TP^*$ triplet state, energy transfer between $^3BP^*$ and TP was used instead. This process was applied in the present paper.

Experimental

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

Fast kinetic measurements have been carried out using 10 ns, 10 MeV, electron pulses from a LAE 10 linear electron accelerator delivering the dose up to 20 Gy per pulse. Some of details of the computer controlled measuring system have already been described [21]. The system presently consists of a new quiet Hamamatsu xenon lamp with appropriate power supply, and a new ORIEL MSH 301 monochromator with two switchable outputs, one with a photomultiplier and the other with ANDOR ICCD camera (intensified charge coupled device) and a new oscilloscope LeCroy 6051A.

The samples in quartz cells, optical path 1 cm, were purged with Ar or N_2O and pulse irradiated by electron beam in the experimental setup. All experiments were carried out at room temperature 20 ± 2 °C. The data were normalized to a dose of 15 Gy per pulse measured by the KSCN dosimeter; this value corresponds to the dose of 17.4 Gy absorbed by R_4NNTf_2 [13, 18].

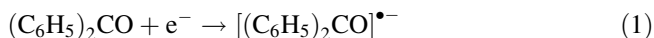
Results and discussion

Pulse radiolysis of 80 mM BP solution

Radiolysis of R_4NNTf_2 leads to production of dry and eventually solvated electrons, protons, radical cations, neutral radicals, and excited states formed by geminate ions recombination [14–18, 29]. The 80 mM concentration of BP in R_4NNTf_2 was used to ensure effective electrons scavenging and possibly excited states of pulse-irradiated solution.

BP reacts with solvated electrons with a rate constant $k = (1.6 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [18]. At a BP concentration of 80 mM, only $\sim 28\%$ of electrons can survive to be solvated [18], the rest are captured in presolvated forms.

Pulse radiolysis of benzophenone solution produces transients characterized by initial broad absorption spectra with maximum at $\sim 700 \text{ nm}$. The results presented in Fig. 1 are similar to those reported before and can be explained by the reaction of BP with electrons (dry and solvated) and H^\bullet radicals followed by protonation of radical anion [17].



The absorption of $[(C_6H_5)_2CO]^{\bullet-}$ radical anion ($BP^{\bullet-}$) is the main component contributing to the absorption spectra observed during the first 200 ns after the pulse. The band with a small maximum at $\sim 460 \text{ nm}$ probably corresponds to $C_6H_5COC_6H_5^\bullet$ radical formed in reaction 2.

The triplet excited state of benzophenone $^3BP^*$ has an absorption band with a maximum in the visible range at 525 nm (in acetonitrile) and molar absorption coefficient of $\varepsilon = 6,700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [36]. In the present experimental conditions, its yield and the ε are too small to have an effect on the absorption spectra of irradiated samples.

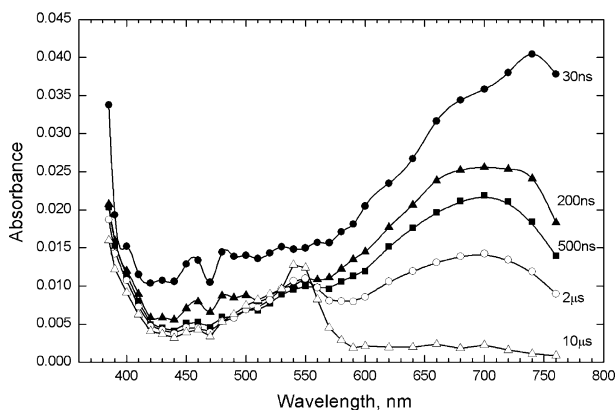
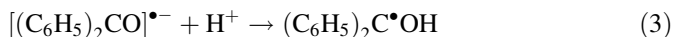


Fig. 1 Absorption spectra in pulse-irradiated Ar saturated 80 mM BP solution in R_4NNTf_2 , measured in 30, 200, 500 ns, 2 μs , and 10 μs after the electron pulse

The overall decrease of the intensity of the spectra in the first 200 ns after the pulse probably corresponds to solvated electrons decaying in reaction 1. In the longer time scale, there is simultaneous decay of absorption with a maximum at ~ 700 nm and formation of more stable absorption characterized by a maximum at ~ 540 nm. The new, more stable, absorption band is described to $(\text{C}_6\text{H}_5)_2\text{C}^\bullet\text{OH}$ radical ($\text{BP}^\bullet\text{H}$) as it was already observed in R_4NNTf_2 [17]. The decay at 700 nm and the formation at 540 nm can be fitted by pseudo-first order kinetics with the same rate constants $k = 2.8 \times 10^5 \text{ s}^{-1}$. The process, also observed before in similar conditions [17], could be explained by protonation of $\text{BP}^{\bullet-}$ radical anion and formation of benzophenone ketyl radical $\text{BP}^\bullet\text{H}$ in reaction 3.



Assuming the molar absorption coefficient at 540 nm of $\text{BP}^\bullet\text{H}$ from acetonitrile solution $\varepsilon = 3,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [36], the radiation yield of ketyl radical will be $G = 2.1 \times 10^{-7} \text{ mol J}^{-1}$. This also corresponds to the total yield of electrons reacting with BP, assuming that all the $\text{BP}^{\bullet-}$ radical anions decay in reaction 3. The present G value is higher than that reported before. However, it was calculated with different value of ε of the $\text{BP}^\bullet\text{H}$ radical [13].

Pulse radiolysis of 80 mM BP solution with addition of TP

Depending on the experimental conditions, several intermediates: radical anions, radical cations, and excited states, can be derived from TP irradiated systems. All of them have absorption spectra in a similar region [37–39] (see Table 1). The presence of 80 mM BP can simplify the interpretation of expected transient spectra.

Absorption of singlet $^1\text{TP}^*$ is too short lived to be observed in actual experimental conditions. The solubility of TP in R_4NNTf_2 is limited to ~ 14 mM. For the maximum concentration of TP and a BP concentration of 80 mM, the electrons should react predominantly with BP, thus diminishing the formation of $\text{TP}^{\bullet-}$ radical anions. Direct radiolytic creation of oxidizing products in R_4NNTf_2 is not very effective, and formation of radical cations of TP with yield comparable to reducing species is not expected.

The spectra at wavelengths >500 nm in argon-saturated, pulse-irradiated 80 mM BP solutions with addition of 3 to 14 mM TP represent all the features described before to BP-derived intermediates. The intensity of that part of the spectrum is slightly diminished at 14 mM TP due to concurrent reactions with electrons.

Figures 2 and 3 show transient absorption spectra in 3 mM and 14 mM TP solution in the presence of 80 mM BP.

Table 1 Position of λ_{max} of absorption spectra of intermediates derived from TP [37–39]

| Intermediate | λ_{max} (nm) |
|------------------------|-----------------------------|
| $^1\text{TP}^*$ | 550 |
| $^3\text{TP}^*$ | 460–450 |
| $\text{TP}^{\bullet-}$ | 440, 470 |
| $\text{TP}^{\bullet+}$ | 426, 462 |

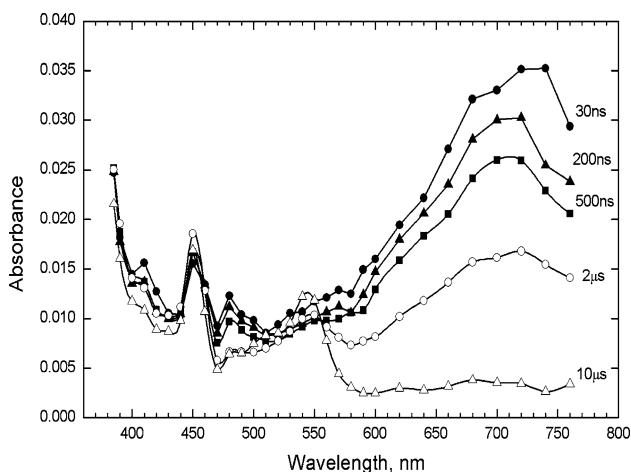


Fig. 2 Absorption spectra in pulse-irradiated Ar saturated, 3 mM TP and 80 mM BP solution in R_4NNTf_2 , measured in 30, 200, 500 ns, 2 and 10 μ s after the electron pulse

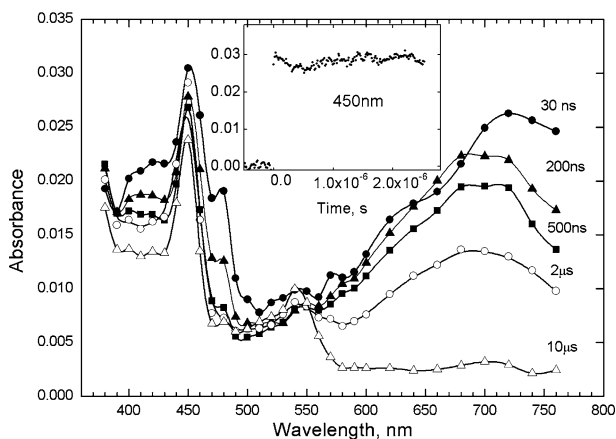


Fig. 3 Absorption spectra in pulse-irradiated Ar saturated, 14 mM TP and 80 mM BP solution in R_4NNTf_2 , measured in 30, 200, 500 ns, 2 and 10 μ s after the electron pulse. *Insert* Absorbance versus time dependence at 450 nm

Absorption connected with TP intermediates is characterized by bands with maxima at ~ 430 , 450 and 480 nm. A band with an absorption maximum at $\lambda = 480$ nm and another at 430 nm indicates formation of the $TP^{\bullet-}$ radical anion. Even at a 3 mM TP concentration some of the electrons react with TP to form the corresponding radical anion.

The most pronounced band with maximum at 450 nm behaves differently from those indicated above. It is formed in two steps, the first immediately during the pulse followed by partial decay in ~ 200 ns, which was the consequence of the background absorption decay of the other components of the spectra, including some leftover absorption of solvated electrons. The second phase of the formation

lasts 2–5 μs , depending on the TP concentration. The plot of the rate constants of pseudo-first order formation as the function of TP concentration gives the second order reaction rate constant of $k = \sim 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. However, the second step corresponds only to $\sim 10\%$ of the total absorption at 450 nm.

From the experiments with TP as the sole component present in R_4NNTf_2 solvent (the results of the radiolysis of TP in IL will be the subject of separate publication) and literature data concerning $^3\text{TP}^*$ absorption [38, 39], there are strong indication that the triplet state of p-terphenyl $^3\text{TP}^*$ is responsible for the intermediate absorption with maximum at 450 nm.

The fast formation could be energy transfer from excited states of the ionic liquid formed due to geminate recombination or other processes discussed later, and the slower step most probably is the effect of TP reaction with $^3\text{BP}^*$ (formed in small yield).



An experiment with a solution saturated in N_2O , a known scavenger of solvated electrons, gives additional evidence on the nature of “450 nm” absorption. The results presented on Fig. 4 indicate that saturation of the system with N_2O completely removes solvated electrons from the irradiated solution. Also, as a consequence the yield of BP^*H is lower; absorption at 540 nm decreases from 0.01 to 0.007 in N_2O saturated samples. Fast formation of the 450 nm absorption is then followed by an increase in next 2 μs , without an intermediate decay. The second step in that case represents $\sim 20\%$ of total absorbance at 450 nm.

The absorbance at 450 nm in 2 μs time in 14 mM TP solution is decreased by N_2O only from 0.029 to 0.027 in comparison to Ar saturated solutions. It means that N_2O very slightly influences only the first step of $^3\text{TP}^*$ excited state formation.

Taking the molar absorption coefficient of $^3\text{TP}^*$ measured in benzene ($\epsilon = 90,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) [38], and the absorbance at 450 nm 2 μs after the

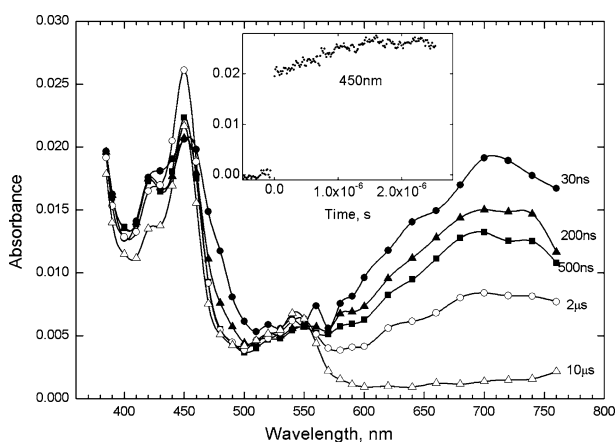


Fig. 4 Absorption spectra in pulse-irradiated N_2O saturated, 14 mM TP and 80 mM BP solution in R_4NNTf_2 , measured in 30, 200, 500 ns, 2 and 10 μs after the electron pulse. *Insert* Absorbance versus time dependence at 450 nm

electron pulse ($OD = 0.029$ in 14 mM TP and 80 mM BP solution), the radiation yield of ${}^3\text{TP}^*$ would be $G = 1.8 \times 10^{-8} \text{ mol J}^{-1}$. This value is ten times smaller than the yield of BP^*H ketyl radicals, under the assumption that both molar absorption coefficients taken from different media could be applied in IL solvent. It seems that the energy transfer from excited solvent to solute is a marginal process in the radiolysis of R_4NNTf_2 . The energy of solvent excited states could instead be involved in fragmentation of particular ions [29].

The other phenomenon leading to formation of solutes excited states also has to be taken into consideration. The 10 MeV electron irradiation is accompanied by Cherenkov light generated in the solution and in the cell. In both compounds, BP and TP excited states are easily formed in photolytical experiments. The fast formation of benzophenone and p-terphenyl excited states could be then caused by direct photolysis. To prove such an assumption more experiments will be needed.

Conclusions

The presented results indicate that energy transfer from excited ions or radicals of the solvents to the solutes in the radiolysis of R_4NNTf_2 is a marginal process. The role of Cherenkov light in the production of solutes excited state has also to be taken into consideration. The observed rate of energy transfer between ${}^3\text{BP}^*$ and TP is close to the rate of the solvated electron's reaction with efficient acceptors and is faster than the macro diffusion limit, again with the assumption that most of the ${}^3\text{BP}^*$ decay is due to reaction 4.

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