Paramagnetic relaxation of adamantane radical cation in solution

V. I. Borovkov<sup>*a,b*\*</sup> and Yu. N. Molin<sup>*a*</sup>

<sup>a</sup> Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk 630090, Russia

<sup>b</sup> Novosibirsk State University, Novosibirsk 630090, Russia

E-mail: borovkov@ns.kinetics.nsc.ru

### Abstract

To measure the rate of spin-lattice relaxation in the Jahn-Teller active adamantane radical cation, the method of time-resolved magnetic effect in recombination fluorescence of spin-correlated radical ion pairs was applied. A very low value of about 6±1 ns was obtained for the relaxation time of the radical cation in magnetic field of 1 T. A rapid spin-lattice relaxation was also found in the cases of 1, 3-dimethyladamantane and hexamethylenetetramine radical cations. Similarly to the case of benzene radical anion and cyclohexane radical cation, the relaxation is attributed to the spin-orbital interaction repeatedly arising in electronically degenerate states.

### Introduction

Polyatomic hydrocarbon radicals are known to have times of paramagnetic relaxation which, when measured in solutions, typically fall into microsecond time range [1]. The main mechanisms of the relaxation are considered to be the modulation of hyperfine interactions or the g-tensor anisotropy as well as spin-rotational interaction. However, a few exceptions from this rule have been discovered. These are radical anions of molecules having threefold or higher axis of symmetry, like benzene or fullerene [2-4]. The time of spin-lattice relaxation in such radical anions was found to be by orders of magnitude shorter as compared with less symmetric radicals. The estimations showed that the above-mentioned relaxation mechanisms cannot provide such a high relaxation rate [3,4].

The unusually rapid relaxation is believed to relate to the degeneracy of the molecular orbital where the unpaired electron appears [3]. In accordance with the Jahn-Teller effect, the symmetry of a radical gets lower as compared to that for the neutral molecule due to a deformation of some molecular bonds, which eliminates the degeneracy. Several Jahn-Teller distorted structures may arise, and the energy barriers for conformational transitions between them are usually not high [5]. It is considered that the degeneracy of the single occupied molecular orbital (SOMO) of the radical ion may be restored due to the radical structure fluctuations and then a strong spin-orbital interaction arises that causes the fast paramagnetic relaxation [3, 6].

Recently, abnormally low values of spin-lattice relaxation times  $T_1$  were observed for radical cations of cyclohexane and its derivatives in *n*-hexane solutions using the method of

Chem. Phys. Lett., 398 (2004) 422-426



**Scheme 1**. The structures of adamantane (AD), 1,3-dimethyladamantane (DMAD), and hexamethylenetetramine (HMT). With the dark spheres, nitrogen atoms are shown.

time-resolved magnetic field effect (TR MFE) of spin-correlated radical ion pairs [7]. In the case of cyclohexane radical cation the measured  $T_1$  value was found to be about 9 ns. Similarly to the case of the radical anions mentioned above [3, 8, 9] the introduction of alkyl substituents to the cyclohexane ring resulted in significant decrease of the relaxation rate.

In the present work, we have measured the spin-lattice relaxation in radical cation of adamantane (AD), whose molecule is known to have a triply degenerate molecular orbital where unpaired electron appears upon ionization. Radical cations of 1, 3-dimethyladamantane (DMAD) and hexamethylenetetramine (HMT) have been also studied. The structures of the molecules are shown in Scheme 1.

### Experimental

The luminescence of *n*-hexane solutions was detected by single photon counting technique using an X-ray fluorimeter described elsewhere [10]. The duration of the ionizing pulse with quantum energy of about 20 keV was < 2 ns. The delayed fluorescence was registered using an optical bandpass filter (260-390 nm). In order to decrease the influence of instrumental drift the fluorescence decays were recorded for periods of 250 s, alternatively, with and without the magnetic field. Zero magnetic field was adjusted to within  $\pm 0.05$  mT.

*n*-Hexane was treated as reported elsewhere [7]. With the use of gas chromatography, we revealed the methylpentanes to be the main impurities (< 1 %) in the *n*-hexane used. Contents of olefin impurities did not exceed 0.01%.

Adamantane, 1,3-dimethyladamantane, hexamethylenetetramine, *cis*-decalin, hexafluorobenzene, and *para*-terphenyl- $d_{14}$  were used as received from Aldrich. The solutions



**Fig. 1**. Decay of delayed fluorescence  $I_0(t)$  for *n*-hexane solutions of 0.01 M C<sub>6</sub>F<sub>6</sub> with the addition of 0.01 M *cis*-decalin (solid line), 0.01 M adamantane (circles) and 0.01 M 1,3-dimethyladamantane (crosshairs). were degassed by repeated freeze-pump-thaw cycles. Temperature of the irradiated samples was stabilized within ±1 K.

#### **Results and discussion**

Fig. 1 shows the delayed fluorescence decays for irradiated *n*-hexane solutions of 0.01 M  $C_6F_6$  with addition of 0.01 M *cis*-decalin (solid line), 0.01 M AD (circles) and 0.01 M 1,3-DMAD (crosshairs). The curves are normalized so that their maxima coincide. It approximately corresponds also to equality of the dose absorbed by solutions. The increase in cycloalkane concentration up to 0.1M does not affect the decay kinetics.

Almost full coincidence of the fluorescence kinetics indicates that in the studied solutions the track recombination of radical ion pairs develops in the similar way. The reactions involved are as follows. Radical anions  $C_6F_6^{-\bullet}$ , owing to a high mobility of excess electrons in *n*-hexane, are formed in subnanosecond time domain. The capturing of primary solvent radical cations by molecules of added cycloalkane (*c*-RH) is defined by their diffusion collisions and at room temperature occurs with a rate constant of about (3-4)·10<sup>10</sup> M<sup>-1</sup>s<sup>-1</sup> [11]. Thus, secondary radical cations *c*-RH <sup>+•</sup> are formed within a range of about 3 ns and the delayed fluorescence of  ${}^{1}C_{6}F_{6}^{*}$ , as shown in a Fig. 1, arises, basically, via reaction

$$c-RH^{+\bullet} + C_6F_6^{-\bullet} \to c-RH + {}^{1,3}C_6F_6^{*}$$
 (1)

Time-resolved magnetic field effect shown in Figs. 2 and 3, is the ratio  $I_B(t)/I_0(t)$  of the fluorescence decays, measured in a magnetic field and without it, accordingly, as a function of time. TR MFE is known to be defined by the dynamics of the spin states of recombining radical



**Fig. 2.** Time-resolved magnetic effect for *n*-hexane solutions of 0.01 M  $C_6F_6$  with the addition of 0.1M *cis*decalin (curve 1), 0.01 M 1, 3-dimethyladamantane (curve 2), 0.01M adamantane (curve 3), observed in a field of 1T at 293K, and 0.01M adamantane registered in a field of 1T at 323K (curve 4) and in a field of 0.1T at 293K (curve 5). Smooth lines are approximations for the long time decay.

ion pairs and to provide information on ESR spectra of radical ions involved. The description of the theory and applications of TR MFE method can be found elsewhere [12-14].

In the present work, no detailed consideration of the spin dynamics of radical pairs at early times is performed, but only the decay of TR MFE curves, which is defined by spin-lattice relaxation, is analyzed. As demonstrated in ref. [7], when the rate of increasing of TR MFE curve exceeds that of the curve decay, TR MFE on longer times is approximately described by expression:

$$\frac{I_B(t)}{I_0(t)} \approx 1 + \theta \cdot e^{\frac{-t}{T_1}}$$
<sup>(2)</sup>

Here  $1/T_1=1/T_{1a}+1/T_{1c}$  is the sum of the spin-lattice relaxation rates for radical anion and a radical cation, as indicated by subscripts *a* and *c*, accordingly.  $\theta$  denotes the fraction of the radical pairs born in the singlet-correlated state.

In Fig. 2 some experimental TR MFE curves as observed in *n*-hexane solutions of  $C_6F_6$  with addition of *cis*-decalin (curve 1), DMAD (a curve 2), and AD (curves 3-5) in the concentrations of 0.01 M are shown in semi-logarithmic coordinates as scatter plots. The absence of an obvious decay of TR MFE curve for *cis*-decalin solution presented demonstrates that the spin-lattice relaxation rates of both  $C_6F_6^{-\bullet}$  radical anion and *cis*-decalin radical cation can be neglected within the time range. Thus, the rapid decay of the TR MFE curves 2-5 is sure to be determined by the spin-lattice relaxation of the AD or DMAD radical cations.

Chem. Phys. Lett., 398 (2004) 422-426

In Fig. 2 solid lines present the best fitting for exponential decay of the curves. From their slopes, the  $T_1$  values for different radical cations have been estimated using Eq. 2. The values obtained are presented in Table 1 together with that for  $C_6F_6^{-\bullet}$  radical anion as determined in our previous work [7]. It was also found that increasing the concentration of added cycloalkanes up to 0.1 M slightly reduced the magnitude of the effect, but did not affect noticeably the TR MFE curve decays.

In order to get a better insight into the relaxation mechanism involved, the TR MFE has been measured in *n*-hexane solutions of HMT whose molecule has structure of the same symmetry as adamantane one. Unfortunately, in solutions containing both  $C_6F_6$  and HMT the delayed fluorescence does not arise. This is because the energy released at recombination of radical ion pairs (HMT<sup>+•</sup>)/ ( $C_6F_6^{-•}$ ) is not enough to form  ${}^1C_6F_6^*$  as in reaction (1) [11, 15, 16]. Therefore, when studying the TR MFE in HMT solutions, *para*-terphenyl-*d*<sub>14</sub> (*p*-TP) as an electron acceptor and luminophor was used. Another experimental complication was a low solubility of HMT in hexane. The maximal HMT concentration reached at room temperature was about  $2 \cdot 10^{-3}$  M. Thus, at this concentration the formation of the secondary radical cation HMT<sup>+•</sup> required about 15 ns. Before the capturing, the TR MFE was defined by *hfc* in radical ion pairs (RH<sup>+•</sup>)/(*p*-TP<sup>-•</sup>), where RH was a molecule of *n*-hexane or impurity, methylpentane.

Results of the TR MFE measurements in *n*-hexane solutions of HMT are shown in Fig. 3. Curve 1 shows the magnetic field effect for *n*-hexane solution of  $3 \cdot 10^{-5}$  M *p*-TP without addition of HMT. The curve's shape is typical for the case of a radical ion pair, which includes both a radical with negligibly small *hfc* constants and a radical with a broad unresolved ESR spectrum [14, 17]. The maximum of TR MFE is placed at 5-6 ns which corresponds to the width of unresolved ESR spectrum of RH<sup>+•</sup> as large as 2 MT. Such spectrum width is significantly less than that observed in low temperature matrixes for radical cations  $C_6H_{14}^{+•}$  because hyperfine interactions in the radicals are partly averaged in solution by fast conformational transitions [14]. As follows from Fig. 3, in the studied time range the spin-lattice relaxation of both RH<sup>+•</sup> and *p*-TP<sup>-•</sup> can be neglected.

Curves 2 and 3 in Fig. 3 show TR MFE at 293 K for solutions of  $3 \cdot 10^{-5}$  M *p*-TP in *n*-hexane with addition of  $10^{-3}$  M and  $2 \cdot 10^{-3}$  M HMT, accordingly. With increasing HMT concentration the formation of HMT<sup>+•</sup> occurs faster and TR MFE curves start earlier to decay due to the fast spin-lattice relaxation of HMT radical cation. The solid lines are the best fits for the decays of the curves and their slope corresponds to T<sub>1</sub> value for HMT<sup>+•</sup> of about 35 ns for both of the HMT concentrations. With decreasing magnetic field strength down to 0.1 T, as well as with increasing temperature up to 323 K, the rate of TR MFE curves decay, unlike that in



**Fig. 3.** Time-resolved magnetic effect for *n*-hexane solutions of  $3 \cdot 10^{-5}$ M *para*-terphenyl- $d_{14}$ , observed in a field of 1T at 293K without addition of HMT (curve 1), with addition  $10^{-3}$ M HMT (curve 2),  $2 \cdot 10^{-3}$  M HMT (curve 3), and also with addition  $2 \cdot 10^{-3}$ M HMT in a field of 0.1T at 293K (curve 4) and  $3 \cdot 10^{-3}$  M HMT in a field of 1T at 323K (curve 5). Smooth lines are approximations for the long time decay.

adamantane solutions, noticeably increases as shown by curves 4 and 5, respectively. Corresponding  $T_1$  values are presented in Table 1.

Thus, the spin-lattice relaxation rate of  $HMT^{+\bullet}$  in solution is fast and comparable with that of  $AD^{+\bullet}$ , which supports the proposition about the decisive role of molecular symmetry in paramagnetic relaxation of the radical cations. A rather strong temperature dependence of

Radical ion	$T_l$ , ns	Conditions
$C_6F_6^{-\bullet}$	350 ±15 <sup>a</sup>	В=1Т; Т=293К
Adamantane <sup>+•</sup>	6.5 ±1	В=1Т; Т=293К
$(AD^{+\bullet})$	6.3 ±1	В=1Т; Т=323К
	5 ±1	B=0.1T; T=293K
1,3-Dimethyladamantane <sup>+•</sup>	8.2 ±1	В=1Т; Т=293К
(DMAD <sup>+•</sup> )	7.5 ±1	В=1Т; Т=323К
	6.8 ±1	B=0.1T; T=293K
Hexamethylenetetramine <sup>+•</sup>	35 ±7	В=1Т; Т=293К
(HMT <sup>+•</sup> )	9 ±3	В=1Т; Т=323К
	19 ±4	B=0.1T; T=293K

Table 1. The spin-lattice relaxation time of the studied radical ions, as estimated from the long time decay of TR MFE curves.

<sup>*a*</sup> From ref. [7]

HMT<sup>+•</sup> relaxation rate indicates that some activation is needed in this case to attend the vibrationally excited states responsible for fast relaxation. The evident dependence of HMT<sup>+•</sup> relaxation on magnetic field strength is most probably to be related to the properties of such states, too. For rough approximation of the correlation time  $\tau_c$  of the perturbation causing the relaxation one can assume that the magnetic field dependence of the relaxation rate is determined by a factor  $1/(1+(\gamma B \tau_c)^2 \text{ similar to that for many relaxation mechanisms described by the Redfield theory [18]. Using the ratio of the relaxation rates measured in fields of 0.1 T and 1T at 293 K, it is easy to estimate the <math>\tau_c$  value to be about 5 ps for HMT<sup>+•</sup>. For both AD and DMAD radical cations where field dependence is less pronounced the corresponding values should be shorter. For quantitative estimations, the relaxation times have to be measured in stronger magnetic fields. The perturbation amplitudes can not be estimated this way because the explicit mechanism of relaxation is unknown.

Note that in the case of  $AD^{+\bullet}$ , unlike cyclohexane<sup>+•</sup> [7], the introduction of two methyl groups affects slightly the relaxation rate. It suggests that in the case of  $\sigma$ -radicals the influence of substituents is not so obvious as compared to  $\pi$ -radicals. The analysis of the influence on the electronic and spin density distribution in  $\sigma$ -radicals using the quantum chemistry calculations seems to be required to account for the difference.

# Conclusions

With the use of the method of time-resolved magnetic field effect in recombination fluorescence, the spin-lattice relaxation times for the radical cations of adamantane, dimethyladamantane and hexamethylenetetramine in *n*-hexane are measured. The relaxation mechanism resulting in the observed very short  $T_1$  values is sure to be more efficient than those typical of organic radicals. Thus, in the present work a novel group of radical ions with an abnormally rapid spin-lattice relaxation was found. The relaxation is attributed to the spin-orbital interaction repeatedly arising in electronically degenerate states of the radicals.

### Acknowledgments

The present work was supported by the Russian Foundation for Basic Research (grant 02-03-32224), INTAS (grant 00-0093), and the program of Leading Scientific Schools (grant NS-84.2003.3).

## References

- 1. D.M. Bartels, R.G. Lawler, A.D. Trifunac, J. Chem. Phys. 83 (1985) 2686.
- 2. M. G. Townsend, S. I. Weissman, J. Chem. Phys. 32 (1960) 309.
- 3. M. R. Das, S. B. Wagner, J. H. Freed, J. Chem. Phys. 52 (1970) 5404.
- A.J. Schell-Sorokin, F. Mehran, G.R. Eaton, S.S. Eaton, A. Viehbeck, T.R. O'Toole, C.A. Brown, *Chem. Phys. Lett.* 195 (1992) 225.
- K. Toriyama, in: A. Lund and M. Shiotani (Eds.), Radical Ionic Systems, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991, p. 99.
- 6. H. M. McConnell, J. Chem. Phys. 34 (1961) 13.
- 7. V.I. Borovkov, Yu.N. Molin, Phys. Chem. Chem. Phys. 6 (2004) 2119.
- 8. R. Das, B. Venkataraman, J. Indian Chem. Soc., 63 (1986) 91.
- 9. M. Brustolon, A. Zoleo, G. Agostini, M. Maggini, J. Phys. Chem. A. 102 (1998) 6331.
- S.V. Anishchik, V.M. Grigoryants, I.V. Shebolaev, Yu.D. Chernousov, O.A. Anisimov, Yu.N. Molin, *Pribory i tekhnica eksperimenta*, 4 (1989) 74 (in Russian).
- 11. V.I. Borovkov, K.A. Velizhanin, Chem. Phys. Lett., 394 (2004) 441.
- 12. B. Brocklehurst, Chem. Soc. Rev. 31 (2002) 301.
- 13. V.A. Bagryansky, V.I. Borovkov, Yu.N. Molin, Phys. Chem. Chem. Phys., 6 (2004) 924.
- 14. V.I. Borovkov, V.A. Bagryansky, I.V. Yeletskikh, Yu.N. Molin, Mol. Phys. 100 (2002) 1379.
- 15. Q.Y. Shang, C. Dion, E.R. Bernstein, J. Chem. Phys. 101 (1994) 118.
- 16. D.W. Werst, Chem. Phys. Lett. 251 (1996) 315.
- 17. K. Schulten, P.G. Wolynes, J. Chem. Phys. 68 (1978) 3292.
- A. Carrington, A.D. McLachlan, *Introduction to magnetic resonance with application to chemistry and chemical physics*. Harper&Row, Publishers, NewYork, Evanston, and London, 1967.