# PHYSICAL CHEMISTRY

Unusual Proton-Transfer Complex between the 2,2,6,6-Tetramethylpiperidine Radical Cation and Neutral Molecule

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As is known, radical cations (RCs) of aliphatic amines are prone to react in solution with their parent neutral molecules. This is accompanied by proton (or hydrogen atom) transfer [1], which leads to the formation of neutral radicals (as a rule, α-aminoalkyl) and ammonium-type cations:

$$RCH_2\overset{\bullet +}{-}NR_2 + R_2N–CH_2R$$
$$\longrightarrow R\overset{\bullet}{C}H–NR_2 + R_2\overset{+}{N}H–CH_2R. \tag{1}$$
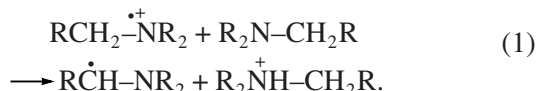
In addition, in some cases (for example, RCs of bicyclic amines with a bridgehead nitrogen atom [2], RCs of triethylamine in zeolite pores [3]), symmetric dimeric RCs with a two-center three-electron σ bond between the nitrogen atoms can form:

$$R_3N^{\bullet +} + NR_3 \longrightarrow R_3N\overset{\bullet +}{\cdots}NR_3. \tag{2}$$
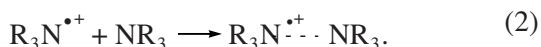
In this study, we showed that the RCs of 2,2,6,6-tetramethylpiperidine (TMP), an aliphatic amine without hydrogen atoms in the α position to the amino group, react with their parent neutral molecules to form dimeric complexes of unusual structure. For the first time, we revealed a dimeric amine RC with spatially separated spin and charge due to proton transfer from the RC to the neutral molecule by the optically detected ESR (OD ESR) and time-resolved magnetic field effect (TR-MFE) methods.

In the OD ESR method, a resonance was detected by monitoring the decrease in the intensity of recombination fluorescence that arises from recombination of radical ion pairs in a resonance microwave field. The signal is a superposition of the spectra of two radical ions that

form a spin-correlated pair. Experiments were carried out on an OD ESR spectrometer [4] built on the basis of a Bruker ER-200D ESR spectrometer, which was equipped with a source of ionizing radiation (X-ray tube) and a photomultiplier for measuring the recombination fluorescence intensity. Spectra were recorded at a microwave power of 5 W and an external magnetic field modulation amplitude of 0.36 mT. To determine HFC constants, the ESR spectra were simulated with the use of the WinSim-2002 program [5].

In the TR-MFE method, the kinetics of decay of the recombination fluorescence intensity $I(t)$ excited by a pulsed ionizing radiation source was measured [6]. In weakly polar solutions, the intensity $I(t)$ is known to be proportional to the product of the geminate recombination kinetics $F(t)$ by the probability of the pair being in the singlet state $W_s(t)$ [7]:

$$I(t) \sim F(t)W_s(t).$$

To separate the $W_s(t)$ function, which determines quantum beats, the $I_B(t)/I_0(t)$ ratio, referred to as the magnetic field effect, was used for analysis. Here, $I_B(t)$ is measured in a strong magnetic field and $I_0(t)$ is measured in a zero magnetic field. Simulation of the magnetic effect decay curves made it possible to determine the spectroscopic parameters of radical ions, in particular, the magnitude and sign of HFC constants.

Squalane (2,6,10,15,19,23-hexamethyltetracosane) was used as a solvent for OD ESR. In the temperature range under consideration, the viscosity of this solvent changed within 17–170 cP [8]. All samples contained a luminescing electron acceptor *para*-terphenyl-d_{14} (PTP).

Figure 1 shows the OD ESR spectra of TMP + PTP solutions in squalane at different temperatures. Spectrum *1* is due to the radical ion pair (PTP$^{\bullet-}$/TMP$^{\bullet+}$). The strong central line in the spectrum arises from the

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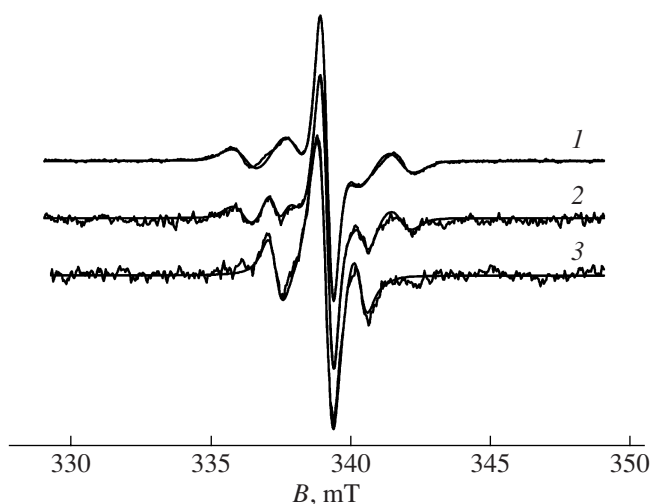 *pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia*

Fig. 1. OD ESR spectra of TMP solutions containing 1.5×10^{-3} M PTP. (*1*) 10^{-2} M TMP, $T = 267$ K, the smooth curve is the simulation result with the parameters $g = 2.0032$, $a_N = 1.8$ mT, and $a_H = 1.9$ mT for the TMP radical cation and $g = 2.0027$ for the PTP radical anion. (*2*) 3×10^{-2} M TMP, $T = 273$ K, the smooth curve is the simulation result with the parameters $g = 2.0032$, $a_N = 1.8$ mT, and $a_H = 2.1$ mT for the TMP radical cation; $g = 2.0044$, $a_N = 1.6$ mT, and $a_H = 0$ for the dimeric complex; and $g = 2.0027$ for the PTP radical anion. (*3*) 3×10^{-2} M TMP, $T = 309$ K, the smooth curve is the simulation result with the parameters $g = 2.0044$, $a_N = 1.5$ mT, and $a_H = 0$ for the dimeric complex and $g = 2.0027$ for the PTP radical anion.

Fig. 2. TR-MFE curves for TMP + PTP solutions. (a) 3×10^{-3} M TMP + 3×10^{-5} M PTP in cyclohexane, $T = 293$ K, $B = 100$ mT. The smooth curve is the simulation result with the parameters of the radical cation $a_N = 1.8$ mT and $a_H = -1.9$ mT. (b) 3×10^{-2} M TMP + 3×10^{-5} M PTP in *n*-octane, $T = 293$ K, $B = 100$ mT. The smooth curve is the simulation result with the parameters of the radical cation $a_N = 1.5$ mT and $a_H = 0$.

PTP radical anion, and the other lines are due to $TMP^{\bullet+}$ with $g = 2.0032$ and the HFC constants $a_N = 1.8$ and $a_H = 1.9$ mT. These values are consistent with the literature data [9].

As the temperature and TMP concentration increase (Fig. 1, curve *2*), the spectrum shows a new signal with $g = 2.0044$ and an HFC constant for only one magnetic nucleus $a_N = 1.46$ mT. With a further increase in temperature and a decrease in the viscosity of a solution, this signal builds up, while the intensity of the initial $TMP^{\bullet+}$ signal decreases. At 309 K, the signal due to $TMP^{\bullet+}$ is already indistinguishable (Fig. 1, curve *3*). In all these spectra, the intensity of the PTP radical anion signal is 50% of the integrated spectral intensity. This means that the change in the OD ESR spectrum is associated with transformations of TMP radical cations.

The TR-MFE experiments were carried out in inviscid solvents, *n*-octane and cyclohexane, in order to ensure fast capture of primary positive charge carriers by TMP molecules. This is necessary for clear observation of quantum beats caused by HFC in secondary radical cations [7]. PTP was also used as an electron acceptor and luminophore. The TR-MFE experiments showed that the change in the shape of quantum beats
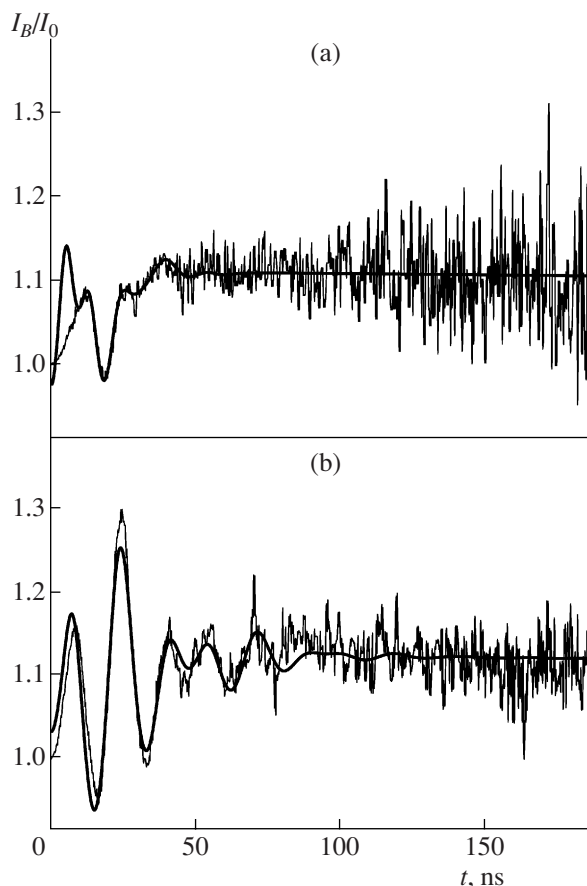
in recombination of the $(PTP^{\bullet-}/TMP^{\bullet+})$ pair with an increase in the TMP concentration completely corresponds to the aforementioned transformation of the OD ESR spectrum. Figure 2 shows the TR-MFE curves for solutions with two different concentrations of TMP. In this case, the oscillations observed in the TR-MFE curves are caused by HFC in the radical cation involved in the spin-correlated pair $(PTP^{\bullet-}/RC^{\bullet+})$. At low TMP concentrations (Fig. 2a), the best-fit parameters are $a_N = 1.8$ mT and $a_H = -1.9$ mT, which corresponds to the results of the OD ESR measurements for $TMP^{\bullet+}$.

An increase in the TMP concentration up to 3×10^{-2} M (Fig. 2b) leads to a radical change in the shape of HFC beats. The experimental curve corresponds to HFC to a single magnetic nucleus with the constant $a_N = 1.5$ mT.

Thus, both methods show that, with an increase in the TMP concentration and/or a decrease in the solution viscosity, which lead to an increase in the frequency of pair encounters of particles in solution, a signal of a new radical cation appears in the spectrum. The fact that this radical cation is observed in TR-MFE spectra is evidence that it is formed from the initial TMP$^{\cdot+}$ with retention of spin correlation in the PTP$^{\cdot-}$/RC$^{\cdot+}$ radical ion pair.

It might be expected that, in pair encounters of RCs with neutral TMP molecules, reactions (1) or (2) take place. However, the principle of signal formation in both methods [7, 10] rules out the possibility of complete separation of spin and charge, as occurs in reaction (1). At the same time, the formation of the dimeric RC by scheme (2) seems to be improbable since the observed ESR spectrum shows a splitting due to a single nitrogen nucleus.

This inconsistency can be removed if we assume that the encounter of the RC and the TMP molecule leads to the formation of an asymmetric dimeric complex. It is worth noting that the characteristics of this radical cation complex—$g = 2.0044$ and $a_N = 1.46$ mT—are close to the parameters of aminyl radical **1** ($g = 2.0048$, $a_N = 1.64$ mT [11]). This means that the required conditions are met by a structure in which the spin and charge are separated due to proton transfer from the TMP RC to its parent neutral molecule (structure **2**).

1   **2**
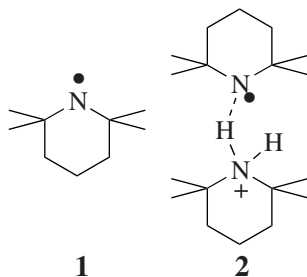
Quantum-chemical PM3 [12] calculations showed that proton transfer when the TMP RC and the neutral molecule approach each other is energetically favorable. The difference between the standard enthalpies of formation of the proton-transfer complex and the free TMP RC and neutral molecule was $\Delta H_r^0 = -22.7$ kcal/mol.

The calculations of HFC constants performed at the UB3LYP/6-31+G*//PM3 level [13] gave $a_N = 1.62$ mT and $a_H = -2.15$ mT for the TMP RC and $a_N = 1.57$ mT and $a_H = -0.03$ mT for the resulting complex. These values are well consistent with the experimental data.

The formation rate of the proton-transfer complex can be estimated from the following reasoning. The TR-MFE curve observed for a 3×10^{-2} M TMP solution in *n*-octane is adequately described assuming the instantaneous formation of the complex, which points

to an insignificant contribution of HFC in TMP$^{\cdot+}$ to the spin dynamics of the radical pair. This is possible if the time of formation of the complex with the neutral molecule in this solution is noticeably smaller than the reciprocal width of the ESR spectrum of TMP$^{\cdot+}$ (about 3×10^8 s^{-1} in frequency units). Hence, the complex formation rate constant should be higher than or on the order of 10^{10} M^{-1} s^{-1}, which is close to the rate constant of a diffusion-controlled reaction.

Thus, using the OD ESR and TR-MFE techniques, we detected for the first time the formation of an unusual complex with proton transfer from the radical cation to the molecule of 2,2,6,6-tetramethylpiperidine.

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