

# Investigation of degenerate electron exchange reactions involving short-lived radicals by the method of time-resolved CIDNP



Maksim P. Geniman<sup>1,2</sup>

<sup>1</sup>ITC SB RAS, Novosibirsk, Russian Federation

<sup>2</sup>NSU, Novosibirsk, Russian Federation



## 1. Abstract

The time-resolved CIDNP method can provide information about degenerate electron exchange reactions involving short-lived radicals. In the temperature range from 8 to 65°C, the degenerate electron exchange reactions of the guanosine-5'-monophosphate cation GMPH<sup>+</sup> with the dication radical GMPH<sup>•+</sup> at pH = 1.3, of the guanosine-5'-monophosphate anion GMP(-H)<sup>•</sup> with the neutral radical GMP(-H)<sup>•</sup> at pH = 11.3, of the N-acetyl tyrosine anion NacTyrO<sup>•</sup> with a neutral radical NacTyrO<sup>•</sup> at pH = 11.7 and of the tyrosine anion TyrO<sup>•</sup> with a neutral radical TyrO<sup>•</sup> at pH = 11.7 were studied. In all cases the radicals were formed in the reaction of quenching triplet 2,2'-dipyridyl. The reorganization energies were calculated using the Arrhenius equation. The rate constant of the reductive electron-transfer reaction in pair GMP(-H)<sup>•</sup>/TyrO<sup>•</sup> was determined at T = 25°C.

The rate of nuclear paramagnetic relaxation was found for the 3,5 and β-protons TyrO<sup>•</sup> and N-AcTyrO<sup>•</sup>, the 8-proton GMPH<sup>•+</sup> and GMP(-H)<sup>•</sup>, the 3,4-protons DPH<sup>•</sup> at each temperature. In all cases, the dependences of the rate of nuclear paramagnetic relaxation on temperature are described by the Arrhenius dependence.

## 2. Reaction scheme

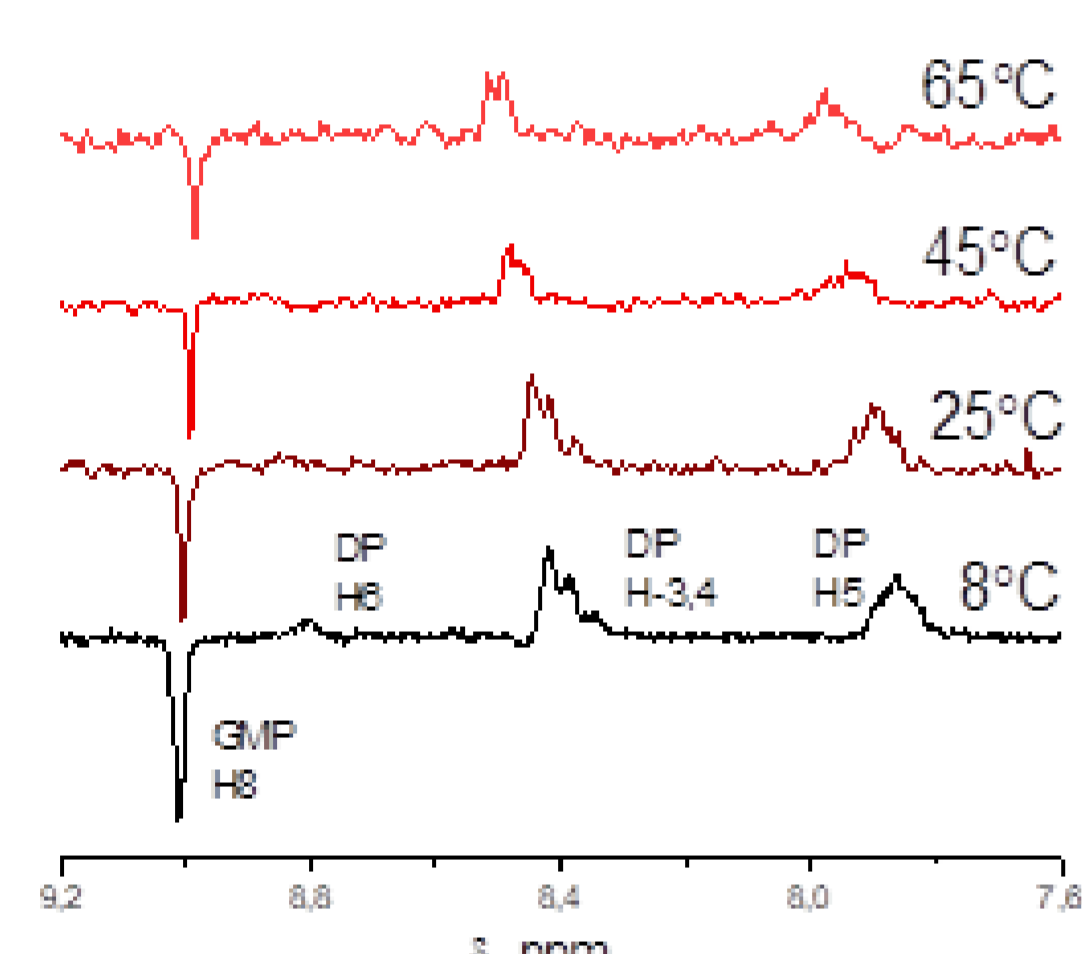
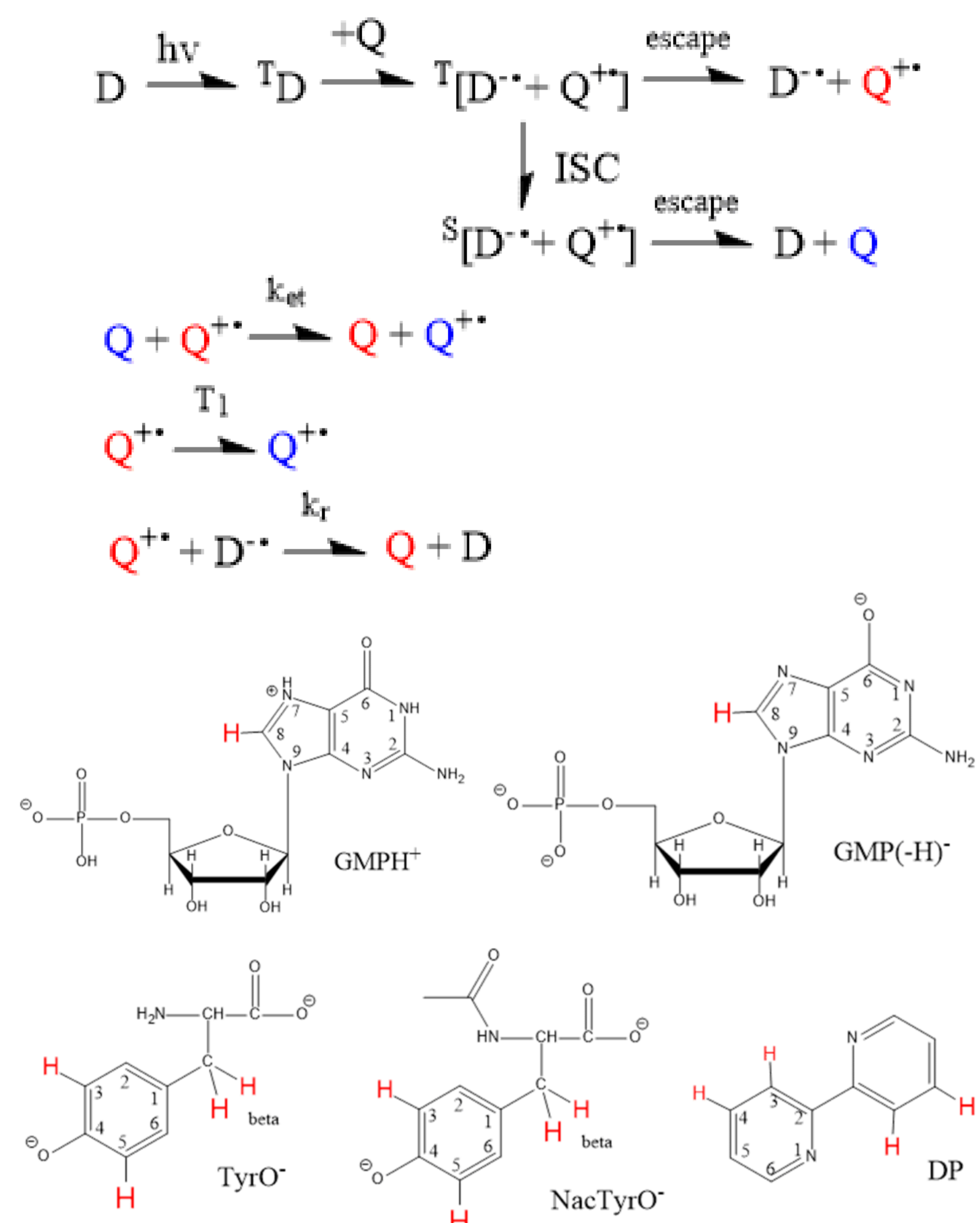


Fig.1. 200 MHz <sup>1</sup>H CIDNP spectra recorded upon the photoirradiation of solutions containing 0.5 mM DPH<sup>+</sup> and 6, 2.3, 2.3, 2 mM GMPH<sup>+</sup> at pH 1.3 and temperature 8, 25, 45, 65°C. The spectra were recorded with the zero delay after a laser pulse.



## 3. CIDNP kinetics

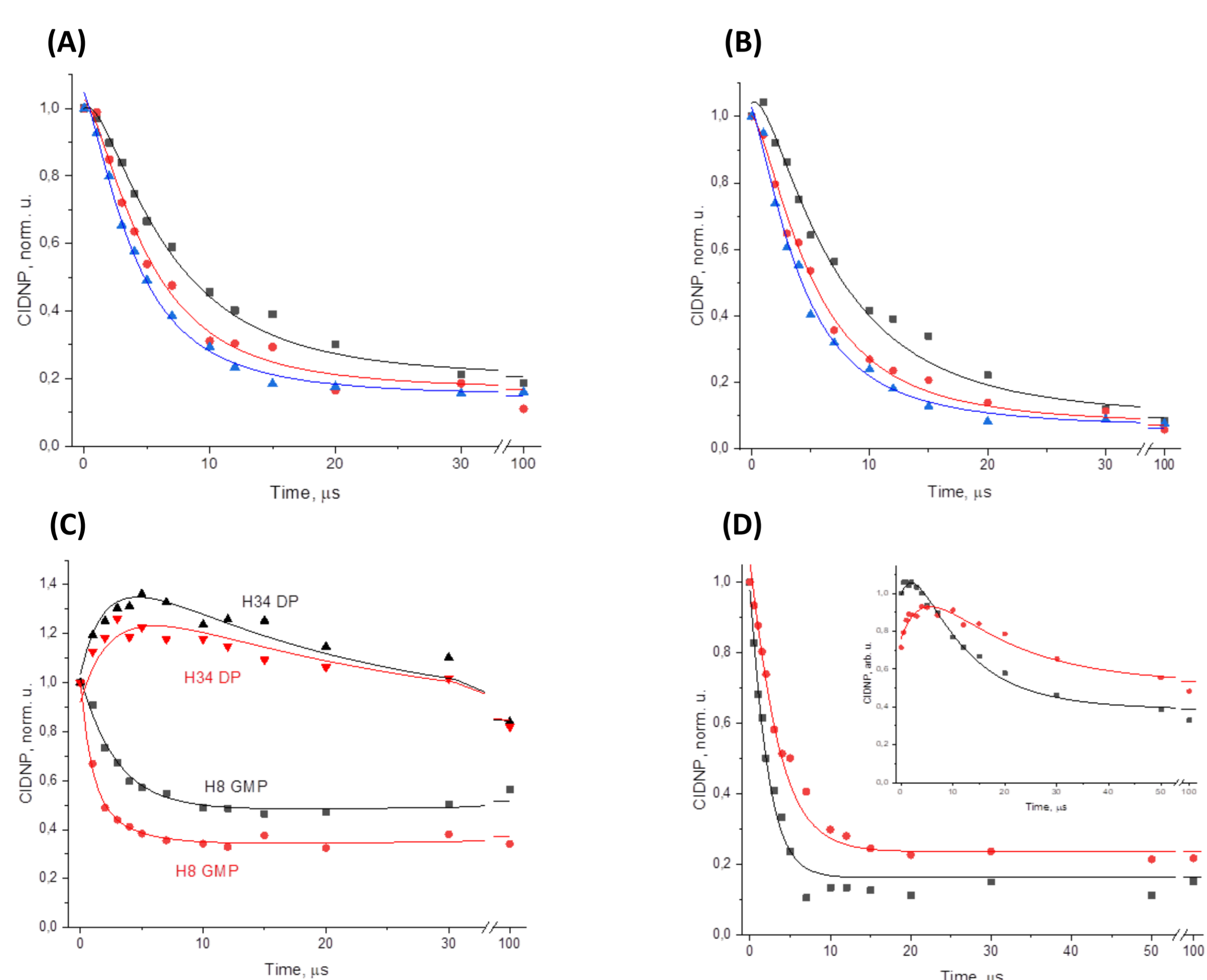


Fig.2. CIDNP kinetic curves obtained in the photoinduced reaction between (A) DP and TyrO<sup>•</sup> at pH 11.7 for the H35 protons of TyrO<sup>•</sup> at T = 55°C, C(TyrO<sup>•</sup>) = 2 mM (black), C(TyrO<sup>•</sup>) = 3.25 mM (red), C(TyrO<sup>•</sup>) = 4.5 mM (blue); C(DP) = 15 mM in all samples; (B) the same as in (A) for H-β protons of TyrO<sup>•</sup>; (C) DPH<sup>+</sup> and GMPH<sup>+</sup> at pH 1.3 for the H8 proton of GMPH<sup>+</sup> and the H34 protons of DPH<sup>+</sup> at T = 8°C, C(GMPH<sup>+</sup>) = 6 mM (black), C(GMPH<sup>+</sup>) = 12 mM (red); C(DPH<sup>+</sup>) = 0.5 mM in all samples; (D) DP, TyrO<sup>•</sup> and GMP(-H)<sup>•</sup> at pH 11.7 for the H8 proton of GMP(-H)<sup>•</sup> and the H35 protons of TyrO<sup>•</sup> (insert) at T = 25°C, C(TyrO<sup>•</sup>) = 1.3 mM (red), C(TyrO<sup>•</sup>) = 2.5 mM (black); C(GMP(-H)<sup>•</sup>) = 4 mM and C(DP) = 15 mM in all samples. Solid lines are calculation, and points are experimental data normalized to the value at the initial moment.

## 4. Degenerate electron exchange

Table 1. Reorganization energies and pre-exponential factors found from the Arrhenius equation.

reaction	ln(A)	λ, eV
GMPH <sup>•+</sup> + GMPH <sup>+</sup>	29.4 ± 0.6	0.81 ± 0.06
GMP(-H) <sup>•</sup> + GMP(-H) <sup>•</sup>	24.8 ± 0.6	0.42 ± 0.05
NacTyrO <sup>•</sup> + NacTyrO <sup>•</sup>	24.4 ± 0.5	0.38 ± 0.05
TyrO <sup>•</sup> + TyrO <sup>•</sup>	27.1 ± 0.4	0.66 ± 0.04

Dependence of the DEE rate constant on temperature:

$$k_{et} = \frac{A}{\sqrt{T}} \exp\left(-\frac{\lambda}{4RT}\right)$$

$$\ln(k_{et}\sqrt{T}) = \ln(A) - \frac{\lambda}{4RT}$$

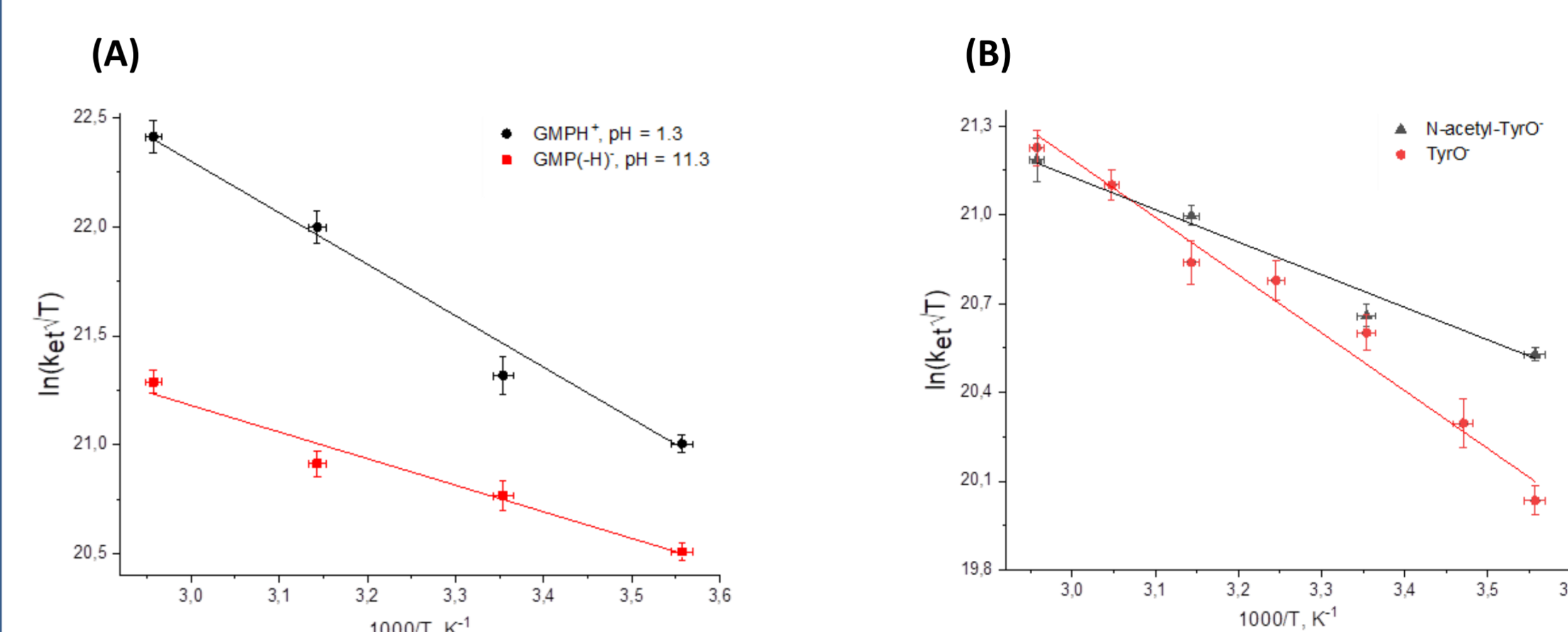


Fig.3. Arrhenius plot (A) for DEE between GMPH<sup>•+</sup> + GMPH<sup>+</sup> (black) and for DEE between GMP(-H)<sup>•</sup> + GMP(-H)<sup>•</sup> (red) (B) for DEE between NacTyrO<sup>•</sup> + NacTyrO<sup>•</sup> (black) and for DEE between TyrO<sup>•</sup> + TyrO<sup>•</sup> (red).

## 5. T<sub>1</sub> relaxation in short-lived radicals

We assume that the main relaxation mechanism is the modulation of the HFI tensor due to the rotation of the whole molecule.

$$\frac{1}{T_1} \propto \frac{\tau}{1 + w^2\tau^2} \approx \tau \quad \tau = \frac{4\pi a^3 \eta}{3kT} \quad \eta(T) = \eta_0 \exp\left(\frac{E}{RT}\right)$$

$$\ln(\eta) = \ln(\eta_0) + \frac{E}{RT} \quad \ln\left(\frac{T}{T_1}\right) = \ln(A) + \frac{E}{RT}$$

Then the temperature dependence of viscosity and T/T<sub>1</sub> should coincide. For H35 TyrO<sup>•</sup>, we assume the contribution of intramolecular rotations to relaxation, Fig. 4E shows a curve in the Lipari Szabo model. For H-β NacTyrO<sup>•</sup> and H-β TyrO<sup>•</sup> T<sub>1</sub> does not depend on T.

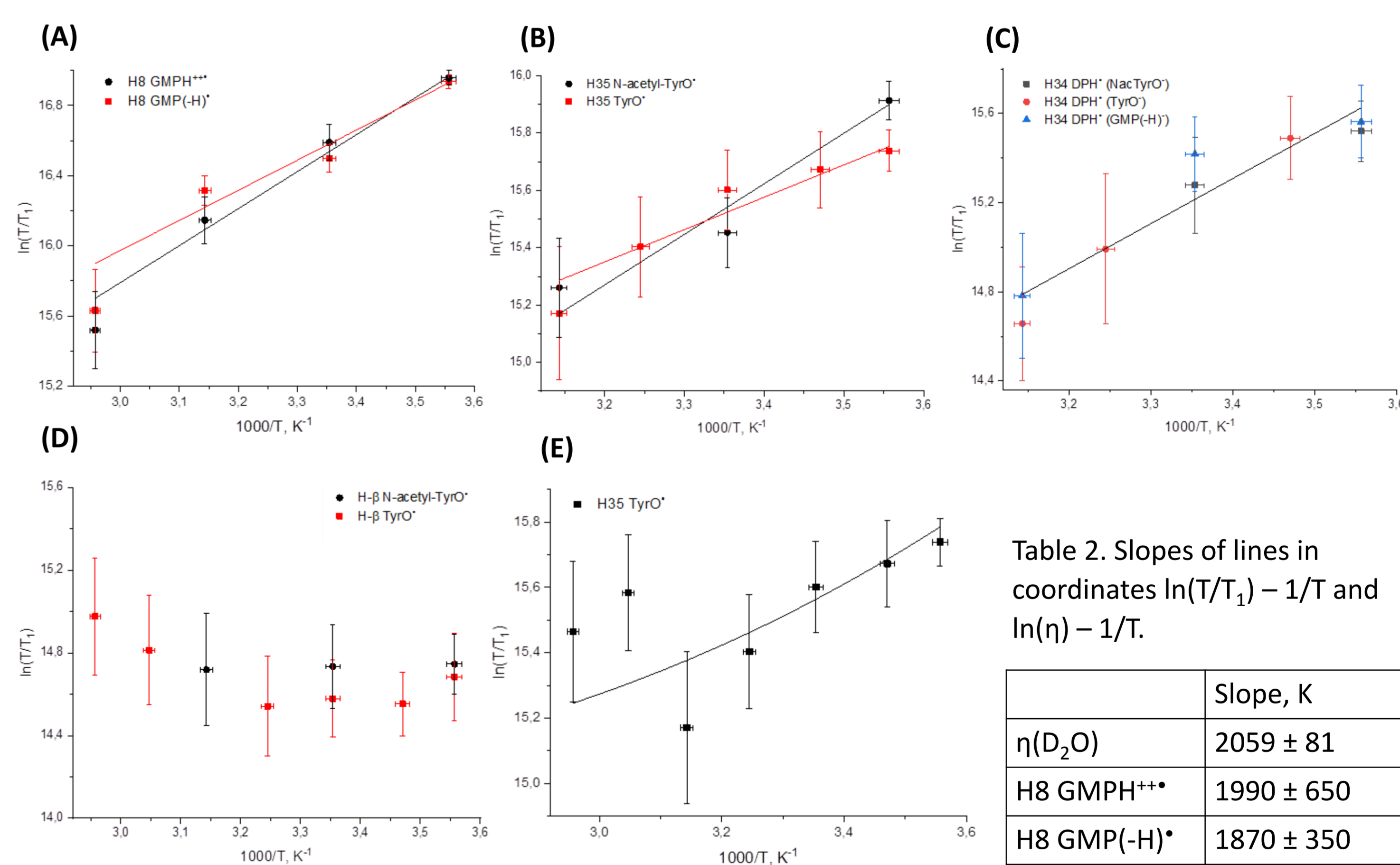


Fig.4. Dependence of T<sub>1</sub> on T in coordinates ln(T/T<sub>1</sub>) - 1/T for protons (A) H8 GMPH<sup>•+</sup> and H8 GMP(-H)<sup>•</sup> (B) H35 NacTyrO<sup>•</sup> and H35 TyrO<sup>•</sup> (C) H34 DPH<sup>•</sup> (D) H-β NacTyrO<sup>•</sup> and H-β TyrO<sup>•</sup> (E) H35 TyrO<sup>•</sup>, the curve is plotted according to the Lipari-Szabo model.

Table 2. Slopes of lines in coordinates ln(T/T<sub>1</sub>) - 1/T and ln(η) - 1/T.

	Slope, K
η(D <sub>2</sub> O)	2059 ± 81
H8 GMPH <sup>•+</sup>	1990 ± 650
H8 GMP(-H) <sup>•</sup>	1870 ± 350
H35 NacTyrO <sup>•</sup>	1760 ± 370
<b>H35 TyrO<sup>•</sup></b>	<b>1130 ± 210</b>
H34 DPH <sup>•</sup>	1790 ± 300

## 6. Conclusions

- The rate constants of the DEE and nuclear paramagnetic relaxation times were determined in four systems in the temperature range 8-65°C.
- The rate constant for the electron transfer from the TyrO<sup>•</sup> to the neutral radical GMP(-H)<sup>•</sup> was determined at T = 25°C, k<sub>red</sub> = 1.48\*10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup>.
- The reorganization energies were calculated using the Arrhenius equation.
- The dependences of the rate of nuclear paramagnetic relaxation on temperature are described by the Arrhenius dependence.