The ESR spectra of the electrochemically generated[3] radical cations, biradicals of systems **1** and **2**, and the neutral radical of *N*-methyl-2,4,6-triphenylpyridinium ($\mathbf{3}^{\cdot}$) are characterized by equal *g* factors of 2.0026 but different linewidths. For molecule **1**, the potentials of formation of the radical cation (−0.82 V) and biradical (−0.95 V) differ.[1] The reduction of molecule **2** occurs *via* one two-electron stage (−1.0 V)[1]; therefore, the radical cations were obtained at −0.85 V (in the region of the predominant generation of monoradicals).

The shape of the ESR line of $\mathbf{3}^{\cdot}$ is due to the unresolved HFS from one N nucleus and protons. The main contribution to the linewidth is made by the splitting from the N nuclei with spin $I = 1$, and the ESR line is well simulated by three Gaussian lines with the width $D = 0.45$ mT with the splitting $a_N = 0.5$ mT. The Gaussian shape of the line indicates the unresolved HFS from protons, and low HFS constants indicate that the unpaired electron is mainly located on the N atom. For radical cation $\mathbf{1}^{\cdot+}$ and biradical $\mathbf{1}^{\cdot\cdot}$, the ESR spectra are narrowed as compared to that of radical $\mathbf{3}^{\cdot}$. Intramolecular collisions of the triphenylpyridinium rings result in narrowing, and the narrowing mechanisms for $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{\cdot\cdot}$ are different. In the case of $\mathbf{1}^{\cdot+}$, the narrowing is due to hole/electron hopping. If the time τ between the hops is sufficiently short, so that the condition is fulfilled:

$$\gamma^2 a_N^2 \tau^2 \ll 1, \tag{1}$$

where γ is the electron gyromagnetic ratio ($1.77 \cdot 10^8$ s^{-1} mT^{-1}), the HFS from two equivalent protons with the constant $a_N{}' = a_N/2$ should be observed. In fact, the spectrum for $\mathbf{1}^{\cdot+}$ is well simulated by the HFS from two equivalent protons with $a_N{}' = 0.2$ mT and $D = 0.44$ mT. Condition (1) is fulfilled at $\tau < 10^{-8}$ s.

In the case of biradical $\mathbf{1}^{\cdot\cdot}$, the narrowing is due to the spin exchange between the triphenylpyridinium radicals at the moment of their intramolecular collisions. This mechanism is characterized by several parameters, such as the value of exchange interaction J and the contact time τ_c of the radicals; therefore, the efficiency of the spin exchange in the narrowing of the ESR line can differ from that of the electron transfer. In fact, the ESR spectrum of biradical $\mathbf{1}^{\cdot\cdot}$, unlike that of radical cation $\mathbf{1}^{\cdot+}$, is sufficiently close to the spectrum of radical $\mathbf{3}^{\cdot}$.

When the temperature decreases from room to −40 °C, the splitting of the a_N lines of both radical cation $\mathbf{1}^{\cdot+}$ and biradical $\mathbf{1}^{\cdot\cdot}$ increases to the a_N value characteristic of radical $\mathbf{3}^{\cdot}$, which agrees with a decrease in the frequency of collisions of the triphenylpyridinium rings.

The temperature changes in the ESR linewidths of system **2** are similar to those of system **1**. It is of interest that, as compared to system **1**, intramolecular electron transfer in radical cation $\mathbf{2}^{\cdot+}$ occurs more slowly because of a longer bridge, while the spin exchange in biradical $\mathbf{2}^{\cdot\cdot}$ results in the same efficient narrowing of the ESR lines.

Analysis of the ESR spectra of the biradicals in frozen solutions makes it possible to determine the exchange interaction value and the distance between spins; therefore, we are planning further experiments in glassy solvents (for example, in ethanol).

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Carbonylation of methyl acetate in the presence of rhodium catalysts based on pyrrolidinopyridine polymers

G. V. Terekhova, N. V. Kolesnichenko, A. E. Batov, E. D. Alieva, N. I. Trukhmanova, E. V. Slivinskii, O. Yu. Pesin, and N. A. Platé*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224. E-mail: Terekhova@tips.aha.ru

Previously,[1] we have studied the hydroformylation of olefins in the presence of a catalytic system based on $RhCl_3$ and the pyrrolidinopyridine polymer (**1**).

This system exhibits high activity in hydroformylation

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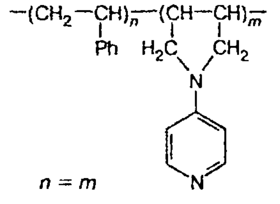
of isobutylene under reaction conditions where commonly used catalysts are not very active.[1] Because polymer **1** is highly resistant to corrosive media and increased temperature, it was interesting to study rhodium complexes heterogenized on this polymer in the carbonylation of methyl acetate.



1

$$\mathrm{MeOAc + CO \xrightarrow{RhCl_3,\ MeI} Ac_2O}$$

It can be seen from Fig. 1 that the carbonylation of methyl acetate in the presence of the polymer-immobilized catalyst proceeds much more rapidly than that catalyzed by a homogeneous system based on $RhCl_3 \cdot 4H_2O$. The higher activity of the polymeric rhodium catalyst compared to that of the homogeneous catalytic system is an uncommon fact, which can be explained by the ability of the polymer to accelerate the rate-limiting stage of carbonylation. It is known that compound **1** has a high basicity[2] and tends to form alkylated or acylated derivatives. Now, it is generally accepted that the rate-limiting stage of carbonylation is the oxidative addition of methyl iodide to a carbonylrhodium complex. Apparently, the polymer accelerates this process because of its capability of being alkylated at the nitrogen atom. Coordination of the alkylated macroligand with the catalytically active $[Rh(CO)_2I_2]^-$ complex[3] favors oxidative addition of methyl iodide to the Rh atom. The rates of carbonylation also increase in the presence of PPh_3 (see Fig. 1, curve *2*), which can form a quaternary salt under the reaction conditions, coordinate with $[Rh(CO)_2I_2]^-$, and accelerate addition of the methyl group.[4]

The role of the acylated form of **1** in the catalysis seems to be in binding acetyl iodide accumulated in the system. This binding prevents the latter from thermal decomposition with the release of iodine, which removes a portion of the rhodium from the catalytic cycle to form inactive Rh^{III} complexes.

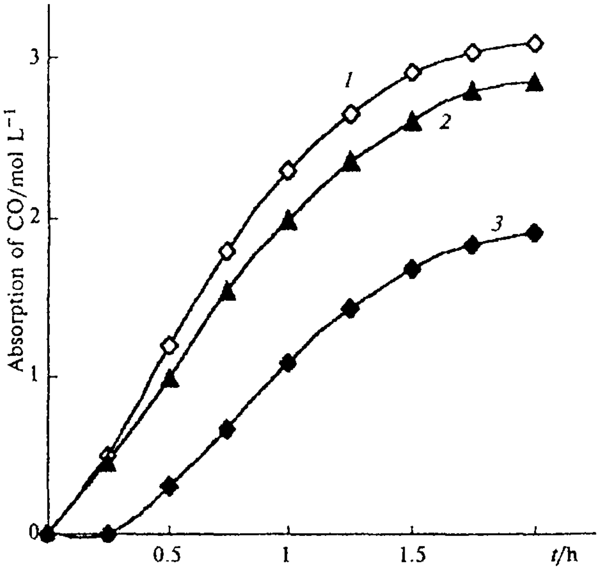


Fig. 1. Carbonylation of methyl acetate in the presence of various catalytic systems: (*1*) $RhCl_3$—**1**; (*2*) $RhCl_3$—PPh_3; (*3*) $RhCl_3 \cdot 4H_2O$ (T = 190 °C, p_{CO} = 5 MPa).

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