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R. O. Matevosyan, E. G. Gabrielyan, A. K. Chirkov, and I. Ya. Postovskii

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Abstract

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Comparative Dehydrogenating Ability of Certain Diarylpicrylhydrazyl Radicals

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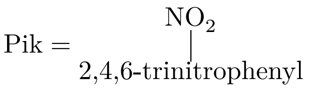
In working with picrylhydrazyl radicals, we observed that N-carbazylpicrylazot (I) dehydrogenates hydroquinone and aromatic amines much more rapidly than α,α-diphenyl-β-picrylhydrazyl (III), being converted in the process into N-carbazylpicrylamine (II) (^{1}).

$$\text{(I)} \quad \longrightarrow \quad \text{(II)} \qquad \text{(III)} \quad R = C_6H_5$$



$$\text{Pik} = \underset{\text{2,4,6-trinitrophenyl}}{\overset{\text{NO}_2}{|}} \qquad \text{(IIIa)}\ R = \text{biphenyl group}$$

$$\text{(IIIb)}\ R = \text{CH}_3\text{O-phenyl-} \qquad \text{(IIIc)}\ R = \text{CH}_3\text{O-biphenyl-}$$

On a more detailed study of the properties of N-carbazylpicrylazot (I), it became clear that this radical dehydrogenates not only the compounds indicated, but even benzene, which cannot be accomplished with radical (III). Thus, a dark-violet solution of radical (I) in benzene becomes orange after several minutes (the color of amine (II)). When a freshly prepared solution of the radical in benzene is chromatographed on Al_2O_3, an orange-colored substance is formed already upon contact with the adsorbent; after development with an excess of benzene and evaporation of the benzene eluate, it gives a substance with m.p. 239–241°, identified by a mixed-melting test with N-carbazylpicrylamine (II).

The high dehydrogenating ability of radical (I) indicates a greater localization in it of the unpaired electron at the β-nitrogen atom than in radical (III). Evidently, this is connected with the fact that the α-nitrogen atom, being part of the coplanar system of the carbazyl residue, has a greater opportunity to supply its electrons for participation in conjugation with the π-electrons of the benzene rings than in the case of (III). In this connection, the interaction of the electrons of the α-atom with the unpaired electron of the β-atom is effected to a lesser degree. This agrees with data obtained from analysis of the hyperfine structure of the electron paramagnetic resonance spectra.

radicals (I) and (III), according to which in radical (III) the unpaired electron is uniformly distributed between the α- and β-nitrogen atoms, whereas in the case of radical (I) it is shifted toward one of them (2). It was therefore of interest, insofar as possible, to characterize quantitatively the dehydrogenating ability of hydrazyl radicals containing residues of different structure (III, IIIa, b, c).

Radicals (IIIb, c) were obtained for the first time; radical (IIIa) was described by us earlier. Radicals were synthesized by the method described in greater detail in earlier communications (1,3,4), according to the scheme:

Fig. 1. Curves of the rate of the dehydrogenation reaction of diphenylamine by radicals: arbanilpicrylhydrazyl (I); diphenylpicrylhydrazyl (III); biphenylphenylpicrylhydrazyl (IIIa), *p*-methoxydiphenylpicrylhydrazyl (IIIb), *n*-methoxybiphenylphenylpicrylhydrazyl (IIIc)

$$\mathrm{R{-}NH_2} \xrightarrow{o\text{-}\mathrm{Cl{-}C_6H_4COOH}} \mathrm{R{-}NH{-}C_6H_4COOH} \rightarrow \mathrm{R{-}NH{-}C_6H_5} \rightarrow \mathrm{R{-}N(C_6H_5){-}N{=}O} \rightarrow$$

$$\rightarrow \mathrm{R{-}N(C_6H_5){-}NH_2} \xrightarrow{\text{picryl chloride}} \mathrm{R{-}N(C_6H_5){-}NH{-}Pik} \xrightarrow{\mathrm{PbO_2}} \mathrm{P{-}N(C_6H_5){-}N{-}Pik}$$

Analyses and constants of the previously undescribed intermediate and final products are given in Table 1.

All radicals are deeply colored substances. In air, chloroform solutions of the radicals do not change the intensity of their color over several hours, as was verified by photocolorimetry of the solutions.

Upon addition of the radicals to solutions of diphenylamine hydrazides, depending on the structure of the radical, dehydrogenation of the amine proceeds at different rates and the radical is converted into an orange-colored hydrazine. This made it possible to follow the dehydrogenation process by photocolorimetry of the solutions. (FEK-M photocolorimeter; concentration of the radical solution $6 \cdot 10^{-2}$ mmol/l,

Table 1

Compound	Y	M.p., °C	Yield, %	Appearance of crystals under the microscope	Empirical formula	N, %, found	N, %, calculated
$CH_3{-}C_6H_4{-}N(Y){-}C_6H_5$	NO	81–82	80	Ash-colored prisms	$C_{13}H_{12}O_2N_2$	12.55	12.27
$CH_3{-}C_6H_4{-}N(Y){-}C_6H_5$	NH_2	43–46	30	Colorless plates	$C_{13}H_{14}ON_2$	13.19	13.08
$CH_3{-}C_6H_4{-}N(Y){-}C_6H_5$	NH−Pik	132–133	70	Red prisms	$C_{19}H_{15}O_7N_5$ *	16.27	16.47
$CH_3{-}C_6H_4{-}N(Y){-}C_6H_5$	N−Pik	96–97	75	Plates of almost black color	$C_{19}H_{14}O_7N_5$	16.38	16.50
$CH_3O{-}C_6H_4{-}C_6H_4{-}N(Y){-}C_6H_5$	$COCH_3$	128–130	45	Colorless needles	$C_{21}H_{19}O_2N$	4.53	4.41
$CH_3O{-}C_6H_4{-}C_6H_4{-}N(Y){-}C_6H_5$	NH	140–141	80	Lustrous pearlescent plates	$C_{19}H_{17}ON$	5.17	5.09
$CH_3O{-}C_6H_4{-}C_6H_4{-}N(Y){-}C_6H_5$	NO	139–140	60	Long needles of light-green color	$C_{19}H_{16}O_2N_2$	9.48	9.21
$CH_3O{-}C_6H_4{-}C_6H_4{-}N(Y){-}C_6H_5$	NH_2	148–150	25	Colorless large needles (bundles)	$C_{19}H_{18}ON_2$	9.89	9.65
$CH_3O{-}C_6H_4{-}C_6H_4{-}N(Y){-}C_6H_5$	NH−Pik	110–112	55	Brick-colored plates	$C_{25}H_{19}O_7N_5$ **	13.81	13.97

Compound	Y	M.p., °C	Yield, %	Appearance of crystals under the microscope	Empirical formula	N, %, found	N, %, calculated
$CH_3O-C_6H_4-N(Y)-N-Pik$	$C_6H_4-C_6H_5$	105−107	40	Small prisms of almost black color	$C_{25}H_{18}O_7N_5$	14.16	14.00

* Found, %: C 53.47; H 3.61
Calculated, %: C 53.65; H 3.55

** Found, %: C 59.78; H 3.98
Calculated, %: C 59.88; H 3.82.

concentration of diphenylamine $6 \cdot 10^{-1}$ mmole/liter, experimental temperature 40.0°, Vobzer thermostat).

The results of the photocolorimetric measurements, indicating the relative rate of dehydrogenation of diphenylamine by different radicals, are given in Fig. 1.

As can be seen from the curves shown in Fig. 1, under the experimental conditions diphenylamine is dehydrogenated most actively by the carbazole radical (I) and is not dehydrogenated by radicals (III ,) containing methoxyl groups. The electron-donor influence of methoxyl is evidently manifested in an increase in the electron density at the α-nitrogen atom, which ensures greater interaction of the unpaired electron of the β-nitrogen atom with the electrons of the α-nitrogen atom, i.e., greater delocalization of the unpaired electron, and thereby accounts for the low reactivity and increased stability of these radicals. Naturally, along with the electronic influence of the groups, the spatial structure of the residues also plays a role. These complex relationships between electronic and spatial structure, on the one hand, and the stability of picrylhydrazyl radicals, on the other, will apparently become clearer as new experimental data are obtained.

Table 2

Radical	$\Delta H_{\text{m.n.}}$
[[structural formula: carbazole-type radical, fused diphenyl residue bonded to $-N-N-Pik$ with an unpaired electron on nitrogen]]	0.52 ± 0.01
[[structural formula: diphenylpicrylhydrazyl radical, $Ph-N(-Ph)-N-Pik$, with an unpaired electron on nitrogen]]	1.0 ± 0.01
[[structural formula: biphenyl-phenyl picrylhydrazyl radical, $Ph-Ph-N(-Ph)-N-Pik$, with an unpaired electron on nitrogen]]	1.11 ± 0.01
[[structural formula: *p*-methoxyphenyl-phenyl picrylhydrazyl radical, $CH_3O-C_6H_4-N(-Ph)-N-Pik$, with an unpaired electron on nitrogen]]	2.6 ± 0.01
[[structural formula: *p*-methoxybiphenyl-phenyl picrylhydrazyl radical, $CH_3O-C_6H_4-C_6H_4-N(-Ph)-N-Pik$, with an unpaired electron on nitrogen]]	7.3 ± 0.01

Table 2 gives the results of measuring the EPR line width of the obtained radicals between the points of maximum slope, $\Delta H_{\text{m.n.}}$. The measurements were carried out in weak fields, $H_0 = 20$ oersted, in crystalline samples of the radicals on an apparatus described earlier (5). As can be seen from the data in the table, the width of the absorption line, characterizing the magnitude of exchange interactions of the unpaired electron in crystalline samples of the radicals studied, falls in the same order as the photocolorimetric data for the process of dehydrogenation of diphenylamine by these radicals.

Ural Polytechnic Institute
named after S. M. Kirov

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