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Mechanism of Autoreduction of Bis(4-methoxyphenyl)-oxoammonium Perchlorate in Aqueous Alkali

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Abstract—Autoreduction of bis(4-methoxyphenyl)oxoammonium perchlorate in aqueous alkali follows a mechanism different from that generally accepted for diaryloxoammonium salts. Bis(4-methoxyphenyl)-oxoammonium cation undergoes hydrolysis to the corresponding quinone imine oxide and methanol, the latter gives rise to methoxide ion which reduces the oxoammonium cation to intermediate bis(4-methoxyphenyl)-hydroxylamine. The reaction of bis(4-methoxyphenyl)hydroxylamine with the initial cation yields bis-(4-methoxyphenyl)nitroxyl, and the quinone imine oxide undergoes disproportionation to *N*-(4-methoxy-phenyl)-1,4-benzoquinone imine and oxidation products.

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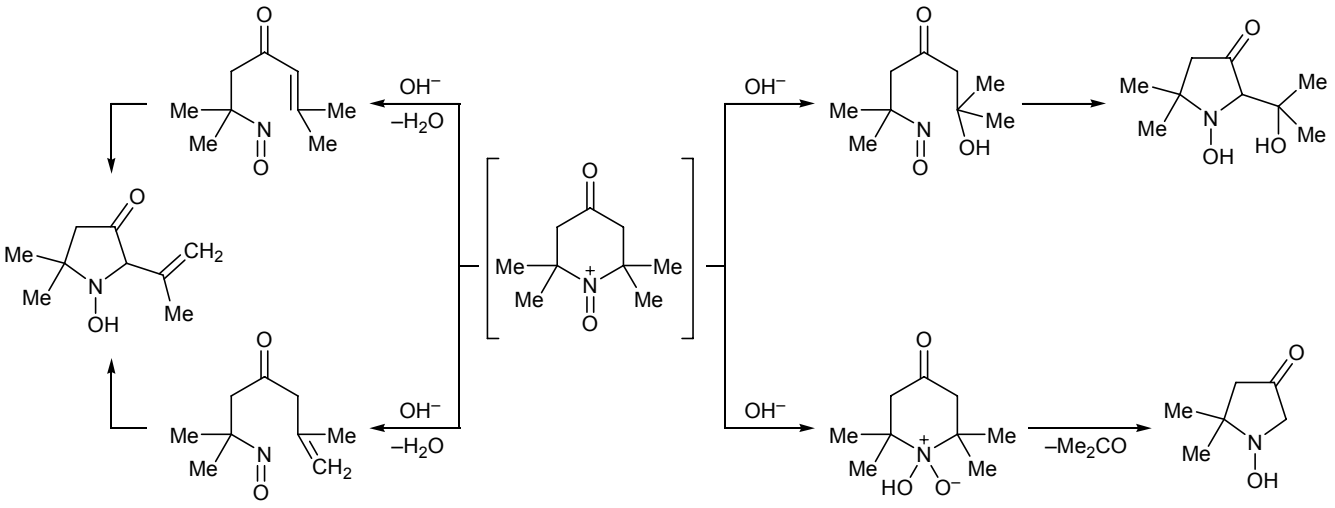
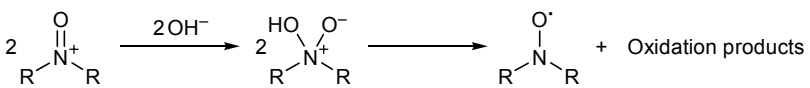
Oxoammonium salts are used as selective stoichiometric oxidants or catalysts in oxidation of alcohols [1–5]. Their catalytic efficiency in aqueous medium is limited by the stability of oxoammonium cations which are converted into nitroxyl radicals and other by-products. The rate of this transformation strongly depends on the structure of oxoammonium ion and pH. For example, autoreduction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium perchlorate in alkaline medium is determined by the transformation of dioxopiperidinium ion into cyclic hydroxylamines as shown in Scheme 1 [6]. Cyclic hydroxylamines reduce dioxopiperidinium ion to nitroxyl radicals, thus being oxidized to the corresponding cyclic nitrones.

Scheme 1.



Scheme 2.



Oxoammonium salts of the aromatic series also undergo one-electron reduction by the action of bases [7, 8]. Meyer and Reppe [8] proposed a hypothetical mechanism for the autoreduction of such salts in alkaline medium, which included addition of hydroxide ion to diaryloxoammonium cation $R_2N^+{=}O$ with formation of *N*-hydroxy *N*-oxide $R_2N(O)OH$. The subsequent disproportionation of the latter yields nitroxyl radical $R_2N{-}O^{\cdot}$ and unidentified oxidation products (Scheme 2).

In the present work we studied in detail the mechanism of autoreduction in aqueous alkali of a typical diaryloxoammonium salt, bis(4-methoxyphenyl)oxoammonium perchlorate (**I**). It was found that the rate of decomposition of salt **I** in alkaline medium strongly increases as the concentration of hydroxide ion rises; at $[OH^-] > 0.1$ M the reaction rate is determined by the rate of salt dissolution. Decomposition of the cation in salt **I** leads to the formation of quinone imine oxide **II**, nitroxyl **III**, quinone imine **IV**, amine **V**, and methanol (Scheme 3, see table).

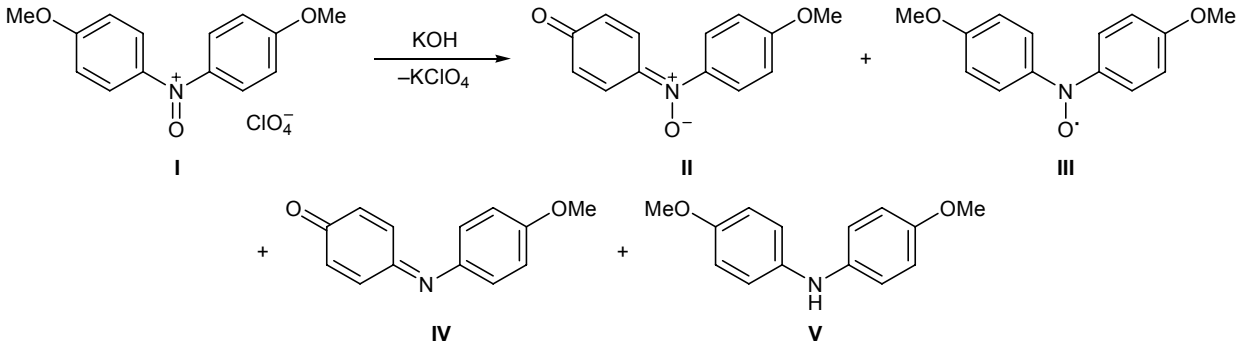
Compounds **II**–**IV** were isolated as individual substances and identified on the basis of spectral data and by comparing with authentic samples (see Experimental). Amine **V** was detected by chromatography and identified by retention volume and UV spectrum. Apart from the above substances, formaldehyde, formic acid, and carbon dioxide were formed as a result of oxidation of methanol. Perchlorate ion does not participate in the process, and it can be recovered quantitatively as potassium perchlorate.

The primary products of the reaction of oxoammonium ion **VI** with hydroxide ion were found to be quinone imine oxide **II** and methanol (yield 70–99%, Scheme 4) but not *N*-oxide $R_2N(O)OH$. Facile hydrolysis of the ether moiety in cation **VI** is likely to be favored by considerable contribution of quinoid structure **VIb**. Increase of the concentration of alkali accelerates hydrolysis of **VI**; however, the yield of quinone imine oxide **II** simultaneously decreases (see table). The yield of **II** also decreases as the initial concentration of salt **I** rises.

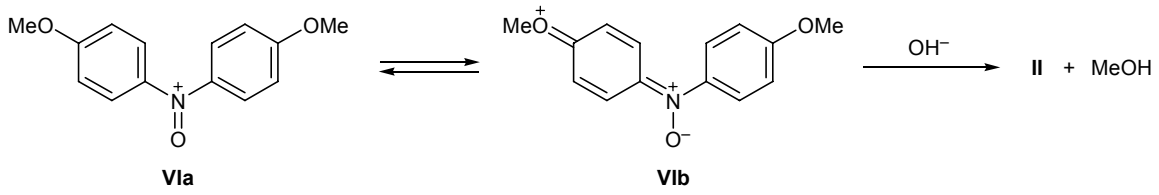
Methanol liberated by hydrolysis of cation **VI** is partly consumed for the reduction of **VI** to radical **III**. This follows from the lower yield of methanol as compared to the yield of quinone imine oxide **II**, as well as from increase in the yield of **III** upon addition of methanol to the reaction mixture (see table). Methanol is a weak reducing agent in neutral and acid media, and it almost does not reduce cation **VI** during the hydrolysis of salt **I**. Therefore, the hydrolysis of **VI** in pure water yields 99±1% of quinone imine oxide **II** and methanol, whereas the yield of radical **III** is less than 0.1% (see table).

Oxoammonium ion **VI** is reduced to radical **III** mainly with methoxide ion according to Scheme 5 [9, 10]. An intermediate product in this reaction is *N*-oxide **A** which undergoes decomposition into formaldehyde and diarylhydroxylamine **B**. Comproportionation of the latter with cation **VI** yields two molecules of **III**. Disproportionation of a small amount of hydroxylamine **B** gives amine **V** and radical **III** [8].

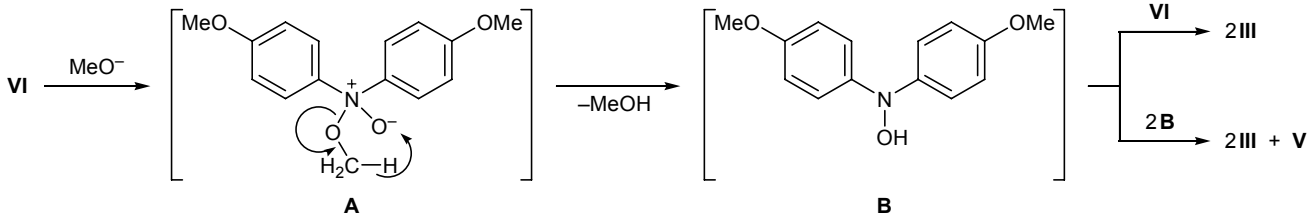
Scheme 3.



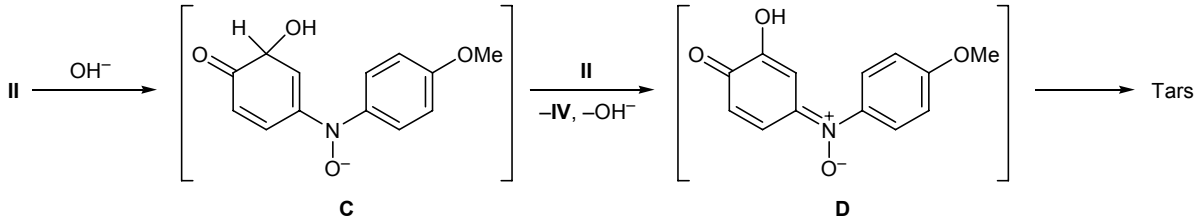
Scheme 4.



Scheme 5.



Scheme 6.



Appreciable accumulation of these species (**V** and **III**) is observed after complete consumption of cation **VI**.

Taking into account that, unlike **II**, the yield of **III** increases with rise in the concentration of alkali, the rate of reduction of **VI** with methoxide ion increases more rapidly than does the rate of hydrolysis of **VI** with hydroxide ion as the concentration of the latter increases. In the reaction with **VI**, methoxide ion is partly oxidized to carbon dioxide through intermediate formation of formaldehyde and formate ion. The yield of **III** increases upon addition of a mixture of CH_2O and HCO_2Na. Judging by the gain in the yield of **III** at $[OH^-] = 0.05$ M, the rate of reduction of **VI** increases in the series formate ion < MeOH < formaldehyde (see table). The same series corresponds to increase in the rate of reduction of 2,2,6,6-tetramethyl-1-oxopiperidinium ions [11].

The fourth decomposition product obtained from cation **VI** is quinone imine **IV** which is formed by reduction of quinone imine oxide **II**. This follows from reduction of the concentration of quinone imine oxide **II** and accumulation of quinone imine **IV** in the reaction mixture after complete consumption of cation **VI**. The stoichiometry and kinetics of transformation of quinone imine oxide **II** in alkaline medium were studied by separate experiments. As a result of disproportionation, ~50% of **II** is reduced to quinone imine **IV**, and its other part is converted into oxidation prod-

Reaction of bis(4-methoxyphenyl)oxoammonium perchlorate (**I**) with KOH at ~20°C

$[\mathbf{I}]_0 \times 10^2$, M	$[OH^-]_0 \times 10^2$, M	Additive (0.1 M)	Yield (HPLC), mol %					Solvent
			II	**III**	**IV**	**V**	MeOH	
1.0	0	–	99±1	<0.1	–	–	98±2	Water
1.0	5.0	–	92±2	5.3±0.3	1.2±0.1	0.3±0.1	[a]	25% MeCN
1.0	50	–	85±2	10±1	2.0±0.2	0.3±0.1	79±3	25% MeCN
1.0	50	–	84±1	11±1	1.6±0.1	0.2±0.05	78±3	Water
50[b]	55	–	69[c]	25[c]	1.2[c]	[a]	[a]	Water
1.0	5.0	MeOH	87±2	10±1	0.8±0.1	<0.1	[a]	25% MeCN
1.0	5.0	CH_2O	77±2	19±1	0.2±0.05	<0.1	[a]	25% MeCN
1.0	5.0	HCO_2Na	85±2	8±2	0.3±0.05	<0.1	[a]	25% MeCN

[a] The yield was not determined.
[b] Sodium hydroxide was used instead of potassium hydroxide.
[c] Yield of the isolated product.

ucts. The reaction rate is proportional to the concentrations of **II** and alkali and is given by the equation $\partial[\mathbf{II}]/\partial\tau = -k[\mathbf{II}][OH^-]$. The bimolecular rate constant in 25% aqueous acetonitrile at 20°C and [KOH] = (5–50)×10^{-2} M is $k = 2.3\times10^{-4}$ l mol^{-1} s^{-1}. A probable mechanism involves addition of hydroxide ion to nitrone **II** with formation of intermediate product **C** and its isomers with alternative position of hydroxy group in the quinoid fragment. Intermediate **C** reduces quinone imine oxide **II** to quinone imine **IV** and is thus oxidized assumingly to quinone imine oxide **D** according to Scheme 6. The transformation **C** → **D** is accompanied by regeneration of hydroxide ion which acts as catalyst. We failed to isolate imine oxide **D** or its isomers because of tarring.

Thus autoreduction of cation **VI** to nitroxyl radical **III** in alkaline medium is not the result of its disproportionation, as was presumed in [8], but the reducing agent is methoxide ion generated by hydrolysis of **VI**. Insofar as the rate of hydrolysis of cation **VI** is higher than the rate of its reduction with methoxide ion, the maximal yield of radical **III** is ~25%. Otherwise, up to 86% of **VI** would be reduced to **III**. The proposed mechanism of autoreduction of salt **I** is likely to be general for all diaryloxoammonium salts having alkoxy groups in the cation.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer. The UV spectra were measured on a Specord UV-VIS spectrophotometer. The NMR spectra were obtained on a Bruker AIII instrument; signals were assigned using two-dimensional HSQC ^{1}H–^{13}C technique. The melting points were determined on a PHMK hot stage. HPLC analysis was performed on a Milikhrom chromatograph [2×64-mm column packed with Nucleosil C18 (5 μm); detection at λ 260 nm; eluent 50% aqueous acetonitrile]; acetanilide (V_{ret} = 110 μl) was used as internal standard for quantitative measurements. Silufol UV-254 plates were used for TLC, eluent chloroform–acetonitrile (10 : 1). The amount of methanol was determined by GLC on an LKhM-80 chromatograph equipped with a flame ionization detector and a 4×1650-mm column packed with Poropak Q (80–100 mesh); oven temperature 130/170°C; carrier gas nitrogen, flow rate 32 ml/min; ethanol was used as internal standard; retention time, s: MeOH, 200; EtOH, 450 s. Bis(4-methoxyphenyl)-amine (**V**) was synthesized according to the procedure described in [12], V_{ret} = 440 μl, R_f 0.79. The kinetics of the reaction of quinone imine oxide **II** with potassium hydroxide were studied in 25% aqueous acetonitrile. The current concentration of **II** was determined by its peak area (HPLC) compared to acetanilide (internal standard).

Bis(4-methoxyphenyl)oxoammonium perchlorate (I) was prepared as described in [7] with account taken of the recommendations given in [13]. The product was purified by double reprecipitation from acetonitrile (spectral grade) with diethyl ether. Decomposition point 166–168°C; published data [7]: decomposition point 155°C. UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 578 (38500), 390 (9670), 259 (7400), 228 (7600), 205 (19800). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 4.14 s (6H, CH_3), 7.32 d (4H, *m*-H, *J* = 9.3 Hz), 8.07 br.d (4H, *o*-H, *J* = 8.6 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 59.08 (CH_3), 135.43 (C^m), 146.51 (C^o), 162.5 (CN), 173.69 (C^p).

Reaction of bis(4-methoxyphenyl)oxoammonium perchlorate (I) with sodium hydroxide. Perchlorate **I**, 1.72 g (5 mmol), was added to 11 ml of an aqueous solution of NaOH (*c* = 0.5 M), and the resulting suspension was stirred for ~20 min at 20°C. A brown material was formed; it was filtered off, washed with water, and dried under reduced pressure. Yield 1.18 g. The filtrate was treated with ethyl acetate (2×5 ml). The extracts were combined and evaporated under reduced pressure to obtain 31 mg of a brown substance. Both products were subjected separately to chromatography in a 28×220-mm column charged with KSK silica gel (40–50 μm). The column was eluted with chloroform–methanol (100 : 3), and the eluate composition was monitored by TLC. From the brown precipitate we isolated 675 mg (59 mol %) of quinone imine oxide **II** and 305 mg (25 mol %) of stable radical **III**. From the extract we isolated 20 mg (1.9 mol %) of quinone imine **IV**.

4-Methoxy-*N*-(4-oxocyclohexa-2,5-dienylidene)-benzenamine oxide (II). Orange needles, mp 126°C (from benzene–hexane); published data [13]: mp 125–126°C; V_{ret} = 155 μl, R_f 0.4. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 385 (27100), 266 (5400), 228 (10500), 202 (22200). IR spectrum (KBr), ν, cm^{-1}: 3108, 3065, 3055, 3032 and 3005 (C–H_{arom}), 2973, 2945, 2908, 2850 (CH_3), 1622, 1608 (quinone), 1598, 1510, 1472, 1448 (arom.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.88 s (3H, CH_3), 6.24 d.d (1H, *m*′-H, *J* = 1.9, 10.25 Hz), 6.62 d.d (1H, *m*′-H, *J* = 1.9, 10.2 Hz), 7.00 m (2H, *m*-H), 7.26 d.d (1H, *o*′-H, *J* =

2.9, 10.25 Hz), 7.44 m (2H, *o*-H), 8.00 d.d (1H, *o*′-H, J = 2.9, 10.3 Hz). ^{13}C NMR spectrum (CD_3Cl), δ_C, ppm: 55.84 (CH_3), 114.46 (C^m), 126.29 (C^o), 126.13, 128.89, 129.89, 131.61 ($C^{o'}$, $C^{m'}$), 138.85 (NC), 143.10 (C^p), 161.88 (N=C), 186.52 ($C^{p'}$).

Bis(4-methoxyphenyl)nitroxyl (III). Copper-red plates, decomposition point 150°C (from aqueous acetone); published data [8]: decomposition point 150°C; V_{ret} = 305 μl, R_f 0.65. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 507 (2450), 334 (17500), 263 (6200), 225 sh (8200), 205 (22600). IR spectrum (KBr), ν, cm^{-1}: 3102, 3070, 3052, 3020 (C–H_{arom}), 2970, 2950, 2920, 2848 (CH_3), 1595, 1498, 1475 (arom.).

4-(4-Methoxyphenylimino)cyclohexa-2,5-dien-1-one (IV). Red plates, mp 84°C (from hexane); published data [8]: mp 84°C; V_{ret} = 220 μl, R_f 0.56. UV spectrum (EtOH), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 500 (8600), 317 (10800), 263 (19700), 234 sh (8800), 203 (18500). IR spectrum (KBr), ν, cm^{-1}: 3130, 3100, 3053, 3005 (C–H_{arom}), 2978, 2960, 2922, 2852 (CH_3), 1648, 1615 (C=O, C=C), 1595, 1580, 1535, 1505, 1475 (arom.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.86 s (3H, CH_3), 6.56 d.d (1H, 3-H or 5-H, J = 2.2, 10.3 Hz), 6.68 d.d (1H, 5-H or 3-H, J = 2.2, 10.0 Hz), 6.93–6.98 m (4H, H_{arom}), 7.21 d.d (1H, 2-H or 6-H, J = 2.7, 10.3 Hz), 7.30 d.d (1H, 6-H or 2-H, J = 2.7, 10.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.57 (CH_3), 114.50 ($C^{m'}$), 123.62 ($C^{o'}$), 128.25, 132.27, 133.07, 142.15 (C^2, C^3, C^5, C^6), 142.81 ($C^{i'}$), 156.50 ($C^{p'}$), 158.99 (C^4), 187.80 (C^1).

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