Brief Communications

Oxidation of aniline with solutions of Mo—V-phosphoric heteropolyacids

M. V. Simonova,[a*] *E. G. Zhizhina,*[a] *V. V. Russkikh,*[b] *and K. I. Matveev*[a]

[a]*G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,*
5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 8056. E-mail: smv@catalysis.nsk.su
[b]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
9 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9752

Mo—V-phosphoric heteropolyacids (HPA) can be used for aniline oxidation to polyaniline or 1,4-benzoquinone. At room temperature and the molar ratio HPA : aniline = 0.67, more than 95% substrate are oxidized to polyaniline. At 90—100 °C and HPA : aniline = 3, the substrate is quantitatively oxidized to 1,4-benzoquinone. Solutions of HPA are regenerated by oxygen in a separate step.

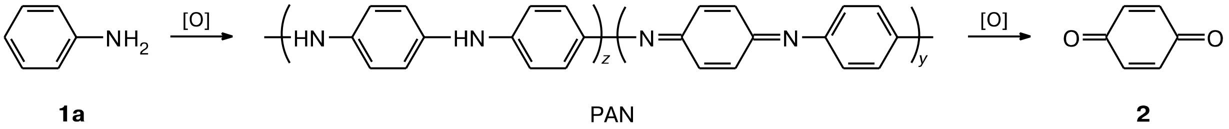
Key words: heteropolyacids, catalytic oxidation, aniline, polyaniline, 1,4-benzoquinone.

Aniline (**1a**) and other aromatic amines are usually oxidized by strong oxidants ($NaClO_3$, $K_2Cr_2O_7$, and others). Depending on the oxidant and process conditions, the products are 1,4-benzoquinone (**2**) or (due to oxidative polymerization) polyaniline (PAN)[1–3] (Scheme 1). The latter can quantitatively be oxidized to quinone **2**.[3]

Electroconducting polymer PAN is used in chemical current sources[4,5] and as a dye.[6] All stoichiometric methods for oxidation of compound **1a** produce large amounts of waste. For instance, when Cr^{VI} compounds are used as oxidants, the products are toxic Cr^{III} compounds and acids that require utilization. Therefore, the development of ecologically safe catalytic methods for aniline oxidation to PAN remains urgent.

In this work, we studied the oxidation of aniline (**1a**) and 2-methylaniline (**1b**) by solutions of Mo—V-phosphoric heteropolyacids (HPA) of composition $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA_x, where x is the number of vanadium atoms in the molecule equal to 3 or 4). These compounds are used as selective catalysts for partial oxidation of various organic compounds by oxygen.[7,8] The reactions in the presence of HPA_x are usually performed

Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1488—1490, June, 2005.

in two steps. In step (1), the substrate (H_2Su) is oxidized by the heteropoly acid to form the reaction product and reduced species of HPA_x (H_mHPA_x). In step (2), HPA_x is regenerated with oxygen.[9] The overall reaction (3) proceeds in the regime of non-stationary catalysis. In these processes, HPA_x acts as a reversible oxidant.

$$m/4\ \mathrm{H_2Su} + m/4\ \mathrm{H_2O} + \mathrm{HPA}_x \longrightarrow m/4\ \mathrm{SuO} + \mathrm{H}_m\mathrm{HPA}_x \tag{1}$$

$$\mathrm{H}_m\mathrm{HPA}_x + m/4\ \mathrm{O_2} \longrightarrow \mathrm{HPA}_x + m/2\ \mathrm{H_2O} \tag{2}$$

$$\mathrm{H_2Su} + \mathrm{O_2} \xrightarrow{\mathrm{HPA}_x} \mathrm{SuO} + \mathrm{H_2O} \tag{3}$$

Mild conditions of reaction (1) and separately performed reactions (1) and (2) usually provide high selectivity of reaction (3).

Results and Discussion

A black precipitate is formed within 30 min upon the addition of substrate **1a** to a solution of HPA_x ($x = 3$) at room temperature. The precipitate is insoluble in organic solvents, organic acids (acetic, oxalic, and tartaric), and concentrated HCl and is weakly soluble in concentrated NaOH and KOH. However, it is soluble in concentrated H_2SO_4 and (with oxidation) in concentrated HNO_3. These properties of the newly synthesized substance coincide with the properties of PAN obtained earlier[2,10] by the non-catalytic oxidation of **1a**. The resulting product has the following elemental composition (%): C, 59.36; H, 4.39; N, 11.98. For the approximate molecular formula of PAN ($z = y$, see Scheme 1) presented in Ref. 2, calculated (%): C, 79.56; H, 4.97; N, 15.47. The synthesized compound differs by relative content of elements (C : N = 4.95) from the known PAN in which C : N = 5.14. This can be a consequence of the fact that, first, our sample has z and y values (see Scheme 1) different from the molecular formula $C_6H_{4.5}N$ ($z = y$)[2]; second, the synthesized sample is found to contain some amount of HPA (~5.5%), which cannot be removed by washing the precipitate.

It can be expected that low amounts of HPA_x incorporated into the PAN composition would modify its properties and determine new potentialities of use. Interest in new materials based on polymers with HPA additives has appeared in recent time. For example, the authors[11] studied the properties of polymers (poly(vinyl alcohol) and poly(methyl methacrylate)) containing additives of molybdenum or tungsten HPA. As shown, these polymers can be used, in particular, in nanolithography and microelectronics. The conducting properties of PAN doped with HPA ($H_4SiW_{12}O_{40}$) to different extents were also studied.[12,13] It is shown[13] that for the same oxidant amount (in this case, $S_2O_8^{2-}$ was used) an increase in the HPA content enhances the conducting properties of the polymer.

To prove the structure of the synthesized compound, we recorded its IR spectrum and compared with the published spectra of PAN. For instance, the formation of poly(*p*-phenyleneamineimine) was shown[10] for the polymerization of **1a**. The IR spectrum of our substance (Fig. 1) in a region of 3200—1100 cm^{-1} coincides with the spectrum of PAN presented previously.[10] However, there are distinctions in the 1100—700 cm^{-1} region. This is explained by the presence of some amount of oxidant (HPA) in our sample.

Our conclusions are confirmed by results of the work[13] where aniline (**1a**) was oxidized with $(NH_4)_2S_2O_8$ in the presence of heteropoly acid $H_4SiW_{12}O_{40}$. This HPA is not an oxidant and is used only for doping PAN. The vibrational spectra of pure PAN and the polymer doped with Si—W-HPA are presented. The spectral pattern remains unchanged but the position of bands somewhat changes in the case of the doped product. The IR spectra (for a region of 1600—1100 cm^{-1}) of our sample and polyanilines (PAN and PAN/$H_4SiW_{12}O_{40}$) obtained in the work[13] are compared in Table 1. It is seen that the synthesized material has absorption bands characteristic of the PAN structure.

The absorption bands at 1100—700 cm^{-1} are assigned[13] to vibrations of $H_4SiW_{12}O_{40}$. In this IR spectral region, the absorption bands of our sample of PAN do not coincide with the previously[13] presented pattern, because we used HPA of different composition ($H_6PMo_9V_3O_{40}$). Therefore, we compared the 1100—700 cm^{-1} region in the spectrum of our PAN with the IR spectra of the crystalline Mo—V-phosphoric HPA presented in another work.[14] In our case, the bands at 1056, 952, 867, and 794 cm^{-1} coincide exactly with those in the spectra of HPA_x. Thus, the data obtained prove convincingly that the sample synthesized by us is PAN containing some amount of HPA_x.

As shown by GLC and ^{1}H NMR, the resulting PAN is dissolved at 90—100 °C in excess HPA_3 or HPA_4 (molar ratio HPA_x : **1a** = 3) to form benzoquinone (**2**). This

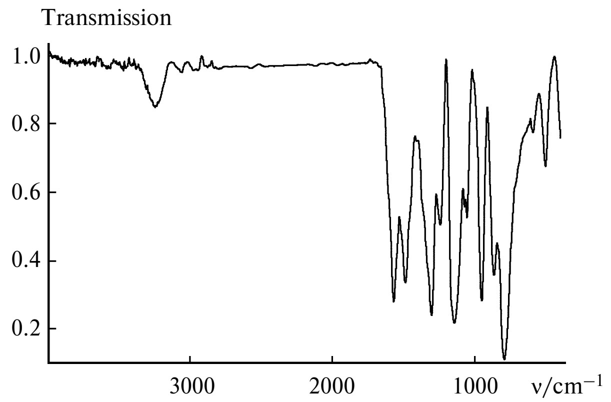


Fig. 1. IR spectrum of polyaniline synthesized in this work (in KBr pellets).

Table 1. Comparative analysis of the IR spectra (KBr pellets, ν/cm^{-1}) of PAN synthesized in this work and polyanilines obtained previously[13]

Sample	ν(N=Q=N)[a]	ν(N—B—N)[b]	ν(Q—B—Q)	ν(Q—B—Q), ν(Q—B—B), ν(B—B—B)	ν(B—B—B)	ν(Q=NH$^+$—B)
PAN	1589	1489	1378	1307	1242	1166
PAN[13]	1573	1490	1306	1306	1244	1145
PAN/$H_4SiW_{12}O_{40}$[13] [c]	1580—1583	1458—1492	1302—1377	1307—1308	1245—1247	1144—1150

[a] Q is quinone ring.

[b] B is benzene ring.

[c] In the case of doped PAN,[13] the band shift is observed, which depends on the ratio **1a** : oxidant : HPA.

agrees with published data[3] and confirms additionally the fact of PAN formation. When substrate **1a** is oxidized in excess HPA_x at temperatures higher than 70 °C, then quinone **2** is formed quantitatively.

The yield of PAN depends on the oxidant (HPA_3) to substrate (**1a**) molar ratio. If the oxidant amount is insufficient, the yield of PAN is low because of an incomplete conversion of the substrate. By contrast, when excess HPA_3 is used, the yield of PAN decreases due to the oxidation of a portion of aniline **1a** to quinone **2**. At an optimum HPA_3 to **1a** molar ratio of 0.67, the mass yield of PAN is 95%.

Compound **1b** was oxidized to the corresponding methylated PAN similarly to amine **1a** (~20 °C, 30 min, molar ratio HPA : **1b** = 0.67). In this case, the amount of the resulting polymer with respect to the starting substrate was 95%. The following composition of this material was established (%): C, 60.62; H, 6.30; N, 6.59.

Thus, it is shown that aromatic amines (aniline and 2-methylaniline) are oxidized in solutions of Mo—V-phosphoric HPA_x to form either PAN or 1,4-benzoquinone, depending on the experimental conditions. A possibility to regenerate HPA_x under oxygen pressure *via* reaction (2)[15] provides challenges for the development of catalytic synthesis of PAN in the presence of HPA_x.

Experimental

Solutions of HPA_x were prepared using a known procedure[16] by the introduction of a freshly prepared $(2.5—5) \cdot 10^{-3}$ *M* solution of $H_6V_{10}O_{28}$ (obtained by the dissolution of V_2O_5 in cold H_2O_2) into a boiling aqueous suspension of $MoO_3 + H_3PO_4$. IR spectra were recorded on a Vector 22 spectrometer (Bruker) in KBr pellets. ^1H NMR spectra were measured on a Bruker WP-200 SY instrument.

Oxidation. A calculated amount of HPA_3 was placed in a conic flask, and freshly distilled aniline **1a** or **1b** (5.5 mmol) was added dropwise with magnetic stirring. After some time, a plenty of black precipitate was formed, which was filtered off and washed with hot water on the filter until the washing waters became colorless. The precipitate was dried in a desiccator above $CaCl_2$ and analyzed by IR spectroscopy and elemental analysis. For the initial HPA_3 to **1a** molar ratios of 0.83, 0.67, and 0.33, the mass yields of PAN were 74, 95, and 18%, respectively.

The products of deep PAN oxidation were extracted with chloroform. Benzoquinone (**2**), ^1H NMR ($CDCl_3$), δ: 6.72 (s). The GLC analysis (flame-ionization detector, capillary column SE-30) of the resulting product exhibited the peak that coincided in retention time with that of an authentic sample of **2**.

References

1. E. M. Geniès, M. Lapkowski, and C. Tsintavis, *New J. Chem.*, 1988, **12**, 181.
2. M. R. Tarasevich, S. B. Orlov, and E. I. Shkol´nikov, *Elektrokhimiya polimerov* [*Electrochemistry of Polymers*], Nauka, Moscow, 1990, 238 pp. (in Russian).
3. R. Willstatter and S. Dorogi, *Ber. Deutsch. Chem. Ges.*, 1909, **42**, 4118.
4. R. de Serville, M. Jozefowicz, and L. T. Yu, *Electrochim. Acta*, 1968, **13**, 1451.
5. P. Novak, K. Müller, K. S. V. Santhanam, and O. Haas, *Chem. Rev.*, 1997, **97**, 207.
6. JP Pat. 2002371219; *Chem. Abstrs*, 2003, **138**, 40858.
7. I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, J. Wiley and Sons, Chichester, 2002, 201.
8. I. V. Kozhevnikov and K. I. Matveev, *Appl. Catal.*, 1983, **5**, 135.
9. E. G. Zhizhina, V. F. Odyakov, M. V. Simonova, and K. I. Matveev, *React. Kinet. Catal. Lett.*, 2003, **78**, 373.
10. F. Wudl, R. O. Angus, Jr., F. L. Lu, P. M. Allemand, D. J. Vachon, M. Novak, Z. X. Liu, and A. J. Heeger, *J. Am. Chem. Soc.*, 1987, **109**, 3677.
11. N. Glezos, D. Velessiotis, Chaidogiannos, P. Argitis, D. Tsamakis, and X. Zianni, *Synth. Met.*, 2003, **138**, 267.
12. J. Gong, J. Yu, Y. Chen, and L. Qu, *Mater. Lett.*, 2002, **57**, 765.
13. J. Gong, X. Cui, Z. Xie, S. Wang, and L. Qu, *Synth. Met.*, 2002, **129**, 187.
14. V. S. Sergienko, L. G. Detusheva, E. N. Yurchenko, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1981, **22**, 37 [*J. Struct. Chem. (USSR)*, 1981, **22**, 32 (Engl. Transl.)].
15. E. G. Zhizhina, M. V. Simonova, V. F. Odyakov, and K. I. Matveev, *Khimiya v interesakh ustoichivogo razvitiya* [*Chemistry in Interests of Stable Development*], 2004, **12**, 683 (in Russian).
16. V. F. Odyakov, E. G. Zhizhina, R. I. Maksimovskaya, and K. I. Matveev, *Kinet. Katal.*, 1995, **36**, 795 [*Kinet. Catal.*, 1995, **36**, 733 (Engl. Transl.)].

Received July 19, 2004;
in revised form March 15, 2005