Reaction of PbO₂ with Solutions of Methylbenzonitriles

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Abstract—The yield of products formed by low-temperature oxidation of methylbenzonitriles with PbO_2 in fluorosulfonic acid solutions was studied in relation to the stabilization factor of the reaction system. The revealed correlation is common for methylbenzonitriles differing in the degree of alkylation and in the oxidation mechanism.

It was shown previously [1, 2] that element oxide layers prepared by molecular layer deposition [3] on the surface of solid matrices can alter the composition and reactivity of organic functional groups grafted to the surface [4]. Due to this fact, e.g., titanium oxide layers can be used as matrices for preparing peptide chains [5], and the systems based on vanadium oxide layers [6], for oxidizing o-xylene and other organic compounds [7, 8]. Interesting opportunities for studying low-temperature reactions are offered by PbO₂, which, similar to other oxides [3], can be prepared by molecular layer deposition from volatile tetrachloride or organic derivatives. Being a powerful oxidant, PbO₂ is used for low-temperature synthesis of organic compounds, in particular, by oxidation of aromatic compounds [9, 10]. These include benzonitriles and their diverse transformation products, widely used for preparing important compounds and formulations. These compounds are also of theoretical interest, since electrophilic radical cations [11] arising after oneelectron oxidation of nitriles in superacids like HSO₃F [12] should undergo further transformations by different pathways depending on their composition and structure. The most probable transformation pathways of methylbenzonitriles in the system HSO_3F-PbO_2 were studied in [13] in relation to the steric and electron donor-acceptor properties of the substituents and to the reaction conditions. However, some problems related to control of the synthesis by dosing definite amounts of PbO₂ by molecular layer deposition require particular consideration. This study is aimed at elucidating the general parameter that governs the completeness of transformations of methylbenzonitriles in the system PbO₂-HSO₃F.

Lead dioxide was of chemically pure grade. Fluorosulfonic acid HSO₃F (D^{18} 1.74 g cm⁻³) was used as solvent. Three series of methylbenzonitriles differing in the number of substituents (Table 1) were prepared

and characterized by procedures described in [13]. The purity of the initial compounds and reaction products was checked by TLC on Silufol UV-254 plates. Voltammograms of oxidation of methylbenzonitriles were taken in the system $HSO_3F-0.1$ M AcOH at $-76^{\circ}C$ on a platinum electrode. The reaction mixtures were separated by column chromatography on silica gel (Chemapol, 40–100 µm). The analytical data were consistent with the composition. The product structures were judged using mass, NMR, and IR spectrometric data from [13]. The conditions of oxidation of methylbenzonitriles and the yields of reaction products are listed in Table 1.

Oxidation of methylbenzonitriles of series 1 (Table 1) at -75° C for 5 h, followed by treatment of the reaction mixture with concentrated HCl, yields chlorinated benzonitriles as shown in scheme (1) (by the example of 2-methylbenzonitrile). This reaction, as in the case of other alkyl-substituted benzonitriles, involves formation of intermediate nonprotonated radical cations [11, 14].



The substituent in the *m*- or *o*-position (Table 1, run nos. 1, 2) does not affect the degree of conversion, whereas with the *p*-substituent the reaction should be performed at a higher temperature $(-40^{\circ}C)$ to attain the same yield.

Oxidation of dimethylbenzonitriles (series II) does not stop at the stage of formation of chlorinated compounds of type A [scheme (1)]. Another transforma-

Run no.	Series		Amount of reagents			Reaction conditions		Product	
		Compound	nitrile, mmol	PbO ₂ , mmol	HSO ₃ F, ml	tempera- ture, °C	time, h	yield, %	Products
1	Ι	2-Methylbenzonitrile	10	15	15	-75	5	29	Α
2		3-Methylbenzonitrile	10	15	15	-75	5	29	Α
3		4-Methylbenzonitrile	8	6	10	-75	6	20	Α
4		4-Methylbenzonitrile	10	15	15	-40	5	28	Α
5	II	2,5-Dimethylbenzonitrile	5	3	10	-70	2	40	A, B, C, D
6		3,5-Dimethylbenzonitrile	4	2	12	-75	2	17	A, D
7		3,5-Dimethylbenzonitrile	7	4	10	-70	2	30	A, D
8	III	2,4,6-Trimethylbenzonitrile	10	10	20	-75	5	94	Ε
9		2,4,6-Trimethylbenzonitrile	5	5	20	-75	5	57	Ε
10		2,4,6-Trimethylbenzonitrile	1	1	20	-75	5	36	Ε
11		2,3,5,6-Tetramethylbenzonitrile	4	2	15	-72	1.5	75	B, I
12	I	2,3,4,5,6-Pentamethylbenzonitrile	5	2.5	20	-75	2	87	Ι

Table 1. Conditions of oxidation of methylbenzonitriles with lead dioxide in fluorosulfonic acid

tion pathway appears for the radical cations [13]: electrophilic attack of the starting molecule, followed by one-electron oxidation of the dimeric radical cation and its deprotonation. This process leads to products of oxidative dimerization (**B**) and then trimerization (**C**), and also to biaryls (**D**), as shown in scheme (2) (by the example of 2,5-dimethylbenzonitrile, Table 1, run no. 5).



Table 1 shows that the structure and yield of the transformation products depend on the mutual location of the substituents. For example, in the case of 3,5-dimethylbenzonitrile, formation of products of types **B** and **C** is impossible, and only product of type **D** is formed as a result of o-o dimerization.



In series III of tri-, tetra-, and pentamethylbenzonitriles, of most interest is oxidation of symmetrical 2,4,6-trimethylbenzonitrile. Firstly, this reaction gives a single final product \mathbf{E} [scheme (3)] whose yield, at increased reactant concentrations, is as high as 94% (Table 1). Secondly, here the cyano group is involved in the transformations, which is a specific feature of oxidative transformations of alkylated benzonitriles [13]. The radical cation formed in the initial stage of oxidation (as in the other cases) attacks the CN group of the starting compound, rather than eliminates pro-

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ton from the methyl group, and yields dimeric radical cation \mathbf{F} and then [scheme (3)] cation \mathbf{G} stable in HSO_3F ; its hydrolysis yields the final product, *N*-arylbenzamide (compound \mathbf{E}).



In the case of tetra- and pentamethylbenzonitriles, oxidation also gives substituted *N*-benzylbenzamides in high yields (Table 1). However, their formation involves deprotonation of *m*-methyl groups [scheme (4) for 2,3,5,6-tetramethylbenzonitrile as example] in the radical cations, followed by oxidation to cation **H**, which reacts with the CN group, yielding compound **I** as final product:



Oxidation of pentamethylbenzonitrile yields similar products.

Thus, low-temperature oxidation of methylbenzonitriles with the PbO₂-HSO₃F system occurs by three

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Fig. 1. Correlation between the oxidation potential φ of methylbenzonitriles and the number *q* of methyl substituents.

pathways depending on the composition and structure of the starting methylbenzonitrile. This fact is probably reponsible for different concentration dependences of the product yields in series I and III and for the lack of such a dependence in series II. This complicates the use of oxidation of alkylated benzonitriles for controllable synthesis with dosed amounts of PbO₂ on the matrix surface and limits the possibility of comprehensive consideration of the substituent effects.

At the same time, the chemical transformations in this series have a common feature, namely, initial formation of intermediate radical cations [11] which subsequently undergo various further transformations [schemes (1)–(3)]. The extent of these transformation and the attainable product yield depend on the capability of various methylbenzonitriles to be oxidized to the radical cation (which can be evaluated by their oxidation potentials [15]) and on the reaction conditions (component concentrations, temperature, etc.). Since the temperature conditions are similar in all the series (Table 1) and the time is sufficient for the reaction completion, we consider the product yield \prod in relation to the oxidation potential φ and concentrations of methylbenzonitrile (m) and PbO₂ (n) only, assuming that the amount of the product formed (p) is proportional to n.

Figure 1 shows the correlation between the oxidation potential φ and the number of substituents q in the methylbenzonitrile molecules. It is seen that φ smoothly decreases from 1.70 V for benzonitrile (φ_0 , q = 0) to 0.90 V for fully substituted (q = 5) pentamethylbenzonitrile.



Fig. 2. Correlation between the product yield \prod in oxidation of methylbenzonitriles and the stabilization factor *R*. Point nos. are run nos. in Tables 1 and 2.

Presumably, the product amount *p* will increase as the methylbenzonitriles will become more susceptible to oxidation with increasing number of methyl substituents, in direct proportion with the difference $\varphi_0 - \varphi$ but in inverse proportion with φ . Let us define the ratio $(\varphi_0 - \varphi)/\varphi = \alpha$ as a parameter characterizing the substrate reactivity (for benzonitrile, $\varphi = \varphi_0$ and

Table 2. Main parameters of low-temperature oxidation of methylbenzonitriles with the system PbO_2-HSO_3F . The nitriles used and reaction conditions are the same as in Table 1

Run	Concentration, M		n/m	φ	α	R	
110.	т	п	р				
1	0.667	1.000	0.193	1.50	1.47	0.156	0.234
2	0.667	1.000	0.193	1.50	1.47	0.156	0.234
3	0.800	0.600	0.160	0.75	1.45	0.172	0.129
4	0.667	1.000	0.187	1.50	(1.45)	0.172	0.258
5	0.500	0.300	0.200	0.60	1.21	0.405	0.243
6	0.333	0.167	0.057	0.50	1.25	0.360	0.180
7	0.700	0.400	0.210	0.57	1.25	0.360	0.205
8	0.500	0.500	0.470	1.00	1.17	0.453	0.453
9	0.250	0.250	0.143	1.00	1.29	0.318	0.318
10	0.050	0.050	0.018	1.00	1.35	0.259	0.259
11	0.267	0.134	0.200	0.50	0.94	0.809	0.405
12	0.250	0.125	0.217	0.50	0.90	0.889	0.445

 $\alpha = 0$). Since $p = \prod m$, we obtain $\prod = c\alpha n/m = cR$ (where *c* is the proportionality coefficient).

The stabilization factors R calculated from the experimental data are listed in Table 2, and the correlation between the stabilization factor and the yield of reaction products for all the three series of methylbenzonitriles is shown in Fig. 2. It is seen that all the data are satisfactorily fitted by a straight line in the coordinates $\prod -R$, deviating by no more than $\pm 3\%$. Mono- and dimethylbenzonitriles (q = 1, 2; series I,II) have R < 0.25, and the compounds with q = 3-5(series III), R > 0.25. The observed significant deviations from the correlation for 4-methylbenzonitrile samples in run no. 3 are probably due to the lower (by half) n/m ratio (Table 2), and in run no. 4, to a considerably higher reaction temperature $(-40^{\circ}C, Table 1)$, which might affect φ ; in the calculation of R for this run, we used the potential obtained at -76° C. For run nos. 9 and 10, which reveal in combination with run no. 8 the influence of the 2,4,6-trimethylbenzonitrile concentration on the yield of oxidation products at equal reactant ratio, the parameters α were calculated from the logarithmic correlation between φ and substrate concentration. As seen from Fig. 2, the points for run nos. 8–10 are also fitted by the same straight line, deviating by no more than $\pm 3\%$.

Thus, the $\prod(R)$ correlation based on the decisive role of radical cation formation in the initial stage of oxidation with PbO₂ is common for all the methylbenzonitriles studied, differing in the degree of alkylation, despite different reaction mechanisms [schemes (1)–(3)] and diversity of products formed.

This result also demonstrates the possibility of using the whole set of methylbenzonitriles with regularly changing number of substituents for studying the reactivity at negative temperatures of oxide systems prepared by molecular layer deposition.

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