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Cyclic trimeric perfluoro-*o*-phenylenemercury: a highly efficient phase transfer catalyst for nitration of aromatic substrates with dilute nitric acid

A.P. Zaraisky[a,*], O.I. Kachurin[a], L.I. Velichko[a], I.A. Tikhonova[b], G.G. Furin[c], V.B. Shur[b,*]

[a] *L.M. Litvinenko Institute of Physical Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, R. Luxembourg Street 70, 83114 Donetsk, Ukraine*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia*
[c] *Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Akad. Lavrent'ev Avenue 9, 630090 Novosibirsk, Russia*

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Abstract

Cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**1**) exhibits a high catalytic activity in the phase transfer nitration of various aromatic substrates (2-methylnaphthalene, 1,3- and 2,6-dimethylnaphthalenes, acenaphthene, anthracene, pyrene) with dilute nitric acid in the presence of sodium nitrite as an initiator and sodium chloride as a promoter. The reactions proceed at room temperature in good or close to quantitative yields. In the absence of the catalyst, the rate of the process is sharply diminished. The best results in the nitration were obtained on using benzene–nitrobenzene mixtures as the organic phase. The replacement of the $PhH/PhNO_2$ mixtures by benzene decreases the reaction rate. An important role in these reactions is played by sodium chloride in the absence of which the catalyst completely loses its activity. Mercury dichloride and bis(perfluorophenyl)mercury do not catalyse the phase transfer nitration with dilute nitric acid even in the presence of sodium chloride. The mechanism of the promoting influence of NaCl on the process of the nitration is discussed. The ability of macrocycle **1** to catalyse the proton transfer from an aqueous phase to an organic phase is also reported.

Keywords: Anticrowns; Aromatic nitration; Phase transfer catalysis; Polymercuramacrocycles; Proton transfer

1. Introduction

One of the outstanding achievements of chemistry of the past decades was the discovery of the fact that some quaternary onium salts as well as crown ethers and their analogues are able to transfer anions from an aqueous phase to an organic phase and, as a consequence, to accelerate two-phase processes occurring with the participation of anionic nucleophiles. This remarkable finding laid a basis for a quite new synthetic methodology and has led to the development of a wide variety of highly efficient phase transfer catalysts for nucleophilic reactions [1–6].

The ability of quaternary onium salts to transport anions through an interface is due to a high lipophilicity of quaternary onium cations capable of extracting anionic species from an aqueous phase. In the case of crown ethers, the process of the anion extraction is preceded by the step of the complexation of its counter cation (usually of alkali metal) with crown ether to form a highly lipophilic complex cation.

In contrast to nucleophilic reactions, the range of known phase transfer catalysts for electrophilic reactions is considerably more narrow. It includes fluorine-containing sodium and tetramethylammonium tetraarylborates, different sodium alkylbenzenesulfonates, sodium 1,4-dialkoxybenzenesulfonates and some others (for reviews, see e.g. [5,7–9]). The presence of a highly lipophilic anion in these salts makes them capable to transport cationic electrophiles through an interface, thereby facilitating their subsequent interaction with a substrate. The observed

* Corresponding authors. Tel.: +7 95 1355024; fax: +7 95 1355085.
E-mail addresses: azar@skif.net (A.P. Zaraisky), vbshur@ineos.ac.ru (V.B. Shur).

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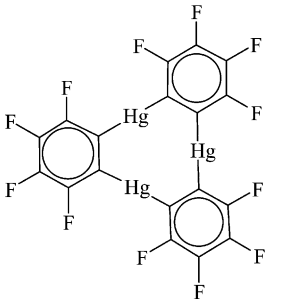
accelerating effects can be here very strong under optimal conditions but due to narrowness of the assortment of suitable catalysts the field of phase transfer catalysis of electrophilic reactions remains so far much less developed than that of nucleophilic processes.

New promising prospects in this important area emerged owing to a rapid progress achieved in latter years in coordination chemistry of macrocyclic multidentate Lewis acids (see e.g. reviews [10–14] and papers cited therein) which can be considered as peculiar antipodes of crown ethers and their thia and aza analogues. A remarkable feature of macrocyclic multidentate Lewis acids is their ability to bind effectively various anions with the formation of lipophilic anionic complexes wherein the anionic species is simultaneously coordinated to all Lewis acidic centres of the macrocycle. This unique property of macrocyclic multidentate Lewis acids makes them very perspective as a potentially new class of phase transfer catalysts for electrophilic reactions.

The first example of the successful application of a macrocyclic multidentate Lewis acid in phase transfer catalysis was described in 1989 when it was reported that cyclic trimeric *o*-phenylenemercury (*o*-$C_6H_4Hg)_3$ containing three Hg atoms in a planar nine-membered cycle is capable of forming complexes with halide anions and catalysing the azo-coupling reaction between benzenediazonium halides $PhN_2^+X^-$ (X = Cl, Br) and β-naphthol in the two-phase H_2O–CH_2Br_2 system [15]. The resulting complexes could not be isolated here due to apparently their insufficient stability and the catalytic effect of the above polymercuramacrocycle in the azo-coupling reaction was not very strong. Nevertheless, the data obtained clearly demonstrated that polymetallamacrocycles of such a type can be employed indeed for interphase transfer of cationic electrophiles.

Much greater efficiency in the phase transfer catalysis can be expected for the perfluorinated analogue of (*o*-$C_6H_4Hg)_3$, viz. cyclic trimeric perfluoro-*o*-phenylenemercury (*o*-$C_6F_4Hg)_3$ (**1**) which also contains three Lewis acidic Hg centres in a planar nine-membered ring [16,17].



(1)

This macrocycle readily reacts with halide (Cl^-, Br^-, I^-) [18–20] and some other anions [10,11,13] to form quite stable and isolable complexes having unusual sandwich, half-sandwich or bipyramidal structures. A high affinity of macrocycle **1** towards anions is due to the presence of the electron-withdrawing fluorine substituents in its molecule which increase the Lewis acidity of the mercury atoms. The same factor results in an enhanced stability of the Hg–C bonds of **1** towards electrophilic attack as compared to those of usual organomercury compounds. According to Ref. [21], macrocycle **1** is insensitive towards the action of 50% H_2SO_4 and 31% HNO_3 at room temperature and remains practically intact on contact with 5% hydrochloric acid at 20 °C for 5–6 h. All these peculiarities of macrocycle **1** are very important for its use in phase transfer catalysis of electrophilic reactions.

In the present paper, data on the catalytic activity of **1** in the phase transfer nitration of aromatic substrates (2-methylnaphthalene, 1,3- and 2,6-dimethylnaphthalenes, acenaphthene, anthracene, pyrene) with dilute nitric acid in the presence of sodium nitrite as an initiator are described in detail. The data demonstrate a high efficiency of **1** in this process. Under optimum conditions, the nitration of such substrates as 1,3-dimethylnaphthalene, acenaphthene and pyrene in the presence of **1** gives at 21 °C good or close to quantitative yields of the nitro products even in several minutes, while in the absence of the catalyst only trace amounts of these products are obtained. The nitration of 2,6-dimethylnaphthalene and 2-methylnaphthalene catalysed by **1** proceeds more slowly but the catalytic acceleration of the process is here also very strong.

For a short preliminary account of a small part of this study, see [22].

2. Results and discussion

The nitration with dilute nitric acid in the presence of nitrite ion as an initiator is often used in organic synthesis for the preparation of nitro derivatives of arylamines, phenols and other highly active aromatic substrates [23]. Under conditions of the phase transfer catalysis by tetra(perfluorophenyl)borates $[(C_6F_5)_4B]^-M^+$ (M = Na, Me_4N), some polycyclic aromatic hydrocarbons (acenaphthene, phenanthrene, pyrene, etc.) can also be involved in this reaction [9,24].

It is usually assumed [23] that the process of the nitration proceeds through a step of nitrosation of the aromatic compound followed by oxidation of the resulting nitroso derivative with nitric acid. The role of nitrosating agents can be played here by nitrosonium cation (NO^+), protonated nitrous acid ($H_2NO_2^+$) and some other species [23]:

$$ArH + HNO_2 \rightarrow ArNO + H_2O$$

$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2$$

According to this mechanism, electrophilic species (NO^+, $H_2NO_2^+$) responsible for occurring the process of the nitration are of cationic character. Therefore, these species could be transferred by **1** through an interface after coordination of their counter anion to the Hg atoms of the macrocycle. With this in mind, we decided to test macrocycle **1** in the phase transfer nitration of aromatic compounds with dilute nitric acid.

In the first experiments, acenaphthene was chosen as an aromatic substrate. The reactions were conducted at 21 °C

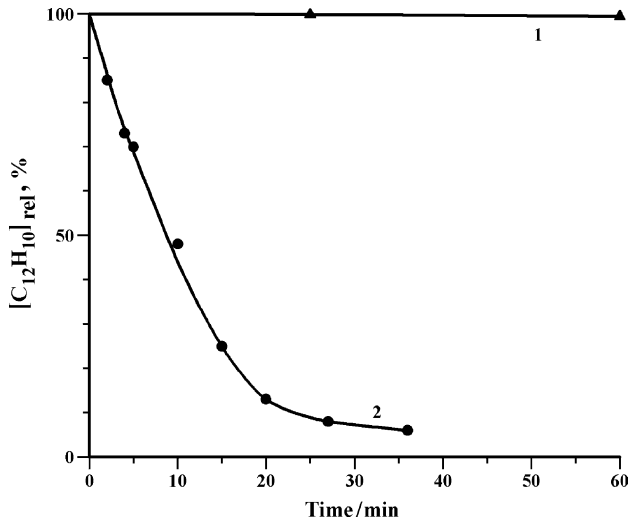
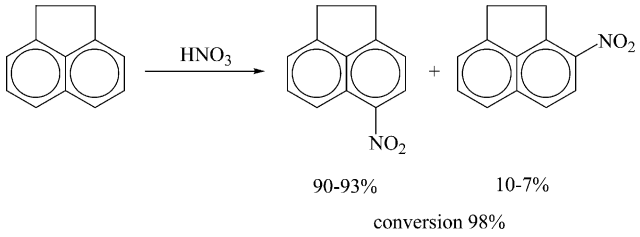


Fig. 1. Kinetic curves of the acenaphthene consumption during its nitration with 21.3% HNO_3 in the absence (curve 1) and in the presence of **1** (31 mg, curve 2). Aqueous phase: 2.5 ml of 21.3% HNO_3 containing $NaNO_2$ (0.33 mmol) and NaCl (1.27 mmol). Organic phase: 5 ml of a 0.5 M solution of acenaphthene in a 87:13 benzene–nitrobenzene mixture.

with the use of a benzene–nitrobenzene mixture (5 ml; the volume ratio is 87:13) as the organic phase and of 21.3% HNO_3 (2.5 ml) as the acidic aqueous phase. The initial concentration of acenaphthene in the organic phase was 0.5 M and the catalyst amount was 31 mg (the acenaphthene:**1** molar ratio = 85:1). A considerable part of this amount of **1** did not dissolve in the organic phase and thus the reaction was started in fact in the suspension of the macrocycle. Sodium nitrite (0.13 mol per mol of acenaphthene, $[NaNO_2]_0 = 0.13$ M) was added to the acidic aqueous phase just before the experiment. Taking into account a high affinity of macrocycle **1** towards halide anions (see above), sodium chloride (44 mol per mol of **1**, $[Cl^-]_0 = 0.51$ M) was introduced additionally into the system.

The results of the experiments have shown that in the absence of **1** the process of the nitration proceeds very slowly and after 3 h about 99% of acenaphthene remains unreacted. However, if 31 mg of **1** is added in the system a rapid consumption of the aromatic substrate occurs and in 35–40 min only small amounts of acenaphthene can be detected in the mixture (Fig. 1). As a result of the reaction, 5-nitro- and 3-nitroacenaphthenes in the 90–93:10–7 ratio are produced in an almost quantitative yield. According to the kinetic data, the addition of **1** increases the initial nitration rate by more than three orders of magnitude.

Still greater efficiency of the acenaphthene nitration can be achieved if the $PhNO_2$:C_6H_6 volume ratio in the benzene–nitrobenzene mixture is increased from 13:87 to 50:50. Under these conditions, nearly all quantity of **1** (31 mg) dissolves in the organic phase (5 ml) and the subsequent stirring with 21.3% HNO_3 (2.5 ml) containing sodium chloride (Cl^-:**1** = 49:1, $[Cl^-]_0 = 0.58$ M) lead to rapid and complete dissolution of the rest of the undissolved macrocycle in the organic layer. As a result, the rate of the acenaphthene nitration in the presence of 31 mg of the catalyst becomes so high that the reaction leads to a substantially quantitative yield of the nitro products even in 2–3 min ($[acenaphthene]_0 = 0.24$ M, $[NaNO_2]_0 = 0.16$ M). When the catalyst is absent, only 10% of acenaphthene are involved in the process of the nitration for the same period of time, and for a quantitative completion of the reaction more than 4.5 h are required.



An important role in the nitration reaction is played by sodium chloride in the absence of which macrocycle **1** shows no activity in this process. Mercury dichloride and bis(perfluorophenyl)mercury do not catalyse the nitration of acenaphthene even in the presence of sodium chloride.

It should be noted that the rate of the acenaphthene nitration practically does not change when the above two-phase system ($PhNO_2$:C_6H_6 = 50:50, 21.3% HNO_3, $NaNO_2$, NaCl) containing 31 mg of **1** is held for 1–3 h under stirring ($[NaNO_2]_0 = 0.18$ M, $[Cl^-]_0 = 0.56$–0.60 M) before the introduction of the aromatic substrate. However, if one enhances the chloride ion concentration in the acidic aqueous phase from 0.56–0.60 to 2.7–2.9 M, the use of such a two-step procedure dramatically reduces the efficiency of the nitration (for more details, see Section 4).

The results obtained are apparently due to a substantial acceleration of the reaction of protolysis of **1** with hydrochloric acid (arising from NaCl and HNO_3) when the concentration of chloride anion in the acidic aqueous phase is augmented to 2.7–2.9 M. Evidently, products formed during the protolysis of **1** exhibit only negligible activity in the phase transfer nitration of acenaphthene or they are totally inactive. The above-mentioned inability of $Hg(C_6F_5)_2$ and $HgCl_2$ to catalyse the acenaphthene nitration are consistent with this assumption.

The replacement of benzene–nitrobenzene mixtures by benzene lowers the efficacy of the nitration of acenaphthene (Fig. 2, curve 2). Here, a close to quantitative conversion of acenaphthene into nitroacenaphthenes in the presence of 31 mg of **1** is attained after 2.5 h ($[acenaphthene]_0 = 0.5$ M, $[NaNO_2]_0 = 0.13$ M, $[Cl^-]_0 = 0.51$ M). An increase in the amount of the catalyst from 31 to 59 mg significantly enhances the efficiency of the process (Fig. 2, curve 1) while its decrease to 12 mg leads to a strong retardation of the nitration reaction (Fig. 2, curve 3). In the absence of **1**, only negligible amounts of nitroacenaphthenes are obtained under the same conditions (Fig. 2, curve 4).

It should be noted that since macrocycle **1** is very poorly soluble in benzene (0.13 g/l at 20 °C [21]) its major part remained undissolved in the organic phase at the beginning of each of the above experiments (Fig. 2). Nevertheless, accord-

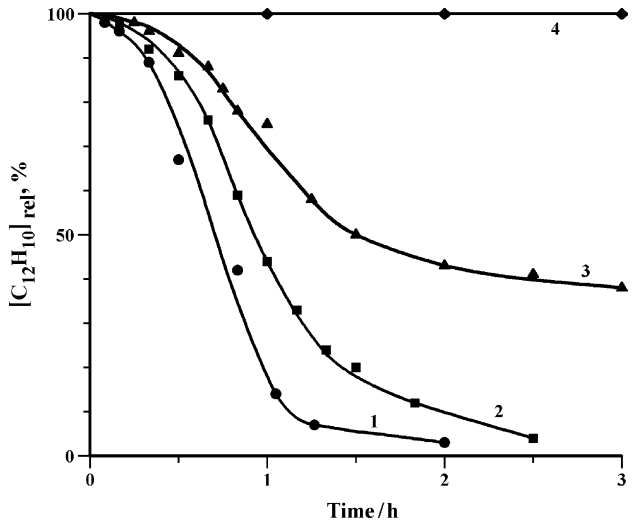


Fig. 2. The effect of the catalyst quantity on the nitration of acenaphthene in benzene as the organic phase. Aqueous phase: 2.5–2.6 ml of 21.3% HNO_3 containing $NaNO_2$ (0.33–0.39 mmol) and NaCl (1.27–1.38 mmol). Organic phase: 5.0–5.3 ml of a 0.48–0.50 M solution of acenaphthene in benzene. Curve 1: 59 mg of **1**, curve 2: 31 mg of **1**, curve 3: 12 mg of **1**, curve 4: no **1**.

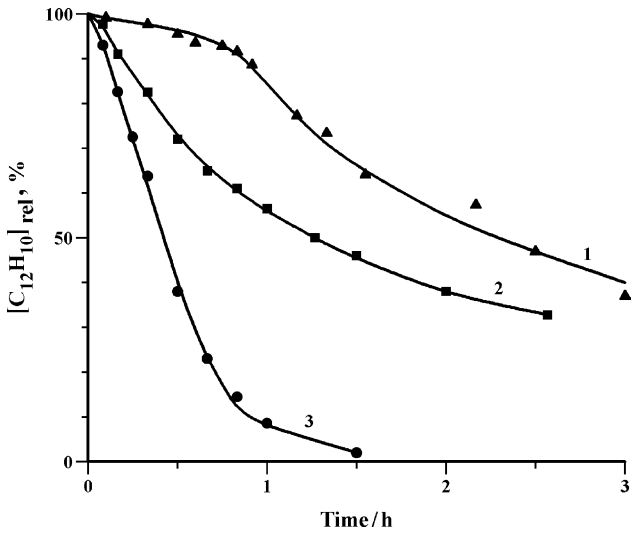


Fig. 3. The effect of the additives of nitroacenaphthenes on the nitration of acenaphthene in benzene as the organic phase in the presence of **1**. Aqueous phase: 2.5 ml of 21.3% HNO_3 containing $NaNO_2$ (0.32–0.36 mmol) and NaCl (1.25–1.27 mmol). Organic phase: 5 ml of a 0.24–0.25 M solution of acenaphthene not containing (curve 1, 12 mg of **1**) or containing 0.14 g (curve 2, 12 mg of **1**) and 0.27 g (curve 3, 32 mg of **1**) of nitroacenaphthenes.

ing to the kinetic measurements, the initial nitration rate in these experiments grows linearly with an increase in the catalyst quantity, thus suggesting the predominant contribution of the solid phase of **1** to the overall kinetics of the process in its early stage.

The nitration of acenaphthene in benzene as the organic phase proceeds with an induction period (Fig. 2) which is absent when the reaction is carried out in a benzene–nitrobenzene mixture. The duration of this induction period decreases with an increase in the amount of the catalyst. An introduction of nitroacenaphthenes into the benzene phase before the reaction results in a disappearance of the induction period and in an increase in the reaction rate (Fig. 3). The observed influence of the additives of nitroacenaphthenes and nitrobenzene on the process of the nitration can be explained by an increase in the solubility of macrocycle **1** in the organic phase due to its complexation with the Lewis basic oxygen atoms of the nitro group. The ability of **1** to form complexes with neutral Lewis bases such as nitriles, carbonyl compounds, dimethylsulfoxide and some others is now well established [10,11,13]. The presence of a nitroarene in benzene should lead also to an increase in polarity of the organic phase and, as a consequence, to an increase in the efficiency of the transfer of a cationic electrophile through an interface owing to an enhancement in the solubility of a chloride complex of **1** in the organic layer. Finally, the rate of the subsequent reaction of a cationic electrophile with the aromatic substrate could grow as well with a rise in polarity of the organic phase. By the end of the induction period, all quantity of the taken **1** dissolves completely in the benzene layer. When the aromatic substrate is absent, macrocycle **1** can be readily recovered in 95% yield after its stirring for 1 h with a mixture of benzene (5 ml) and 21.3% HNO_3 (2.5 ml) in the presence of sodium nitrite ($[NaNO_2]_0 = 0.13$ M) and sodium chloride ($[NaCl]_0 = 0.51$ M).

The phase transfer nitration of 1,3-dimethylnaphthalene with 21.3% HNO_3 is also catalysed by macrocycle **1** and leads to the formation of 4-nitro-1,3-dimethylnaphthalene together with two unidentified nitro isomers in the 90:5:5 ratio. According to the literature data [25], the nitration of the same substrate with 100% HNO_3 in acetic anhydride affords a 81.8:9.9:8.3 mixture of 4-nitro-, 5-nitro- and 2-nitro-1,3-dimethylnaphthalenes. Therefore, one may suggest that the above-mentioned minor isomers formed under conditions of the phase transfer nitration of 1,3-dimethylnaphthalene are 5-nitro- and 2-nitro-1,3-dimethylnaphthalenes.

The kinetic curves of the 1,3-dimethylnaphthalene consumption during its nitration in the absence and in the presence of **1** at 21 °C are given in Fig. 4. In these experiments, a 0.12 M solution of the aromatic substrate in a 50:50 benzene–nitrobenzene mixture was used as the organic phase, and the initial $NaNO_2$ concentration in the acidic aqueous phase was 0.26 M. The obtained data show that under such conditions an introduction of 98 mg of the catalyst into the system ($[Cl^-]_0 = 1$ M) results in a very strong acceleration of the reaction which is quantitatively completed here even in 15–25 min. In the absence of **1**, only 2% of the aromatic substrate undergo the nitration for the same period of time. An increase in the chloride ion content in the system allows the accomplishment of the nitration with high rates using lesser amounts of the catalyst. Thus, if one enhances the initial concentration of NaCl in the acidic aqueous phase by a factor of 2.8, only 50 mg of **1** are required for a close to quantitative (95–98%) conversion of 1,3-dimethylnaphthalene into the products of its nitration for 10–15 min.

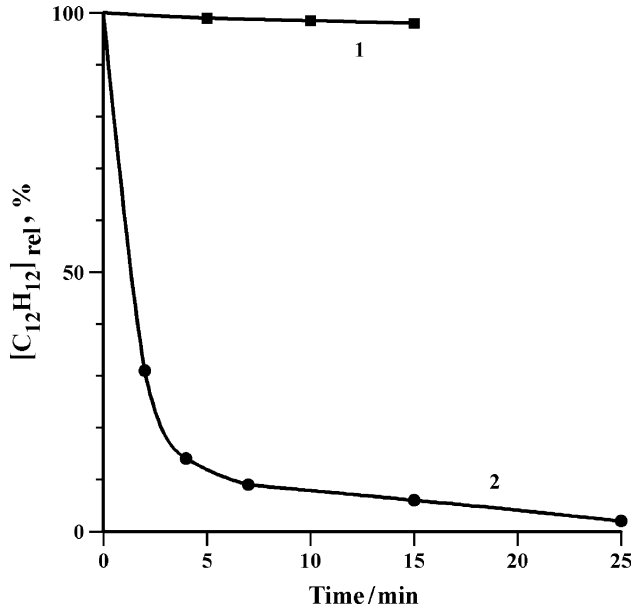
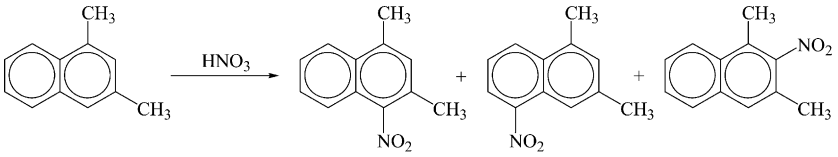


Fig. 4. Kinetic curves of the 1,3-dimethylnaphthalene consumption during its nitration with 21.3% HNO_3 in the absence (curve 1) and in the presence of **1** (98 mg, curve 2). Aqueous phase: 2.5 ml of 21.3% HNO_3 containing $NaNO_2$ (0.65 mmol) and NaCl (2.51 mmol). Organic phase: 5 ml of a 0.12 M solution of 1,3-dimethylnaphthalene in a 50:50 benzene–nitrobenzene mixture.



Experiments on the nitration of 2,6-dimethylnaphthalene with 21.3% HNO_3 were also conducted using a 50:50 benzene–nitrobenzene mixture as the organic phase. The catalyst was taken here in the amount of 78 mg ($[Cl^-]_0 = 0.74$ M). The initial concentration of the aromatic substrate in the organic phase was 0.1 M and the $NaNO_2$ concentration in the acidic aqueous phase was 0.24 M. It turned out that under these conditions (see Fig. 5), the process of the nitration of 2,6-dimethylnaphthalene is practically completed after about 1 h at 21 °C. On carrying out the reaction without catalyst, no nitration occurs for at least 1.5 h (Fig. 5).

According to Ref. [25], the nitration of 2,6-dimethylnaphthalene with 100% HNO_3 in acetic anhydride results in the formation of a 81.6:16.5:1.9 mixture of 1-nitro-, 4-nitro- and 3-nitro-2,6-dimethylnaphthalenes. In our experiments too, 1-nitro isomer is a major product (80%) of the nitration of 2,6-dimethylnaphthalene. In addition, small amounts of two unidentified nitro isomers (19–20% and <1%) are also obtained. Apparently, these minor isomers are 4-nitro- and 3-nitro-2,6-dimethylnaphthalenes. The overall yield of the nitro products is close to 100%.

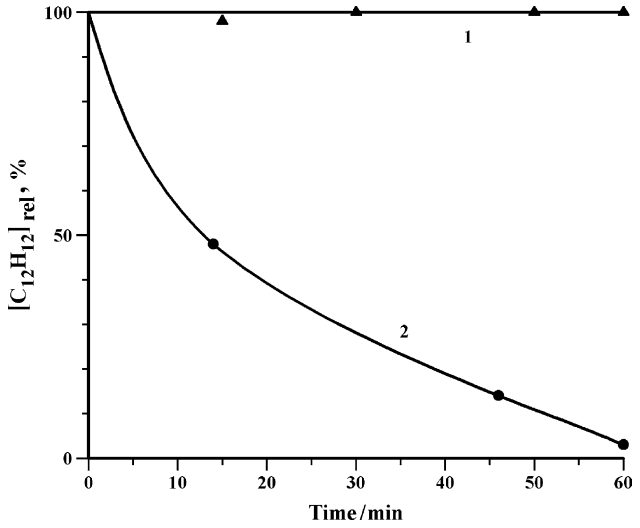


Fig. 5. Kinetic curves of the 2,6-dimethylnaphthalene consumption during its nitration with 21.3% HNO_3 in the absence (curve 1) and in the presence of **1** (78 mg, curve 2). Aqueous phase: 2.5 ml of 21.3% HNO_3 containing $NaNO_2$ (0.61 mmol) and NaCl (1.86 mmol). Organic phase: 5 ml of a 0.1 M solution of 2,6-dimethylnaphthalene in a 50:50 benzene–nitrobenzene mixture.

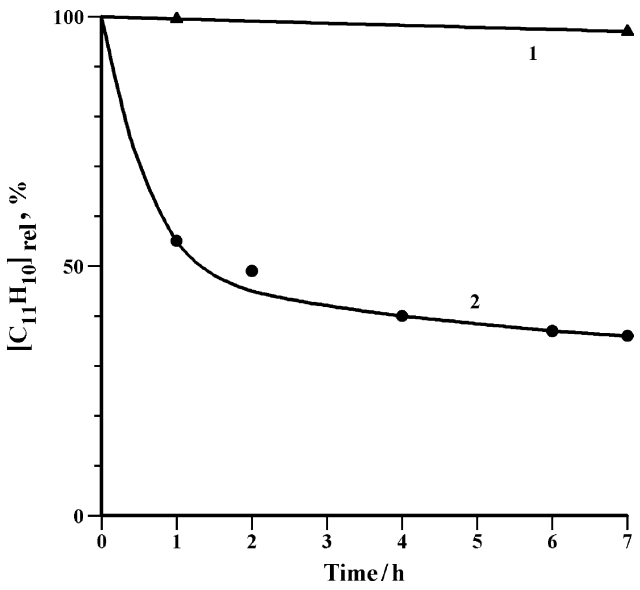
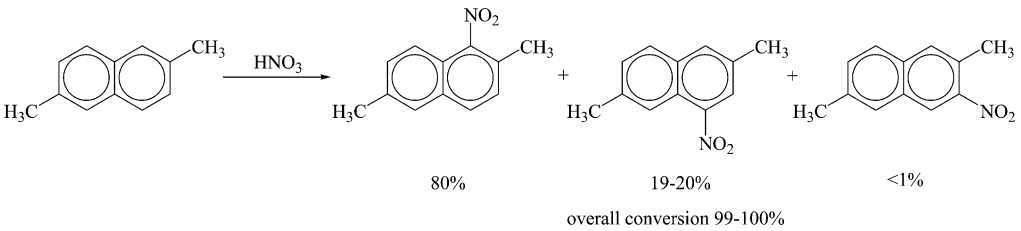
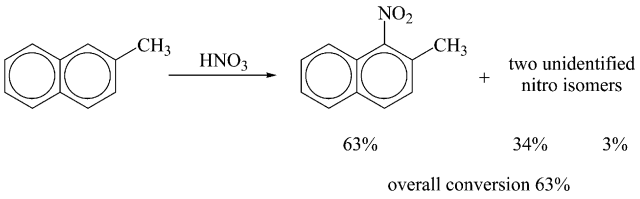


Fig. 6. Kinetic curves of the 2-methylnaphthalene consumption during its nitration with 21.3% HNO_3 in the absence (curve 1) and in the presence of **1** (0.17 g, curve 2). Aqueous phase: 3 ml of 21.3% HNO_3 containing $NaNO_2$ (0.88 mmol) and NaCl (7.07 mmol). Organic phase: 6 ml of a 0.21 M solution of 2-methylnaphthalene in a 17:83 benzene–nitrobenzene mixture.



2-Methylnaphthalene is less active than acenaphthene and dimethylnaphthalenes in reactions of electrophilic substitution and so it is nitrated with 21.3% HNO_3 at 21 °C with a lower rate than these substrates even on using rather large amounts of the catalyst and an increased nitrobenzene content in the organic phase. Nevertheless, the catalytic effect of the macrocycle looks here also quite impressive. As seen from Fig. 6, if the reaction is carried out in the presence of 0.17 g of **1** with the use of a 17:83 benzene–nitrobenzene mixture ($[Cl^-]_0 = 2.83$ M, $[NaNO_2]_0 = 0.29$ M) the conversion of 2-methylnaphthalene after 6 h reaches 63%; then the process practically stops due to apparently the decomposition of the catalyst and irreversible consumption of nitrous acid for side reactions. In the absence of **1**, the conversion of 2-methylnaphthalene into its nitro derivatives does not exceed 3% even after 7 h (Fig. 6). As result of the nitration, 1-nitro-2-methylnaphthalene together with two unidentified minor isomers are produced in the 63:34:3 ratio.



In the case of the anthracene nitration, the best results were obtained on using 14.5% HNO_3 and a 93:7 benzene–nitrobenzene mixture as the organic phase ($[NaNO_2]_0 = 0.21$ M). Under these conditions, an introduction of 10 mg of **1** into the system ($[Cl^-]_0 = 2.73$ M) leads to a 93% conversion of the aromatic substrate in 1 h at 21 °C (Fig. 7), and if 45 mg of **1** is added about 97% of the initial amount of anthracene can be transformed into the reaction products even after 1–2 min. On carrying out the nitration without catalyst, the conversion of anthracene attains 67% after 20 min (Fig. 7) but then the process stops as in the case of the 2-methylnaphthalene nitration catalysed by **1** (see above). According to GLC, the reaction products both in the presence and in the absence of **1** contain 9-nitroanthracene, anthraquinone and a small quantity of an unidentified compound in the ratio of 77:19:4. Thus, the nitration of anthracene with dilute nitric acid in the two-phase system is accompanied by its partial oxidation to anthraqui none.

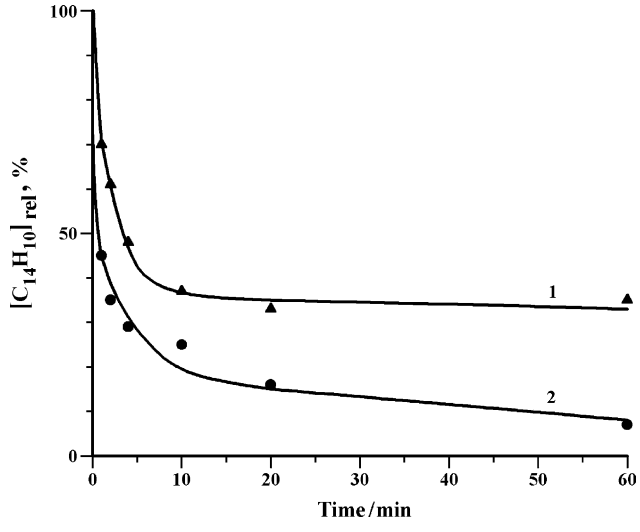


Fig. 7. Kinetic curves of the anthracene consumption during its nitration with 14.5% HNO_3 in the absence (curve 1) and in the presence of **1** (10 mg, curve 2). Aqueous phase: 2.5 ml of 14.5% HNO_3 containing $NaNO_2$ (0.53 mmol) and NaCl (6.86 mmol). Organic phase: 5.4 ml of a 0.07 M solution of anthracene in a 93:7 benzene–nitrobenzene mixture.

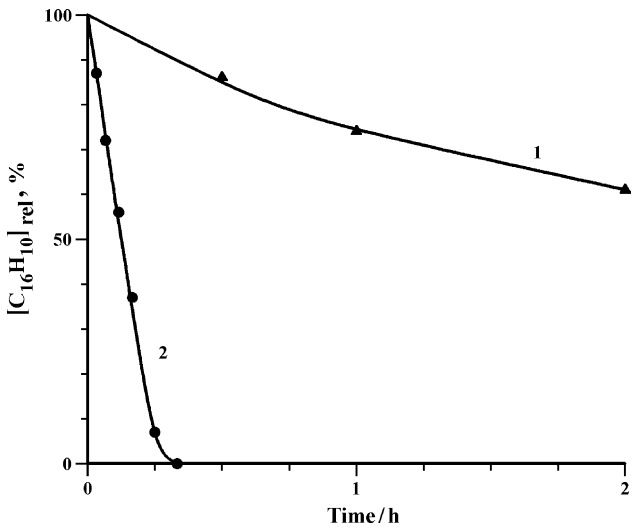
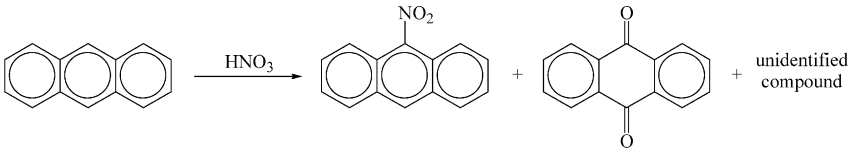


Fig. 8. Kinetic curves of the pyrene consumption during its nitration with 21.3% HNO_3 in the absence (curve 1) and in the presence of **1** (55 mg, curve 2). Aqueous phase: 2.5 ml of 21.3% HNO_3 containing $NaNO_2$ (0.43 mmol) and NaCl (1.68 mmol). Organic phase: 5.05 ml of a 0.09 M solution of pyrene in a 89:11 benzene–nitrobenzene mixture.

Table 1
Comparison of the reactivities of the aromatic substrates (ArH) in the phase transfer nitration with dilute nitric acid in the presence of sodium nitrite as an initiator, macrocycle **1** as a catalyst and sodium chloride as a promoter[a]

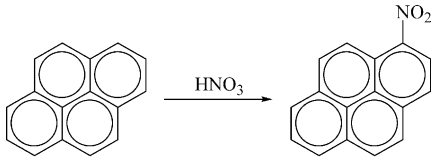
No.	ArH	**1** (mg)	$[ArH]_0$ (M)	$[HNO_3]_0$ (%)	$[NaNO_2]_0$ (M)	[NaCl] (M)	$[PhNO_2]$ (vol.%)	$\tau_{1/2}$ (min)
1	2-Methylnaphthalene	170	0.21	21.3	0.29	2.8	83	75
2	2,6-Dimethylnaphthalene	78	0.10	21.3	0.24	0.74	50	12
3	1,3-Dimethylnaphthalene	98	0.12	21.3	0.26	1.0	50	1.5
4	1,3-Dimethylnaphthalene	50	0.30	21.3	0.26	2.8	50	1.5
5	Acenaphthene	48	0.30	21.3	0.25	2.8	50	<1
6	Acenaphthene	31	0.24	21.3	0.16	0.58	50	ca. 1
7	Pyrene	55	0.09	21.3	0.17	0.67	11	7.5
8	Pyrene	56	0.09	21.3	0.17	2.9	11	2
9	Anthracene	45	0.07	14.5	0.21	2.7	7	<1

[a] 21 °C, the aqueous phase containing nitric acid, sodium nitrite and sodium chloride; the organic phase containing ArH in a benzene/nitrobenzene mixture.



overall conversion 97%

The phase transfer nitration of pyrene with 21.3% HNO_3 at 21 °C affords 1-nitropyrene and is sharply accelerated on the addition of even small amounts of nitrobenzene to benzene. The catalytic effect of the macrocycle is here also very strong (Fig. 8). Thus, if the reaction is conducted in the presence of 55 mg of **1** using a 89:11 benzene–nitrobenzene mixture only 15–20 min are required for the complete transformation of pyrene into 1-nitropyrene at the chloride ion concentration of 0.67 M ($[NaNO_2]_0$ = 0.17 M, $[pyrene]_0$ = 0.09 M). In the absence of **1**, the conversion of pyrene attains only 40% even in 3 h. Still higher nitration rate is observed when the chloride ion content in the acidic aqueous phase is increased to 2.9 M. Under these conditions, a practically all quantity of the taken pyrene is converted into the product of its nitration in the presence of 56 mg of the catalyst even in 4 min.



conversion 100%

A comparison of the reactivities of the above aromatic substrates in the phase transfer nitration catalysed by **1** is strongly complicated because of the difference in the reaction conditions for most of the substrates. Nevertheless, some qualitative conclusions can be made here. As seen from Table 1, acenaphthene is noticeably more active in the nitration than 1,3-dimethylnaphthaline under the same conditions (cf. runs 5 and 4). With smaller quantities of **1**, $NaNO_2$, NaCl and nitrobenzene, pyrene demonstrates, nevertheless, markedly greater reactivity than 2,6-dimethylnaphthalene (cf. runs 7 and 2). Using similar reasonings, one may conclude also that in the case of anthracene the rate of the reaction is higher than in the case of pyrene (cf. runs 9 and 8) and 2,6-dimethylnaphthalene is apparently less reactive than acenaphthene (cf. runs 6 and 2). The least activity in the nitration among the aromatic substrates tested is exhibited by 2-methylnaphthalene (run 1) that is nitrated with very low rate despite the use of very large amounts of **1**, nitrobenzene and sodium chloride.

3. Conclusion

The results obtained show that macrocycle **1** exhibits a high catalytic activity in the phase transfer nitration of various aromatic substrates with dilute nitric acid in the presence of sodium nitrite as an initiator and sodium chloride as a promoter. The reactions proceed at room temperature in good or close to quantitative yields. In the absence of the catalyst, the rate of the nitration is sharply diminished.

The role of chloride ions in these reactions consists in their coordination with the macrocycle (see [18–20]) to form lipophilic complex anions capable of extracting cationic electrophiles (responsible for occurring the process of the nitration) from an acidic aqueous phase to an organic phase. One may suggest that nitrate anions either are unable to form complexes with **1** or these complexes are insufficiently lipophilic for the effective transfer of cationic electrophilic species through an interface. In all probability, it is this which is the reason why the catalytic effect of macrocycle **1** in the phase transfer nitration is manifested only in the presence of sodium chloride in the system.

The addition of nitrobenzene to benzene enhances the solubility of macrocycle **1** in the organic phase owing to, appar-

ently, a complexation of its nitro group with the Hg atoms of **1**. Similar complexes are probably formed also in the interaction of **1** with the nitro derivatives arising during the nitration. The presence of chloride anions in the system leads to further increase in the solubility of **1** in the organic layer. The ability of **1** to coordinate nitro compounds is evidenced by the recent isolation of a complex of **1** with 1-nitropyrene [26]. In this complex, $\{[(o\text{-}C_6F_4Hg)_3](C_{16}H_9NO_2)_3\}$, both the oxygen atoms of the nitro groups and the C=C bonds of the aromatic rings of the nitropyrene ligands are involved in the coordination to the Hg centres of the macrocycle. The syntheses and structures of this complex as well as complexes of **1** with other nitro compounds will be described in detail elsewhere. The complexation of **1** with aromatic hydrocarbons (including unsubstituted pyrene) has previously been established by Gabbaï and coworkers [13].

The proposed mechanism of the promoting influence of chloride ions on the phase transfer nitration reactions catalysed by **1** is in a good accord with the data on the catalytic activity of this macrocycle in the proton transfer from an aqueous phase to an organic phase. The process of the proton transfer can be easily monitored if trityl alcohol is introduced as an indicator into an organic phase. As is known, this colourless compound is readily transformed into yellow trityl cation under the action of sufficiently strong acids.

$$Ph_3COH + H^+ \leftrightarrows Ph_3C^+ + H_2O$$

Using this indicator method we found that macrocycle **1** is able to transfer protons into benzene from 25 to 35% hydrochloric acid. However, if hydrochloric acid is replaced by 21.3% nitric or 31% sulfuric acids no proton transfer takes place. The ability of macrocycle **1** to accomplish the proton transport through an interface opens a way to the use of macrocycles of such a type in the phase transfer catalysis of acid-catalysed reactions.

4. Experimental

The starting macrocycle **1** was synthesized according to the published procedure [16]. Commercial acenaphthene was additionally purified by recrystallization from ethanol (or aqueous ethanol) with subsequent sublimation in vacuum. Commercial pyrene was repeatedly recrystallized from the mixture of xylenes. Commercial anthracene (mp 216 °C), 2-methylnaphthalene (mp 34.5 °C), 1,3- and 2,6-dimethylnaphthalenes (98%, Fluka) and $HgCl_2$ were used without additional purification. Nitric acid of the required concentration (21.3 and 14.5%) was prepared by dilution of 60% HNO_3 with distilled water. Purity of sodium nitrite as determined by the permanganate titration was 97–98%. Nitrobenzene was distilled in vacuum prior to use. Commercial benzene of high quality was employed without further purification.

Experiments on the nitration were carried out at 21 ± 1 °C in a kinetic region. The course of the reactions was monitored by means of GLC using LHM-8/3 and Tswett-104 chromatographs with flame ionization detectors (carrier gas He). The analyses were performed on columns (3 m × 3 mm) with 5% OV-17 or 3% SE 30 on Inerton Super (0.16–0.20 mm) in the temperature interval of 155–260 °C.

4.1. General procedure for the nitration

Definite amounts of macrocycle **1**, benzene or benzene–nitrobenzene mixture, nitric acid, sodium chloride, aromatic substrate and a higher alkane (internal standard) were charged into a 20 ml two- or three-necked flask placed into thermostat and the resulting two-phase system was intensively stirred at 21 ± 1 °C for 10–20 min. Then stirring was stopped, the appropriate amount of solid sodium nitrite was added and the reaction mixture was vigorously stirred in a closed system at 21 ± 1 °C. From time to time, probes (∼0.05 ml) were taken from the organic layer. The probes were treated with $NaHCO_3$, dried over anhydrous $MgSO_4$ and analysed by GLC for the content of the starting substrate and products of the nitration. The results of the analyses were averaged over 3–10 measurements. The standard deviations from the averaged values did not exceed 3–5%. The volume of an organic phase was usually ∼5 ml while that of an aqueous phase was ∼2.5 ml.

4.2. Two-step procedure for the nitration

Special experiments with the use of the two-step procedure for the nitration were carried out in order to examine the dependence of the efficiency of the nitration upon the time of the preliminary contact of **1** with the nitration system in the absence of the aromatic substrate. In these experiments, the initial chloride ion concentration in the aqueous phase was 0.56–0.64 and 2.7–2.9 M. On the step of the nitration, acenaphthene was used as the substrate.

In the case of the 0.56–0.64 M chloride ion concentration, the experiments were performed in the following manner. Two-phase system consisting of 21.3% HNO_3 (2.5 ml), sodium nitrite ($[NaNO_2]_0 = 0.18$ M), NaCl ($[Cl^-]_0 = 0.56$–0.60 M) and 31 mg of **1** in a 50:50 benzene–nitrobenzene mixture (5 ml) was stirred at 21 °C for 1 and 3 h, respectively. Then acenaphthene (1.19–1.21 mmol) was dissolved in the separated organic phase and the resulting 0.24 M solution of acenaphthene was subjected to the phase transfer nitration with the freshly prepared nitration system containing 21.3% HNO_3 (2.5 ml), sodium nitrite ($[NaNO_2]_0 = 0.19$ M) and NaCl ($[Cl^-]_0 = 0.63$–0.64 M). The results of GLC analyses showed that when the duration of the preliminary contact of **1** with the nitration system is 1 h, the acenaphthene conversion into the nitro products attains 64% after 1 min and 95% after 3 min which practically coincides with the corresponding values (62 and 98%, respectively) observed on the use of the standard procedure for the nitration under the same conditions. Close results (99%

conversion after 3 min) are obtained if the time of the preliminary contact of **1** with the nitration system is increased to 3 h.

In the case of the 2.7–2.9 M chloride ion concentration, the following series of the experiments was carried out. In one of these experiments, the nitration was conducted in the usual manner. A 0.24 M solution of acenaphthene in a 91:9 benzene–nitrobenzene mixture (5.5 ml) was introduced in the reaction with a 21.3% solution of HNO_3 (2.5 ml) containing sodium nitrite ($[NaNO_2]_0 = 0.13$ M) and sodium chloride ($[Cl^-]_0 = 2.9$ M). Under such conditions, the presence of 13 mg of **1** in the system gave a 79% conversion of acenaphthene into the nitro products in 30 min after which the process ceased to proceed. In the absence of **1**, only traces of nitroacenaphthenes were formed even for 1.5 h. In two other experiments, 34 mg of **1** in a 50:50 benzene–nitrobenzene mixture (5 ml) was stirred at 21 °C with 21.3% HNO_3 (2.5 ml), sodium nitrite ($[NaNO_2]_0 = 0.24$ M) and NaCl ($[Cl^-]_0 = 2.74$ M) for 1 and 2.5 h, respectively. Then acenaphthene (1.15 mmol) and 3.3 ml of benzene was added to 1.7 ml of the separated organic phase (containing 12 mg of **1** theoretically) and the resulting 0.23 M solution of acenaphthene underwent the phase transfer nitration with 21.3% HNO_3 (2.5 ml) in the presence of sodium nitrite ($[NaNO_2]_0 = 0.14$ M) and sodium chloride ($[Cl^-]_0 = 2.8$ M), i.e. under conditions of the above experiment carried out in the usual manner. It was found that when a solution of **1** is in touch with the nitration system for 1 h (before introducing the aromatic substrate) the subsequent nitration gives after 30 min only 20% conversion of acenaphthene into the nitro products and then the reaction stops. Even greater fall in the efficiency of the nitration is observed when the time of the preliminary contact of **1** with the nitration system is enhanced to 2.5 h. In this case, the conversion of acenaphthene into nitroacenaphthenes does not exceed 7–8% within 30–60 min.

4.3. Identification of the reaction products

3-Nitroacenaphthene and 5-nitroacenaphthene, 1-nitro-2-methylnaphthalene, 9-nitroanthracene and anthraquinone were identified by GLC using authentic samples of these compounds. 1,3-Dimethyl-4-nitronaphthalene, 1-nitro-2,6-dimethylnaphthalene and 1-nitropyrene were isolated from the reaction mixtures and identified by a comparison of their melting points with those described in the literature.

1,3-Dimethyl-4-nitronaphthalene, mp 80 °C (after double chromatography on a column with silica gel; CCl_4 and $CHCl_3$ as eluents), lit. mp 80 and 83 °C [25].

1-Nitro-2,6-dimethylnaphthalene, mp 67 °C (after double column chromatography on silicagel; CCl_4 and $CHCl_3$ as eluents), lit. mp 67–67.5 °C and 68 °C [25].

1-Nitropyrene, mp 155 °C (after sublimation in vacuum and recrystallization from EtOH–PhH mixture), lit. mp 155 °C [27].

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