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Phase-transfer Catalysis in Electrophilic Substitution Reactions: IX.* Kinetics and Mechanism of Nitration of Polycyclic Arenes under Conditions of Phase-transfer Catalysis in a System Benzene–Aqueous Sulfuric Acid–Sodium Nitrite

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Abstract—Nitration of polycyclic arenes under conditions of the phase-transfer catalysis in a system benzene–aqueous sulfuric acid–sodium nitrite involves reagent activation stage with formation of its active forms $H_2NO_2^+$ and $H_2O \cdot NO^+$ in the polar phase. The limiting reaction stage is presumably interphase transport of the active reagent form.

We investigated in [1] preparative aspects of nitro-arenes production under conditions of phase-transfer catalysis by treating aromatic substrate with nitrous acid. The stereochemistry of the process was studied. The reaction is efficient at mild conditions for a wide range of arenes, but its kinetics and mechanism were not sufficiently elucidated. This study was undertaken in order to fill this gap at least partially.

The reagent (nitrous acid) suffers decomposition under the reaction conditions. To reveal the kinetic law of the nitration the initial reaction rates were measured. On Fig. 1 are shown the kinetic curves of acenaphthene (**I**) nitration in systems of various acidity. As catalyst of interphase transfer we used tetramethylammonium tetrakis(perfluorophenyl)-

Fig. 1. Kinetic curves of acenaphthene (**I**) nitration. (Runs numbered as in Table 1).

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* For communication VIII see [1].
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borate (**II**) [2]. The results of experiments are compiled in Table 1. The initial reaction rates were determined by the slope of tangents to the kinetic curves at the time moment $\tau = 0$. In case of the largest reaction rates the order of reaction with respect to acenaphthene was close to zero (Fig. 2).

The data obtained indicate that under all conditions studied the acenaphthene nitration is limited by transfer of the active reagent species or of its precursor into the organic phase. The limiting stage cannot occur in the polar phase, for it would have excluded the phase transfer catalysis. As seen from Fig. 3, within the concentration range of sulfuric acid 10–45% the reaction rates follow the Hammett's acidity function providing a kinetic equation below is valid:

$$(d[\mathbf{I}]/d\tau)_0 = -k[\mathbf{II}][NaNO_2]_0 \ h_0 \equiv -k_0 \qquad (1)$$

where h_0 is nonlogarithmic Hammett's acidity function (index "0" at the term k_0 means zero order in substrate, in the other cases it indicates the initial moment of the reaction). The first order of reaction in nitrite (nitrous acid) was confirmed in [1]. The first order in catalyst follows from the comparison of runs nos. *5* and *6* (Table 1). The same conclusion follows from the data on nitration of fluorene and phenanthrene which are not reported here, and from the general considerations of the catalysis theory [4].

In the concentration range 10–45% of H_2SO_4 (see Fig. 3) the possible active species of the reagent is a protonated nitrous acid (**III**). Above 45% of H_2SO_4
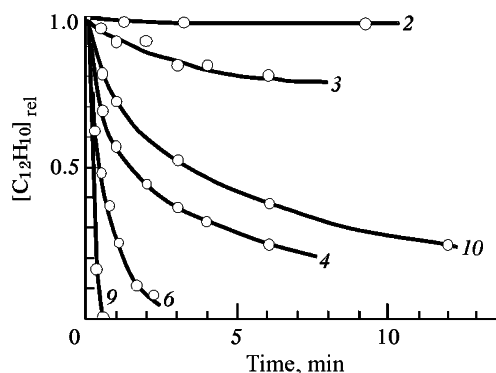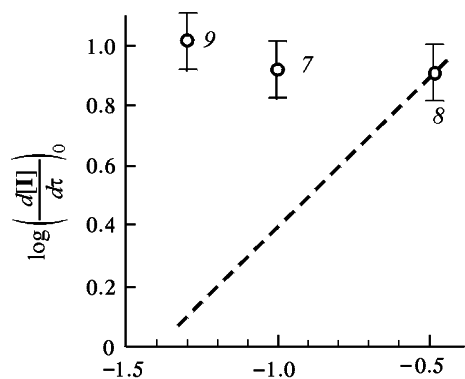
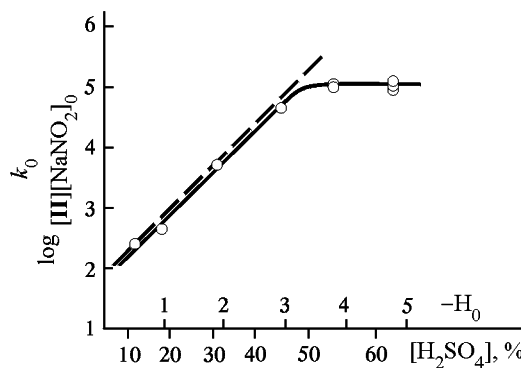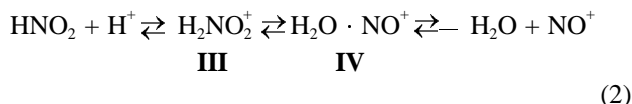**Fig. 2.** The reaction order in acenaphthene is close to zero (Runs numbered as in Table 1).
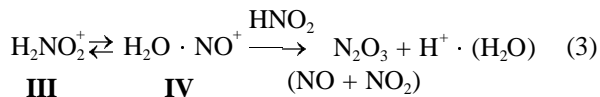

Fig. 3. Acenaphthene nitration rate as a function of acidity [3]. The unit slope is shown by dashed line.

the curve on Fig. 3 gradually attains a plateau, and the effect of the acidity becomes negligible. According to literature data this fact may be rationalized as a result of total transformation of the nitrous acid into nitrosonium cation at H_2SO_4 concentrations above 50–55% [5]. This transformation should proceed through a stage of water-solvated nitrosonium (**IV**).

$$HNO_2 + H^+ \rightleftarrows \underset{\textbf{III}}{H_2NO_2^+} \rightleftarrows \underset{\textbf{IV}}{H_2O \cdot NO^+} \rightleftarrows H_2O + NO^+$$

$$(2)$$

The reorganization of nitrosacidium ion (**III**) into the water-solvated cation **IV** should occur through a considerable energy barrier. It is presumable that the first order on the path of nitrous acid decomposition [6] is due to the slow decomposition of **III** species followed by fast attack on the second HNO_2 molecule:

$$\underset{\textbf{III}}{H_2NO_2^+} \rightleftarrows \underset{\textbf{IV}}{H_2O \cdot NO^+} \xrightarrow{\ HNO_2\ } N_2O_3 + H^+ \cdot (H_2O) \quad (3)$$
$$(NO + NO_2)$$

The decomposition of cation **IV** along the above scheme (2) is not energetically favorable [7] and gradually proceeds in the region of 60–90% of H_2SO_4 [8] at transition to nitrosylsulfuric acid [9]. However the strongly shifted to the left side dehydration equilibrium exists also at lower concentrations of H_2SO_4, but is apparently affected by the proton acidity of the medium. It was found [10] that the nitration rate of *m*-xylene in the sodium nitrite solutions in sulfuric acid increased 40 times in going from sulfuric acid concentration of 55.3% to 64.9%, all the other conditions being equal. At this acidity in the phase-transfer nitration of acenaphthene the reaction rate is totally independent of the reaction mixture composition (see Fig. 3). It is presumable that with acenaphthene the process is carried out by **IV** species which is the main form of the reagent at the given acidity whereas the *m*-xylene in the sulfuric acid is nitrated by NO^+ ion present in a low equilibrium concentration (cf. [7]). The *m*-xylene is virtually unreactive under the conditions of phase-transfer

Table 1. Initial rates of acenaphthene nitration in a system benzene–aqueous sulfuric acid–sodium nitrite, 25°C

Run no.	[H₂SO₄], %	Initial concentrations, mmol l⁻¹			(d[I]/dτ)₀, mol l⁻¹ h⁻¹
		acenaphthene (**I**)	catalyst **II**	NaNO₂	
1	10.9	4.55	0.399	97.4	0.0103
2	18.1	209	0.800	396	0.14
3	31.0	109	0.406	209	0.425
4	44.4	101	0.413	206	3.85
5	54.0	78.8	0.199	154	3.06
6	54.0	101	0.399	213	8.09
7	61.8	100	0.399	201	8.59
8	61.8	321	0.399	203	8.17
9	61.8	51.0	0.399	197	10.23
10	61.8	100	–	202	2.28

catalysis used in the runs nos.*7–9* for acenaphthene. The growth of the nitration rate of *m*-xylene in the solutions of sodium nitrite in sulfuric acid may be rationalized relying on a scheme (4) of equilibrium with a participation of a hypothetical virtual dication (A). Activity of a nitrosonium ion in this scheme is proportional to the acidity function h_0 and varies inversely with water activity. These values change for H_2SO_4 of 55.3–64.9% concentration 16.5-fold [3] and 2.6-fold [11] respectively corresponding to the increase in NO^+ activity by a factor of ~40.

$$H_2O \cdot NO^+ \rightleftarrows [H_3O^+ ...NO^+] \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} H_2O + NO^+ \qquad (4)$$
$$\textbf{IV} \qquad\qquad A$$
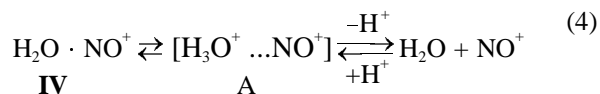
Thus in the two-phase system under study the active form NO^+ does not operate in reaction with acenaphthene.

It is important to note that in the noncatalyzed run no. *10* (Table 1) where the catalysis by acid is also exhausted the reaction is significantly decelerated, 5-fold as compared with run no. *9* where the compound **II** provides transport of the active cation. This fact unambiguously evidences the capability of catalyst **II** to transfer through the phase boarder not only protons [2] but also active reagent species.

The limiting stage of the reaction hardly occurs in this process in the organic phase for both an efficient extraction of the nitrous acid from the acid–water phase is dubious and the above-described specific reaction features are unlikely to be observed in nonpolar benzene. The involvement into the analogous reaction of the nitrogen trioxide is *a fortiori* excluded since the reaction rate in this case should be the second and not the first order in the reagent.

It is obvious that the great source in raising the reaction efficiency lies in application of more powerful means for electrophile transport. It should have both accelerated the reaction and retarded the nitrous acid decomposition that occurs along the first order process [6].

The mechanism of nitration is closely related to the character of the substrate reactivity. As show the specific features of nitration kinetics treated above the estimation of relative reactivity of substrates by comparing their nitration kinetics cannot provide unambiguous data. Therefore the relative reactivity was studied by the method of concurrent reactions: an appropriate pair of substrates (see EXPERIMENTAL) was subjected to nitration, and the running concentration of each component was measured in the course of the process.

Table 2. Substrate ratios for nitration in the system benzene–aqueous sulfuric acid–sodium nitrite, 20–25°C

Run no.	Substrate	k/k_{naph}
1	Biphenyl	0.0058
2	Naphthalene	(1)
3	Phenanthrene	10.2
4	Fluoranthene	13.3
5	Fluorene	13.0
6	2-Methylnaphthalene	33.9
7	1,3-Dimethylnaphthalene	2500
8	Acenaphthene	84000
9	Pyrene	24500000
10	Anthracene	1800000000

The relative reactivity (substrate ratio) calculated from these data as independent of conversion, i.e. of the sampling time, of the medium acidity, of the type of the phase-transfer catalyst, of the presence or absence of the latter in the system. For the transport of the active reagent species were used the approved formerly [1, 2] phase-transfer catalysts tetramethylammonium and sodium tetrakis(perfluorophenyl)borates and also cyclic trimer of perfluorophenylenemercury and pentamer of perfluoropropylidenemercury.

The pair anthracene–pyrene was an exception: the substrate ratio in this case decreased with time and sometimes even became less than unity. However the values extrapolated to the initial reaction moment were in agreement. These averaged figures were taken as the most probable. We do not intend to discuss here the behavior of this the most reactive pair.

The substrate ratio obtained in the experiments on concurrent reactions (see EXPERIMENTAL) permitted the calculation of reactivity of the arenes under study with respect to naphthalene. These values are given in Table 2.

The logarithms of these values correlate with the energy of substrate ionization measured experimentally by photoionization and photoelectron spectroscopy methods which have given similar results [12].

$$\log(k/k_{naph}) = (105.1 \pm 0.8)I, \qquad (5)$$
$$r = -0.995, \ n = 7,$$

As seen from Fig. 4, for fluorene, fluoranthene, and phenanthrene the deviations from the empirical relationship far exceed the errors in the rate measure-

Table 3. Substrate ratios in experiments of nitration under concurrent kinetics (system benzene–aqueous sulfuric acid–sodium nitrite, 20–25°C)

Run no.	Concurrent pair (1/2)	Concentration of H_2SO_4, %	$k_{(1)}/k_{(2)}$ [a]	Number of runs/number of samples
1	Phenanthrene/naphthalene	54.0	10.4 ± 0.7	5/10
2	Fluorene/phenanthrene	54.0	1.30 ± 0.14	7/21
3	2-Methylnaphthalene/phenanthrene	54.0	3.31 ± 0.4	3/9
4	Acenaphthene/1,3-dimethylnaphthalene	25.6; 54.0	33.6 ± 0.9	6/10
5	1,3-Dimethylnaphthalene/2-methylnaphthalene	54.0	73.5 ± 6.1	4/9
6	Fluoranthene/naphthalene	54.0	13.2 ± 0.5	3/11
7	Phenanthrene/fluoranthene	31.2; 54.0	0.92 ± 0.08	2/3
8	Biphenyl/naphthalene	31.2	0.0058 ± 0.0006	1/3
9	Pyrene/acenaphthene	25.6; 54.0	265 ± 50	3/6
10	Anthracene/pyrene	25.6	80 ± 10 [b]	3/5

[a] Standard deviations from the average values are given.
[b] Determined by extrapolation to the initial moment of the reaction.

ments and likely also in the estimation of the ionization energy of arene molecule. These three points are not included into expression (5), and the observed deviations are as yet unclear.

However the relation presented on Fig. 4 suggests the early character of the transition state in the first stage of reactant interaction in the organic phase. For instance, the crucial substrate form in this stage is likely a charge-transfer complex or arene cation-radical (cf. [13, 14]). Interestingly, no nitroso compounds were detected in the system under study. The investigation of the fine mechanism of the reaction will be the subject of further research.

EXPERIMENTAL

Analyses were carried out by GLC on chromatograph LKhM-MD3 equipped with a flame-ionization detector, stainless steel column 3000×3 mm, stationary phase OV-17 on Inerton Super (0.16–0.20 mm), carrier gas helium, vaporizer temperature 300–380°C. Analysis temperatures from 130°C (naphthalene) to 270°C (1-nitropyrene). The analytical procedure, description of kinetic experiments, preparation of reagents used were published in [1,13].

The procedure of kinetic experiments with concurrent pairs was the same as in purely kinetic runs. The pairs were selected from compounds not strongly differing in reactivity; otherwise at the nearly total conversion of the active substrate the occurrence of reaction with the less active one would not be observed (p-acenaphthene–phenanthrene). Another condition

of selection was no overlapping of chromatographic peaks belonging to substrates, reaction products, and internal references used (n-alkanes from C_{11} to C_{24}). If the conversion in reaction α was of the same order of magnitude as the common precision of the analysis (for instance, α = 10–20% at analysis accuracy about 5%), then the measurements were performed with respect to reaction products, and in such or similar cases as a rule these were controlled by analyses by substrates.

Thus the substrate ratios were calculated from the experimentally measured residual fractions of compounds belonging to the given concurrent pair. The latter values were the ratios of the running concentra-
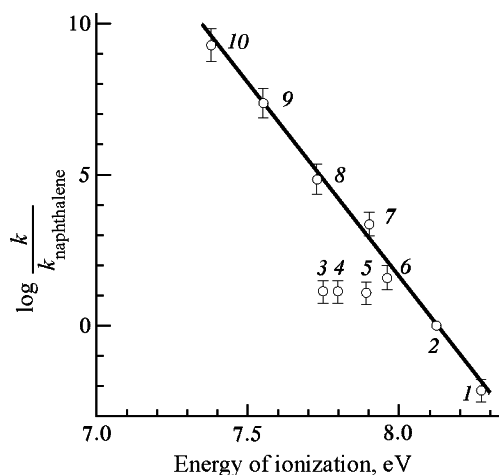
Fig. 4. Correlation between logarithms of substrate reactivity and ionization energy of arene molecules. The numbering as in Table 2.

tions of a substrate to its initial concentration. The calculations were done by a formula:

$$k_1/k_2 = [\log(100-\alpha_1)-2]/[\log(100-\alpha_2)-2], \qquad (6)$$

where the values in parentheses are just the residual fractions of substrates (%). The results are collected in Table 3.

The first order in substrate at the stage of active species attack on the substrate underlies expression (6). For an elementary reaction investigated by the concurrent reactions method this assumption should be valid in the majority of cases.

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