Kinetics and Catalysis, Vol. 42, No. 4, 2001, pp. 471–473. Translated from Kinetika i Kataliz, Vol. 42, No. 4, 2001, pp. 523–525.
Original Russian Text Copyright © 2001 by Mil'to, Orlov, Mironov, Kopeikin.

Kinetics of the Reactions of 4-Nitrochlorobenzene with Substituted Phenols in the Presence of Potassium Carbonate

V. I. Mil'to, V. Yu. Orlov, G. S. Mironov, and V. V. Kopeikin

Yaroslavl State University, Yaroslavl, 150000 Russia

Received February 9, 2000

Abstract—The kinetics of 4-nitrochlorobenzene (4-NCB) reactions with substituted phenols in the presence of potassium carbonate in *N*,*N*-dimethylacetamide was studied. Depending substituents, the reactivity of the phenols is changed in the series 3-NO_2 > 4-Cl > H > 4-Br > 3-CH_3 > 3-NH_2, which is consistent with the series of their acidity. The reaction rates satisfactorily correlate with the pK_a values of the corresponding substituted phenols. Based on kinetic data (first-order and zero-order reactions with respect to phenol and 4-NCB, respectively, and the consistency of the reactivity and acidity of substituted phenols), the deprotonation of phenols is considered as the rate-determining step of the overall reaction under the test conditions. A reaction scheme was proposed for the synthesis of diaryl ethers in the presence of potassium carbonate. It involves a heterogeneous step of phenol deprotonation, which takes place on the surface of potassium carbonate, and a homogeneous step of the interaction of potassium phenolates with 4-NCB. Under the reaction conditions, the resulting bicarbonate decomposes with the formation of potassium carbonate and with the release of carbon dioxide and water.

INTRODUCTION

Earlier [1], we studied the reactions of 4-nitrochlorobenzene (4-NCB) with substituted phenolates to form nitro derivatives of diphenyl oxide. The preparative synthesis of nitroaryl ethers is performed by the *in situ* generation of phenolates from corresponding phenols and alkaline agents [2]. Among these agents, potassium carbonate is most widely used. The reaction kinetics of the formation of dinitrophenyl oxide derivatives under the conditions of real syntheses (substrate, substituted phenol, and alkaline agent) was poorly studied. The aim of this work was to fill this gap.

EXPERIMENTAL

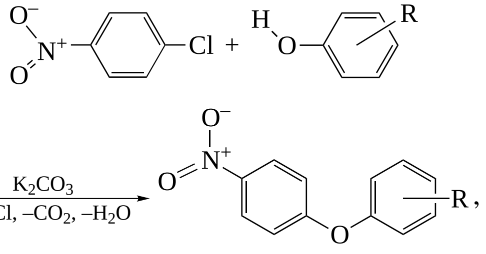
The kinetics of the reactions of 4-NCB with substituted phenols in the presence of potassium carbonate was studied in a thermostatically controlled flask equipped with a stirrer, a reflux condenser, a capillary for admitting nitrogen, and a thermostatically controlled dropping funnel. The initial reactant concentrations were equal to 4×10^{-2} mol/l; *N*,*N*-dimethylacetamide (DMAC) was used as a solvent. The flask was maintained at a constant temperature and purged with nitrogen; the solvent, 4-NCB, and potassium carbonate were loaded in a flask, and a solution of the relevant substituted phenol in DMAC was added from the thermostatically controlled funnel and stirring in a nitrogen atmosphere. To determine whether or not the reaction is by kinetics, the stirring intensity of the reaction mixture was monitored with a strobotachometer. In the course of reaction, samples were taken, cooled, and analyzed for 4-NCB by GLC (Chrom-4 chromatograph with a flame-ionization detector; carrier gas, nitrogen; column length, 3 m; column diameter, 3 mm; stationary phase, polyethylene glycol adipate; solid support, NAW; column and injector temperatures, 170 and 280°C, respectively; internal standard, nitrobenzene).

Solvents (reagent grade) were additionally dried with alkali metal hydroxides and calcium chloride and distilled in a vacuum.

The starting chemicals (chemically pure) were additionally recrystallized.

RESULTS AND DISCUSSION

The kinetics of the interactions of 4-NCB with substituted phenols in the presence of potassium carbonate in a DMAC medium was studied at 130–160°C. The reaction takes place according to the following scheme:



where R = 3-NH_2, 3-CH_3, H, 4-Cl, 4-Br, or 3-NO_2.

In this case, the yields of aryl ethers were as high as 91–95 mol %.

The general features of the process were determined for a reaction of 4-NCB with phenol in the presence of potassium carbonate.

0023-1584/01/4204-0471$25.00 © 2001 MAIK "Nauka / Interperiodica"

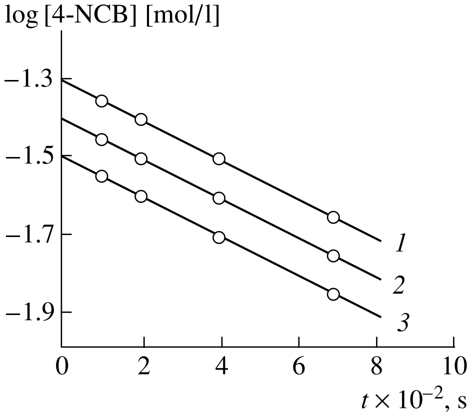


Fig. 1. Semilogarithmic kinetic curves for the reaction of 4-nitrochlorobenzene with phenol in the presence of K_2CO_3 (DMAC; 140°C; 4-NCB : K_2CO_3 = 1 : 5; $d \leq 0.25$ mm; n = 1500 rpm; $[4\text{-NCB}]_0 = [\text{phenol}]_0$ = (*1*) 0.05, (*2*) 0.04, or (*3*) 0.03 mol/l).

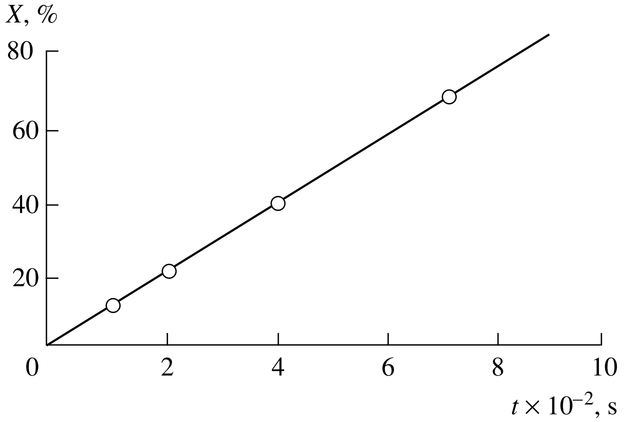


Fig. 2. Conversion of 4-nitrochlorobenzene (X) as a function of time in the reaction with phenol in the presence of potassium carbonate (DMAC; 140°C; 4-NCB : K_2CO_3 = 1 : 5; $d \leq 0.25$ mm; n = 1500 rpm; $[4\text{-NCB}]_0 : [\text{phenol}]_0$ = 1 : 10).

Because potassium carbonate is almost insoluble in DMAC, its solubility or the accessibility of its surface for contact with reactants can be responsible for the reaction rate. We found the process parameters at which the reaction is not controlled by diffusion (the conversion of reactants is independent of the stirring intensity n, the molar ratio between potassium carbonate and phenol, and the carbonate particle size d) (Table 1).

Data in Table 1 indicates that the following conditions are responsible for the kinetic region of the reaction between 4-NCB with phenol in the presence of potassium carbonate: K_2CO_3 : phenol ≥ 1 : 1 mol/mol, $d \leq 0.5$ mm, and $n \geq 1500$ rpm.

The time dependence of the current concentration of 4-NCB at equimolecular ratios between 4-NCB, phenol, and K_2CO_3 and different initial concentrations of the reactants is described by a first-order rate law (Fig. 1).

The linear dependence of the conversion of 4-NCB (X) on time with an excess of phenol indicates that the reaction is of zero order with respect to 4-NCB (Fig. 2).

The apparent rate constants k_{app} for 4-NCB reactions with substituted phenols (Table 2) were found from the kinetic curves similar to those shown in Fig. 1.

It follows from the above data that, depending on the nature of substituents, the reactivity of phenols is changed in the order $3\text{-NO}_2 > 4\text{-Cl} > \text{H} > 4\text{-Br} > 3\text{-CH}_3 > 3\text{-NH}_2$, which is consistent with their acidity series. The reaction rate satisfactorily correlates with the pK_a values of phenols (Table 2). The correlation parameters are as follows: the constant that characterizes the reaction type $\rho = 0.242 \pm 0.010$, the correlation coefficient r = 0.983, and the standard deviation s = 0.08. It is likely that the low absolute value of ρ for the test reaction in comparison with $\rho = 3.46$ for the dissociation of phenols in dimethyl sulfoxide [3] is due to the fact that the effect of substituents in a reactant on the reaction rate is inhibited under heterogeneous reaction conditions.

A comparison of the above results with published data [1] allowed us to notice that the effects of the same substituents on the reaction rate were inverted on going from the reactions of 4-NCB with phenols in the pres-

Table 1. Conversion of 4-nitrochlorobenzene in the reaction with phenol depending on the rate of stirring n, the K_2CO_3 particle size d, and the K_2CO_3 : phenol ratio

Conversion of 4-NCB, %												
K_2CO_3 : phenol (d = 0.25 mm; n = 1500 rpm)						d, mm (K_2CO_3 : phenol = 1 : 1, n = 1500 rpm)			n, rpm (K_2CO_3 : phenol = 1 : 1, d = 0.25 mm)			
0	0.05	0.50	1.00	5.00	10.00	1.50	0.75	0.25–0.50	100	300	1500	2500
0	20	50	65	75	75	33	53	75	58	72	80	80

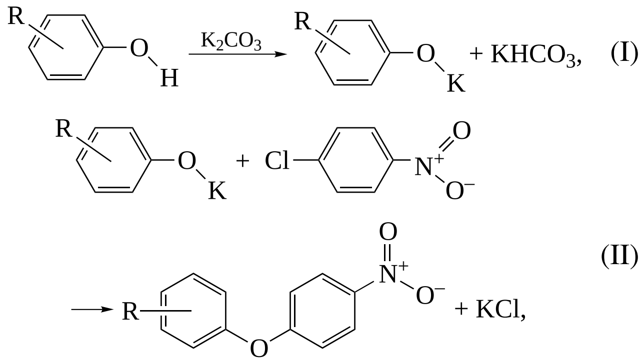
Note: Reaction conditions: DMAC; 140°C; 4-NCB : phenol = 1 : 1; duration, 30 min. Molar ratios between components are given.

ence of potassium carbonate to the reactions with potassium phenolates.

Based on kinetic data for the reactions of 4-NCB with substituted phenols in the presence of potassium carbonate (first-order and zero-order reactions with respect to phenols and 4-NCB, respectively, and the consistency between the reactivity and acidity of substituted phenols), we may believe that the deprotonation of phenols is a rate-determining step in the overall reaction under the test conditions. Esikov and Yufit [4, 5], who studied the alkylation of acetoacetic ester in the presence of various alkaline agents, including potassium carbonate, have drawn a similar conclusion. These authors believe that the partial orders of reaction with respect to the reactants (first and zero orders with respect to acetoacetic ester and the alkylating agent, respectively) indicate that deprotonation is the rate-limiting step of the test process.

It is well known [6] that deprotonation in the presence of K_2CO_3 results in the degradation of the crystal lattice of potassium carbonate. The surface becomes coated with an inactive layer of $KHCO_3$, and the reaction is gradually decayed. However, in the processes under consideration, the reaction was completed in 1.0–1.5 h with no signs of completion. This is due to the fact that above 100°C (the experiments were performed at 130–160°C) bicarbonate decomposes and forms carbonate, water, and carbon dioxide [7].

To interpret the above kinetic results and our previous data [1], we can propose the following scheme for the synthesis of diaryl ethers in the presence of potassium carbonate:



$$2KHCO_3 \longrightarrow K_2CO_3 + H_2O + CO_2. \qquad \text{(III)}$$

Step (I) is a heterogeneous process, which depends on deprotonation and takes place on the surface of potassium carbonate. The reaction rate increases with an increase in the acidity of phenols. Under the conditions of this synthesis, the resulting bicarbonate decomposes to form potassium carbonate and to release carbon dioxide and water (step (III)). Potassium phenolates react with 4-NCB under homogeneous conditions (step (II)). These reactions are described by the *SN*Ar-type kinetics, and they are orbital-controlled [1]. If the energy of the highest occupied molecular orbital of the reagent is close to the energy of the lowest unoccupied molecular orbital of the substrate, as is the case with potassium resorcinate [1], the radical ions of reactants are formed, and the reaction occurs with the participation of these species.

Table 2. Rate constants of the reactions of 4-nitrochlorobenzene with substituted phenols in the presence of potassium carbonate

Substituent *R*	pK_a [3]	$k_a \times 10^4$, s^{-1}
3-NO_2	12.1	16.60 ± 0.17
4-Cl	12.7	15.00 ± 0.14
4-Br	13.2	9.60 ± 0.11
H	13.7	11.40 ± 0.12
3-CH_3	13.6	7.50 ± 0.11
3-NH_2	–	5.20 ± 0.13

Note: Reaction conditions: DMAC; 140°C; 4-NCB : K_2CO_3 = 1 : 5; d = 0.25 mm; n = 1500 rpm; $[\text{4-NCB}]_0 = [\text{phenol}]_0 = 4.0 \times 10^{-2}$ mol/l.

REFERENCES

1. Mil'to, V.I., Mironov, G.S., Kopeikin, V.V., *et al.*, *Kinet. Katal.*, 2001, vol. 42, no. 3, p. 518.
2. US Patent 4287372.
3. Kreshkov, A.P., Aldarova, N.Sh., Tatasov, A.I., *et al.*, *Reakts. Sposobn. Org. Soedin.*, 1970, vol. 7, p. 279.
4. Esikov, I.A. and Yufit, S.S., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 3, p. 507.
5. Esikov, I.A. and Yufit, S.S., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 3, p. 515.
6. Yufit, S.S., *Mekhanizm mezhfaznogo kataliza* (The Mechanism of Phase-Transfer Catalysis), Moscow: Nauka, 1984.
7. *Spravochnik khimika*, Nikol'skii, B.P., Ed., 1971, vol. 2.