

INFLUENCE OF MEDIUM ON REACTIVITY OF 2,4-DINITROFLUORO- AND CHLOROBENZENES DURING REACTION WITH *m*- AND *p*-SUBSTITUTED ANILINES

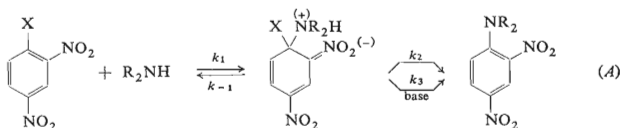
J. KAVÁLEK, J. HAASOVÁ and V. ŠTĚRBA

Department of Organic Chemistry,
Institute of Chemical Technology, Pardubice

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The reactions of 2,4-dinitrofluoro- and chlorobenzenes with *m*- and *p*-substituted anilines have been studied kinetically in methanol and acetonitrile media. The differences in reactivities and base catalysis have been discussed from the mechanistic point of view.

The reactions of primary and secondary amines with nitrohalogenobenzenes follow the addition-elimination mechanism, Eq. (A).



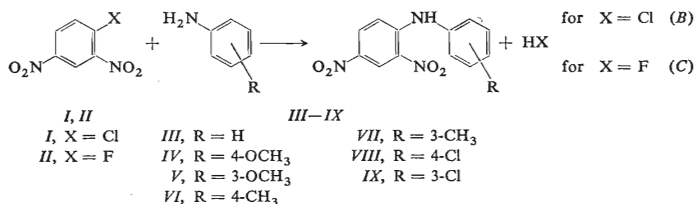
The constant k_2 represents the velocity of non-catalyzed resp. solvent-catalyzed decomposition of the intermediate *A* into products. The value k_3 represents the rate constant of the respective base-catalyzed decomposition. The proper nucleophile or another added basic catalyst can act as the base. The experimental bimolecular constant k_A is given by Eq. (I).

$$v/([RX][R_2NH]) = k_A = (k_1 k_2 + k_1 k_3 [B]) / (k_{-1} + k_2 + k_3 [B]) \quad (I)$$

If $k_2 + k_3[B] \gg k_{-1}$, then $k_A = k_1$. The reaction is not base catalyzed, and the first step (formation of intermediate) is rate-determining. In the opposite case the decomposition of the intermediate is rate-determining and the reaction is linearly dependent on the base concentration. If the velocities of decompositions of the intermediate into starting substances and into products are comparable, the curve of the dependence of k_A on base concentration has a non-linear concave course. In the reactions of dinitrochlorobenzene with amines the first reaction step is rate-determining¹⁻³. The rate constant does not depend on the base concentration or changes relatively little which is explained by a stabilization of the activated complex by substances capable of formation of hydrogen bonds⁴. The reaction of dinitrochlorobenzene with aniline in acetone⁵ is the only case where the base-catalyzed decomposition of the intermediate is considered to be the rate-determining step. The ratio of the rate constants of fluoro and chloro derivatives (k_F/k_{Cl}) is (besides the base catalysis) the second criterion frequently used for determination of the rate-

determining step in the case of fluoro derivatives, which can exhibit a change of the rate-determining step on changing the reaction conditions. Whereas in polar protic solvents the first step is usually rate-determining, the second step is rate-determining in non-polar aprotic media⁶. In the case of the first step being rate-determining for the both halogeno derivatives the fluoro derivative reacts faster than the chloro derivative by two or more orders of magnitude. If the second step is rate-determining with the fluoro derivative, the reaction can be slowed down to such an extent, that the reactivity order will reverse⁷. There are, however, reactions³ which have the second reaction step rate-determining, and, in spite of it, $k_F/k_{Cl} = 10^2 - 10^3$.

The aim of this work was to compare the reactivities of 2,4-dinitrofluorobenzene (*II*) and 2,4-dinitrochlorobenzene (*I*) with *m*- and *p*-substituted anilines *III*–*IX* in two polar solvents having close dielectric constants and differing in that one is protic and the other is aprotic.



Though the splitting of the F—C bond, which affects k_2 and k_3 , is far easier in protic solvents than in aprotic ones, the solvents have been appreciated mainly by the value of their dielectric constants up to now⁶. The pair methanol–acetonitrile was chosen for our work.

RESULTS AND DISCUSSION

We have found that the reactions (*B*) and (*C*) in methanol were first order in both the halogeno derivative and amine even at the highest base concentrations (Table I). The ratio k_F/k_{Cl} was 230 for aniline (*III*). This considerable difference in reactivities and absence of the base catalysis indicates that the first step is rate-determining. The rate constant is given by equation $k_A = k_1$. The rate constants measured were correlated with the Hammett σ constants⁸. The values ρ obtained for the reactions (*B*) and (*C*) were -2.2 and -3.3 respectively. Although the fluoro derivative *II* is more reactive, it has a higher value of the constant ρ , too. A similar study was carried out in ethanol earlier⁹. The reaction was first order in the both components, too, and the ratio k_F/k_{Cl} equaled 63 at 50°C. The ρ values found were -3.4 and -2.8 for the fluoro and chloro derivatives respectively, *i.e.* greater with the more reactive fluoro derivative, too.

In the medium of acetonitrile only two amines (*III* and *IV*) were used as nucleophiles in the reaction (*B*). The reaction is first order in both the components in the whole concentration range studied (Table II) and the values of rate constants are about 4 times smaller than in methanol medium. The reaction (*C*) was, in the case of amines *III–VIII*, first order in the fluoro derivative *II*, but the rate constant k_A increased non-linearly with the increasing amine concentration (Fig. 1). Therefrom it follows that the reaction is base-catalyzed. From Fig. 1 it is obvious that the bimolecular rate constant $k_A = 0$ for all the amines *III–VIII* when extrapolating the constants to zero concentration of amine. The value of k_2 is thus far smaller than $k_3[B]$ (*B* denotes the amine *III–VIII*) and can be neglected (the decomposition of the intermediate into products proceeds only through the base-catalyzed step).

The rate constants k_1 and k_{-1}/k_3 (for amines *III–VII*) (Table III) were determined graphically from the linear dependence $1/k_A$ vs $1/[B]$ in Eq. (2).

$$1/k_A = 1/k_1 + k_{-1}/k_1 k_3 [B]. \quad (2)$$

For the reaction of the fluoro derivative *II* and amine *III* in acetone medium⁵ at 50°C the values $k_1 = 3.15 \cdot 10^{-1} \text{ l mol}^{-1} \text{ min}^{-1}$ and $k_{-1}/k_3 = 1.6$ were found which are close to our values for the same reaction (Table III).

The values k_1 calculated correspond to the same reaction step as the rate constants k_A of the reaction (*B*) in acetonitrile (Table II). Their ratio (k_F/k_{CI}) for aniline (*III*) has the value of 300 which is close to an analogous value found in methanolic solution (230). The Hammett correlation of k_1 gave graphically the constant $\rho - 4.5$. The ratio k_{-1}/k_3 is the same for all the anilines *III–VII* within experimental error.

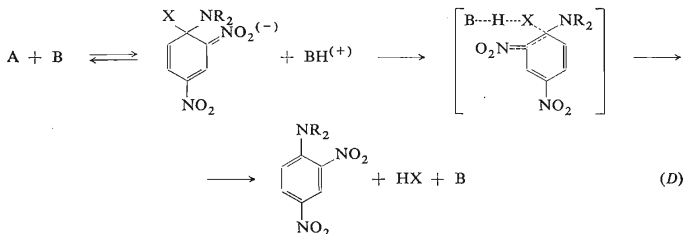
TABLE I

Rate Constants k_1 of Reactions (*B*) and (*C*) in Methanol at 20°C
 $[I]_0 = 1 \cdot 10^{-4} \text{ mol/l}$, $[II]_0 = 0.5 \cdot 10^{-4} \text{ mol/l}$.

Substituted aniline (<i>c</i> , mol/l)	$10^4 k_1^{(B)}$ l/mol min	$10^4 k_1^{(C)}$ l/mol min	Substituted aniline (<i>c</i> , mol/l)	$10^4 k_1^{(B)}$ l/mol min	$10^4 k_1^{(C)}$ l/mol min
<i>VI</i> (1.0)	36.0	—	<i>III</i> (0.3)	14.7	33.6
<i>VI</i> (0.3)	37.0	10.6	<i>III</i> (0.1)	15.3 ^a	33.0 ^b
<i>VI</i> (0.1)	34.0	10.8	<i>VIII</i> (1.0)	3.24	—
<i>VII</i> (0.6)	23.0	—	<i>VIII</i> (0.1)	—	3.36
<i>VII</i> (0.1)	22.0	60.8	<i>IX</i> (1.0)	1.32	1.20
<i>III</i> (0.8)	13.8	—	<i>IX</i> (0.8)	—	1.26
<i>III</i> (0.6)	—	32.4	<i>IX</i> (0.5)	—	1.32
<i>III</i> (0.4)	14.4	34.0			

^a $[I]_0 = 0.5 \cdot 10^{-4} \text{ mol/l}$; ^b $[II]_0 = 1 \cdot 10^{-4} \text{ mol/l}$.

This can be explained as follows. Mechanism (D) is generally accepted for base catalysis¹⁰.



The increase of basicity of the amine B results in increasing the difficulty of its reverse splitting off from the intermediate A (Scheme A) (k_{-1} is lowered), but, at the same time, the splitting of the C—F bond is slowed down, too, because the conjugate acid BH^+ , being derived from a stronger base, is weaker and has thus lower catalytic effect. The influences of the basicity change of the amine on the velocities of the both steps (k_{-1} and k_3) cancel each other. The ratio k_{-1}/k_3 of the reaction with aniline (III) did not change on rising the temperature from 20° to 80°C either (Table III). Therefrom it follows that the difference in the activation energies of the both steps is small.

The reaction (C) gives a dipolar intermediate from the two non-polar starting substances, and the reaction product involves an amonium salt. It is presumed^{6,11}

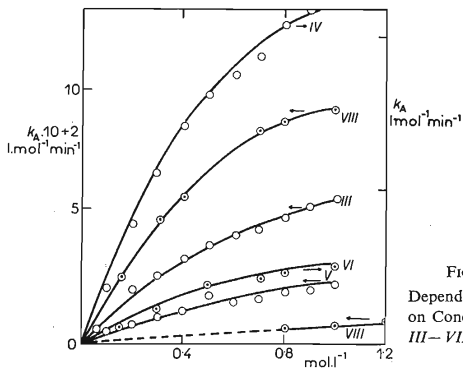


FIG. 1
Dependence of k_A Value of Reaction (C) on Concentration of Substituted Anilines III—VIII in Acetonitrile at 20°C

for such a type of nucleophilic aromatic substitution that an increase of solvent polarity causes an increase of the constant k_1 and decrease of the ratio k_{-1}/k_3 (the formation of the intermediate becomes rate-determining). The value of dielectric constant was chosen as a measure of polarity for these reactions⁶. Although acetonitrile has a higher value of dielectric constant than methanol (36.5 and 32.6 respectively), the k_1 value found by us for the reaction (C) in acetonitrile is three times smaller than that in methanol, and the reaction is strongly catalyzed by bases (the decomposition of the intermediate into products makes itself felt kinetically). The higher k_1 value in methanol medium can be explained by stabilization of the activated complex by formation of hydrogen bond with oxygen atom of methanol^{4,10}. The operation of the base catalysis during the reaction (C) in acetonitrile is a consequence of the decrease of decomposition velocity of the intermediate to products. In con-

TABLE II

Rate Constants k_1 of Reaction (B) in Acetonitrile at 20°C
 $[I]_0 = 5 \cdot 10^{-5}$ mol/l.

Substituted aniline (c, mol/l)	$10^4 k_1$ 1/mol.min	Substituted aniline (c, mol/l)	$10^4 k_1$ 1/mol.min
III (0.3)	3.6	IV (0.6)	24
III (0.7)	3.8	IV (1.0)	22
III (1.0)	3.5 ^a		

^a $[I]_0 = 1 \cdot 10^{-4}$ mol/l.

TABLE III

Rate Constants k_1 and k_{-1}/k_3 Calculated from Eq. (2) for Reaction (C) in Acetonitrile at 20°C
 $[II]_0 = 1 \cdot 10^{-2}$ mol/l.

Substituted aniline	$10k_1$ 1/mol min	k_{-1}/k_3^a	Substituted aniline	$10k_1$ 1/mol min	k_{-1}/k_3^a
III	1.1	0.80	VII	1.4	0.50
III	2.5 ^b	0.90 ^b	V	0.40	0.80
III	5.5 ^c	0.75 ^c	IV	25	0.90
VI	5.0	0.85			

^a Mean error ± 0.15 ; ^b at 40°C; ^c at 80°C.

trast to methanol, acetonitrile has no acid proton and hence cannot facilitate the splitting of the C—F bond by formation of hydrogen bond.

The results obtained cannot, however, be generalized even to other reactions of fluoronitrobenzenes with amines, as it can be seen from the following comparison of our results with the values obtained for the reaction of 4-nitrofluorobenzene with piperidine in the same solvents⁶. In the both solvents the reaction with piperidine is first order in the base and proceeds about 200 times slower in methanol than in acetonitrile. The reasons of this very different behaviour are not yet known to us.

EXPERIMENTAL

Reagents. 2,4-Dinitrochlorobenzene, p.a. (I) (Reanal, Budapest) m.p. 53–54°C. 2,4-Dinitrofluorobenzene p.a. (II) (Lachema, Brno) was redistilled at 151°C/8 Torr. The substituted anilines III–IX (commercial samples) were purified by distillation or crystallization from water. Methanol p.a. (Lachema, Brno) was distilled. Acetonitrile p.a. (Laborchemie, Apolda) was dried and distilled at 80°C (ref.¹²).

Kinetic measurements. In the kinetic experiments the concentration increase of the coloured 2,4-dinitrodiphenylamine derivative formed was followed spectrophotometrically using a VSU-2P apparatus (Zeiss, Jena). The measurements in methanol were carried out by direct analysis of the samples withdrawn at suitable time intervals from the reaction mixture closed in the flasks immersed in a thermostat bath ($\pm 0.2^\circ\text{C}$). In acetonitrile medium $[II]_0$ was about $100\times$ higher and, therefore, 0.1 ml samples were withdrawn by means of a microproportioner MD 100 (Laboratorní přístroje) from the reaction mixture, and after a 250 fold dilution with benzene (whereby the reaction was stopped) the extinction was measured. The experiments at 80°C were carried out in sealed test tubes which were, one by one, removed from the thermostat at definite time intervals, and their content was analyzed after cooling. The rate constant k_A was calculated graphically according to Eq. (3), where E_t and E_∞ are the extinctions measured at a time t and $t = \infty$ (corresponding to six half-lives) respectively.

$$k_A t = 2.303 \log (E_\infty / (E_\infty - E_t)). \quad (3)$$

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