

REACTIVITY OF CYANURIC CHLORIDE AND FLUORIDE  
DURING REACTION WITH *meta*- AND *para*-SUBSTITUTED ANILINES

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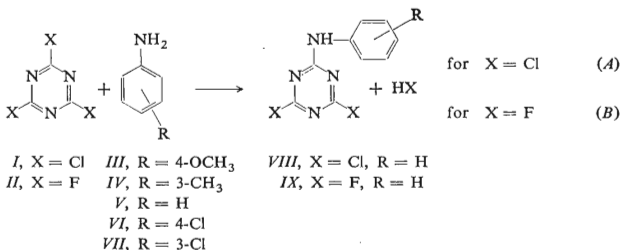
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The reaction of cyanuric fluoride with substituted anilines has been studied in diethyl ether medium. By comparison with the experimental results of the analogous substitution of cyanuric chloride ( $k_F < k_{Cl}$ ;  $\rho_F > \rho_{Cl}$ ) it can be judged that the both reactions differ in the rate-determining step.

Of the symmetrical halogenotriazines cyanuric chloride (*I*) has attracted the greatest attention so far. More recently papers appeared which dealt with preparation<sup>1-6</sup> and reactivity<sup>1,7</sup> of cyanuric fluoride (*II*). The practical use of cyanuric fluoride derivatives was described in the region of herbicides and fungicides<sup>8</sup> as well as reactive dyestuffs<sup>9</sup>. Kinetics of the nucleophilic substitution of cyanuric chloride is dealt with in papers<sup>10-13</sup>.

The aim of this work was to determine the basic kinetic data of the reaction of cyanuric fluoride with a series of substituted anilines *III-VII* and to compare them with analogous data for cyanuric chloride (reactions (A) and (B)).



The diethyl-ether medium was chosen for the measurements, because the substitution of the first fluorine atom can be studied independently under these conditions, 2-anilino-4,6-difluoro-1,3,5-triazine (*IX*) being the reaction product. This compound had already been prepared<sup>8</sup> from equimolar amounts of analogous starting materials *II* and *V* in toluene solution at a temperature  $-10$  to  $+50^\circ\text{C}$ . Cyanuric fluoride reacts with aniline at a molar ratio 1 : 6 in tetrahydro-

furan medium at room temperature to give 2,4,6-trianilino-1,3,5-triazine<sup>1</sup>. Another advantage of ether in the role of solvent would be also that no acid autocatalysis was observed in its solutions in the concentration range used<sup>14</sup>.

TABLE I

Rate Constants of Reaction (A) Obtained from Eq. (5)

[I] 10 <sup>3</sup> mol/l	Subst. aniline (init. conc. 10 <sup>3</sup> mol/l)	<i>t</i> , °C	<i>k</i> · 10 <sup>-5</sup> l/mol h
0.50	V (0.36)	0	30
2.0	V (2.1)	0	33
0.50	V (0.54)	- 5	15
0.50	V (0.52)	-10	7.0
0.52	V (0.52)	-15	4.8
0.50	V (0.45)	-20	3.2
0.50	V (0.80)	-20	3.0
0.60	V (0.20)	-20	2.9
1.0	III (0.75)	-10	30
1.0	IV (0.75)	-10	10.6
1.0	VI (0.75)	-10	0.86
1.0	VII (0.75)	-10	0.50

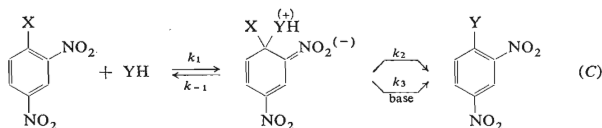
TABLE II

Rate Constants of Reaction (B) Obtained from Eq. (5)

[II] 10 <sup>3</sup> mol/l	Subst. aniline (init. conc. 10 <sup>3</sup> mol/l)	<i>t</i> , °C	<i>k</i> · 10 <sup>-4</sup> l/mol h
1.5	V (1.0)	0	4.2
1.5	V (1.0)	- 5	3.0
4.0	V (0.69)	-10	2.2
2.0	V (0.70)	-10	2.3
1.0	V (0.75)	-10	2.0
2.2	V (0.60)	-10	2.4
2.2	V (1.0)	-10	2.0
2.2	V (2.6)	-10	2.2
1.5	V (1.0)	-15	1.46
1.0	III (0.55)	-10	14.4
1.0	IV (0.78)	-10	3.9
1.0	VI (0.75)	-10	0.30
1.0	VII (0.75)	-10	0.06

## RESULTS AND DISCUSSION

From the results of our kinetic measurements it follows that both the reactions (A) and (B) are first order in the both reaction components during substitution of halogen by aniline (Tables I, II). It was also remarkable to find that cyanuric fluoride reacted more slowly than cyanuric chloride in the medium chosen (diethyl ether). The ratio of the reaction rates was 30 for aniline at  $-10^{\circ}\text{C}$ . A higher reactivity of a chloro derivative as compared to the respective fluoro derivative has already been observed during aromatic nucleophilic substitution: *e.g.*  $k_{\text{Cl}}/k_{\text{F}} = 1.5$  and 15 for the reactions of the 2,4-dinitrohalogenobenzenes with N-methylaniline in ethanol and nitrobenzene respectively<sup>15</sup>, and  $k_{\text{Cl}}/k_{\text{F}} = 17$  for the reaction of the same substrates with potassium iodide in acetone<sup>16</sup>. A change of the rate-determining step in Scheme (C) is given as the reason<sup>12</sup>.



YH = nucleophile

Eq. (1) holds generally for the bimolecular rate constant  $k_{\text{A}}$  of the reactions (A) and (B), *i.e.* nucleophilic aromatic substitutions proceeding by an addition-elimination mechanism (which was proved by finding the respective intermediate in the reactions of triazine derivatives, too<sup>17</sup>).

$$v/([\text{RX}][\text{ArNH}_2]) = k_{\text{A}} = (k_1 k_2 + k_1 k_3 [\text{ArNH}_2]) / (k_{-1} + k_2 + k_3 [\text{ArNH}_2]) \quad (1)$$

As no basic catalysis by amine was found in the case of the reactions (A) and (B) studied, the Eq. (1) can be simplified to Eq. (2):

$$k_{\text{A}} = k_1 k_2 / (k_{-1} + k_2). \quad (2)$$

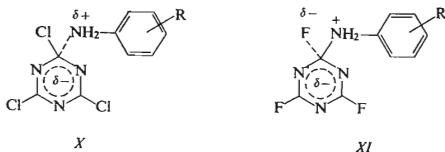
If  $k_{-1} \ll k_2$ , as it is the case with nucleophilic substitutions of chloro derivatives (the reaction (A) in our case), the constant measured will be

$$k_{\text{A}} = k_1. \quad (3)$$

In the case of the fluoro derivative we can presume that the reaction (B) proceeds either by the same mechanism ( $k_{-1} \ll k_2$ , *i.e.* Eq. (3) holds), or by a mechanism having  $k_2 \ll k_{-1}$  for which Eq. (4) holds.

$$k_A = k_1 k_2 / k_{-1} \quad (4)$$

A lower reactivity of cyanuric fluoride as compared to cyanuric chloride indicates<sup>12</sup> that Eq. (4) holds for the reaction (B). This view is also supported by the values of the Hammett  $\rho$  constants found in the series of substituted anilines III–VII. In the case of the reaction (A) having the first reaction step rate-determining (*i.e.* the substituent R in aniline molecule exerts its influence only until the formation of the activated complex X leading to the intermediate formation) the  $\rho_A$  constant found has a value of  $-2.5$ . (According to Eq. (3)  $\rho_A = \rho_1$ ). In the case of the reaction (B) the substituent R affects not only the intermediate formation but also its decomposition into products, *i.e.* it operates until the formation of the second activated complex XI.



According to Eq. (4)  $\rho_B = \rho_1 + \rho_2 - \rho_{-1}$ . If we assume  $\rho_1 = -2.5$  (found for the reaction (A)), a negative  $\rho_2$  and a positive  $\rho_{-1}$ , we can accept the higher experimental value  $\rho_B = -3.8$ ,  $\rho_2$  and  $\rho_{-1}$  being approximately  $-0.3$  and  $1$  respectively. A large difference in  $\rho$  values caused by a change of the rate-determining step was observed during aromatic nucleophilic substitution<sup>18</sup> and analogous electrophilic substitution, too<sup>19</sup>.

## EXPERIMENTAL

**Reagents.** Cyanuric chloride (I) (VCHZ-Synthesia) was purified by crystallization from light petroleum, m.p.  $142-143^\circ\text{C}$ . Cyanuric fluoride (II) was prepared from the chloro derivative (I) and  $\text{SbF}_3\text{Cl}_2$  (ref.<sup>2</sup>), b.p.  $73-74^\circ\text{C}$ . The substituted anilines III–VII, usual commercial samples, were purified by distillation or crystallization. 2-Anilino-4,6-dichloro-1,3,5-triazine (VIII) was prepared from cyanuric chloride and aniline<sup>20</sup>, m.p.  $134-135^\circ\text{C}$ . 2-Anilino-4,6-difluoro-1,3,5-triazine (IX):  $0.67$  g ( $0.05$  mol) cyanuric fluoride was dissolved in  $50$  ml dry ether, cooled at  $-10^\circ\text{C}$ , and a solution of  $0.93$  g ( $0.01$  mol) aniline in  $50$  ml ether was added drop by drop thereto. The aniline hydrofluoride precipitated was filtered off, ether was distilled from the filtrate under reduced pressure, and the residue was purified by vacuum sublimation. Yield  $0.9$  g ( $88\%$ ), m.p.  $145-147^\circ\text{C}$  (ref.<sup>8</sup>  $143-146^\circ\text{C}$ ). Diethyl ether p.a. (Lachema, Brno) was dried over sodium and twice distilled.

**Kinetic measurements.** The course of the reactions (A) and (B) was followed by measuring the concentration changes of amines III–VII. The spectrophotometric analytic method using the rapid reaction of anilines with *p*-dimethylaminobenzaldehyde (to give coloured Schiff's bases)

was described in a previous report<sup>10</sup>, where the course of the proper kinetic measurement was given, too. The measurements of the fluoro derivative *II* had to be carried out in perfectly anhydrous media to prevent its eventual hydrolysis. It was proved that the reactions studied follow the mechanism (*A*) or (*B*): the reaction products *VIII* or *IX* were isolated under the conditions of kinetic experiments and identified by their melting points. The values of rate constants were calculated from the integrated form (6) of the kinetic equation (5):

$$dx/dt = k(a - x)(b - 2x), \quad (5)$$

$$k = \frac{2.303}{t(b - 2a)} \log \frac{a(b - 2x)}{b(a - x)}, \quad (6)$$

where *k* is the rate constant to be found, *a* and *b* are the initial concentrations of compound *I* (or *II*) and aniline respectively, and *x* stands for the amount of products at a time *t*. The experimental error of the rate constants determination was 7 and 10% for the reactions (*A*) and (*B*) respectively.

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