

## 2,4-이니트로할로벤젠과 치환된 아닐린의 반응속도에 대한 용매효과 (제 3 보)

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## Influence of Solvents on Rates of Reactions of 2,4-Dinitro Substituted Halobenzenes with Substituted Anilines (III)

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**요 약.** 2,4-Dinitrohalo (F, Br) benzene 과 파라치환아닐린간의 반응속도를 아세토니트릴-메탄올 혼합용매 하에서 측정하였다. 2,4-Dinitrobromobenzene 과 치환아닐린간의 반응에서 메탄올은 친핵촉매 현상만을 보였으며, 2,4-dinitrofluorobenzene 과 치환아닐린간의 반응에서는 메탄올은 양쪽성(친핵 및 친전자)촉매현상을 보였다. 메탄올에 의한 친핵촉매현상은 아마도 천이 상태에서 알코올기의 수소와 이탈기의 플루오르사이의 수소결합에 의해 설명될 수 있으며 친전자촉매현상은 알코올기의 산소와 아닐린의 아민기 수소사이의 수소결합에 기인되는 것임을 알았다.

**ABSTRACT.** Rates of reactions of 2,4-dinitrofluorobenzene and 2,4-dinitrobromobenzene with para substituted anilines in acetonitrile-methanol binary mixtures have been measured. It has been shown that methanol acts as nucleophilic catalyst upon reaction of 2,4-dinitrobromobenzene with anilines and as bifunctional catalyst upon reaction of 2,4-dinitrofluorobenzene with anilines. The electrophilic catalysis by methanol probably consists of formation of hydrogen bond in the transition state between alcoholic hydrogen and leaving group, fluorine. Nucleophilic catalysis by methanol may be ascribed to formation of hydrogen bond between alcoholic oxygen and amine hydrogen in the transition state.

### 1. INTRODUCTION

Recently, increasing attention has been focussed on isodielectric solvents in an attempt to

understand better the nature of specific solvent effects. Rates of reactions between polar molecules are quite insensitive to the change from dipolar aprotic to protic solvent of the same dielectric constant when there exists only electrostatic interactions between reactants (or tran-

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sition states) and solvents.<sup>1</sup> But when there exists specific solvation between them, the rate is remarkably changed in the same solvent transfer.<sup>2</sup>

In order to clarify the mechanism of specific solvation for the reaction between polar molecules, 2,4-dinitrohalo (F, Br) benzenes and anilines (*p*-toluidine, aniline, *p*-chloroaniline), isodielectric solvent mixtures, acetonitrile (dipolar aprotic,  $D=36.02$ )—methanol (protic,  $D=32.63$ ), are used in connection with the previous papers.<sup>3,4</sup>

## 2. EXPERIMENTAL

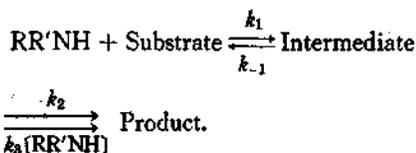
**1. Materials.** 2,4-Dinitrofluorobenzene was purified by distillation under reduced pressure. 2,4-Dinitrobromobenzene was prepared from bromobenzene by dinitration and the final product had m. p  $72.5\sim 73^\circ\text{C}$  (lit.<sup>5</sup>  $72.5^\circ\text{C}$ ). Methanol, acetonitrile, *p*-toluidine, aniline and *p*-chloroaniline were purified as in the previous work.<sup>3</sup>

**2. Rate Measurements.** Kinetic measurements were done by conductivity method as described before.<sup>3</sup> In the case of experiments between 2,4-dinitrofluorobenzene and anilines, the initial concentration of substrate was  $2.5\times 10^{-4}\sim 6.9\times 10^{-4}$  M and base  $8.3\times 10^{-3}\sim 1.6\times 10^{-1}$  M. In the case of reactions between 2,4-dinitrobromobenzene and anilines, the initial concentration of substrate amounted to  $1\times 10^{-3}\sim 5\times 10^{-3}$  M and salt  $9\times 10^{-2}\sim 4.2\times 10^{-1}$  M.

**3. Calculations.** CNDO/2 method was used in calculations and the standard values of the bond distances and bond angles were adopted.<sup>6</sup>

## 3. RESULTS AND DISCUSSION

For the nitro activated aromatic bimolecular nucleophilic substitution reactions when either primary or secondary amines are the nucleophiles the accepted mechanism is as follows:



Two criteria can be used to determine whether the bond formation step or the bond breaking step is rate determining. The first is a kinetic criterion. If the decomposition of the intermediate is rate determining, base catalysis is observed and the observed second order rate constant increases with the increase in the concentration of base. If the formation of the intermediate is rate determining, then the reaction is not base catalyzed.

The second criterion is reactivity ratios. If the rate constant sequence  $\text{F} \gg \text{Cl}, \text{Br}, \text{I}$  is observed, then breaking of the carbon-halogen atom is not involved in the rate determining step.

In a point of view of kinetic criterion, we found that the second order rate constants for the reaction between 2,4-dinitrobromobenzene and anilines are nearly independent on the concentration of anilines in all the solvent system studied, thus the bond formation is rate determining in this reaction system as in the case of reactions of 2,4-dinitrochlorobenzene<sup>3</sup> and 2,4-dinitroiodobenzene<sup>4</sup> with anilines. In the reactions between 2,4-dinitrofluorobenzene and anilines, the second order rate constants are not affected by changing the concentration of anilines in methanol rich solvent (<50 vol. % of methanol; see Table 1) but as it becomes acetonitrile rich (>35 vol. % of methanol\*) the reaction is base catalyzed in which the rate constants increase with increasing aniline concentration. The reactions of 2,4-dinitrofluoroben-

\*Although we failed to obtain the exact rate constant near 35% (vol) of methanol because of nonlinearities in Guggenheim plot, we investigated the increasing tendencies of the rate constants when the concentration of aniline increases.

Table 1. Reaction rate constants of 2,4-dinitrofluorobenzene and *p*-toluidine in (a) pure methanol and in (b) 50 vol. % CH<sub>3</sub>CN-CH<sub>3</sub>OH mixture at 25 °C.

	2,4-Dinitrofluorobenzene (mole/l)	<i>p</i> -Toluidine (mole/l)	$k_1$ (sec <sup>-1</sup> )	$k_2$ (l/mole·sec)
(a) Pure methanol	$2.98 \times 10^{-4}$	$1.25 \times 10^{-2}$	$3.94 \times 10^{-4}$	$3.15 \times 10^{-2}$
	$2.98 \times 10^{-4}$	$2.53 \times 10^{-2}$	$7.39 \times 10^{-4}$	$2.92 \times 10^{-2}$
	$2.98 \times 10^{-4}$	$3.65 \times 10^{-2}$	$1.08 \times 10^{-3}$	$2.96 \times 10^{-2}$
	$2.98 \times 10^{-4}$	$4.22 \times 10^{-2}$	$1.30 \times 10^{-3}$	$3.08 \times 10^{-2}$
	$3.47 \times 10^{-4}$	$2.28 \times 10^{-2}$	$7.08 \times 10^{-4}$	$3.11 \times 10^{-2}$
	$3.47 \times 10^{-4}$	$4.92 \times 10^{-2}$	$1.43 \times 10^{-3}$	$2.91 \times 10^{-2}$
			mean: $3.02 \times 10^{-2}$	
(b) 50 Vol. % CH <sub>3</sub> CN-CH <sub>3</sub> OH	$3.27 \times 10^{-4}$	$8.37 \times 10^{-3}$	$7.76 \times 10^{-5}$	$9.26 \times 10^{-3}$
	$3.27 \times 10^{-4}$	$1.45 \times 10^{-2}$	$1.36 \times 10^{-4}$	$9.32 \times 10^{-3}$
	$3.27 \times 10^{-4}$	$1.78 \times 10^{-2}$	$1.63 \times 10^{-4}$	$9.14 \times 10^{-3}$
	$3.27 \times 10^{-4}$	$4.14 \times 10^{-2}$	$3.92 \times 10^{-4}$	$9.47 \times 10^{-3}$
	$3.27 \times 10^{-4}$	$5.73 \times 10^{-2}$	$5.32 \times 10^{-4}$	$9.29 \times 10^{-3}$
			mean: $9.30 \times 10^{-3}$	

Table 2. Kinetics of the reactions of 2,4-dinitrofluorobenzene with anilines in CH<sub>3</sub>CN-CH<sub>3</sub>OH mixed solvents.

Nucleophile	Vol. % of MeOH	Temp. (°C)	$k_2$ (l/mole·sec)	$\Delta H^\ddagger$ (kcal)	$-\Delta S^\ddagger$ (e. u.)
<i>p</i> -Toluidine	100	50	$8.22 \times 10^{-2}$	6.91	42.3
		40	$5.56 \times 10^{-2}$		
		25	$3.02 \times 10^{-2}$		
	75	50	$3.79 \times 10^{-2}$	4.71	50.6
		40	$2.85 \times 10^{-2}$		
		25	$1.85 \times 10^{-2}$		
	50	50	$1.83 \times 10^{-2}$	4.33	53.3
		40	$1.39 \times 10^{-2}$		
		25	$9.30 \times 10^{-3}$		
Aniline	100	50	$1.89 \times 10^{-2}$	6.02	48.0
		40	$1.35 \times 10^{-2}$		
		25	$7.88 \times 10^{-3}$		
	75	50	$8.57 \times 10^{-3}$	4.99	52.7
		40	$6.32 \times 10^{-3}$		
		25	$4.01 \times 10^{-3}$		
	50	50	$4.10 \times 10^{-3}$	4.77	54.9
		40	$3.05 \times 10^{-3}$		
		25	$1.97 \times 10^{-3}$		
<i>p</i> -Chloroaniline	100	50	$2.82 \times 10^{-3}$	8.78	43.2
		40	$1.72 \times 10^{-3}$		
		25	$8.03 \times 10^{-4}$		
	75	50	$1.27 \times 10^{-3}$	6.60	51.5
		40	$8.44 \times 10^{-4}$		
		25	$4.70 \times 10^{-4}$		

	50	50	$5.45 \times 10^{-4}$	5.02	58.1
		40	$4.03 \times 10^{-4}$		
		25	$2.55 \times 10^{-4}$		

Table 3. Kinetics of the reactions of 2,4-dinitrobromobenzene with anilines in CH<sub>3</sub>CN-CH<sub>3</sub>OH mixed solvents.

Nucleophile	Vol. % of MeOH	Temp. (°C)	$k$ (l/mole·sec)	$\Delta H^\ddagger$ (kcal)	$-\Delta S^\ddagger$ (e. u.)
<i>p</i> -Toluidine	100	50	$1.03 \times 10^{-4}$	10.5	39.9
		40	$5.92 \times 10^{-4}$		
	75	50	$7.04 \times 10^{-4}$	11.5	37.5
		40	$3.85 \times 10^{-4}$		
	50	50	$5.39 \times 10^{-4}$	11.6	37.7
		40	$2.93 \times 10^{-4}$		
	14.3	50	$3.36 \times 10^{-4}$	11.5	39.1
		40	$1.84 \times 10^{-4}$		
0	50	50	$1.88 \times 10^{-4}$	10.7	42.7
		40	$1.07 \times 10^{-4}$		
	100	50	$3.28 \times 10^{-4}$	10.2	43.0
		40	$1.91 \times 10^{-4}$		
75	50	$2.30 \times 10^{-4}$	10.1	44.2	
	40	$1.35 \times 10^{-4}$			
50	50	$1.61 \times 10^{-4}$	11.1	41.7	
	40	$8.98 \times 10^{-5}$			
14.3	50	$1.01 \times 10^{-4}$	11.2	42.3	
	40	$5.60 \times 10^{-5}$			
0	50	$4.36 \times 10^{-5}$	10.4	46.5	
	40	$2.52 \times 10^{-5}$			
<i>p</i> -Chloroaniline	100	50	$8.42 \times 10^{-5}$	12.5	38.8
		40	$4.39 \times 10^{-5}$		
	75	50	$6.42 \times 10^{-5}$	11.4	42.5
		40	$3.52 \times 10^{-5}$		
	50	50	$4.42 \times 10^{-5}$	12.9	38.9
		40	$2.26 \times 10^{-5}$		
	14.3	50	$1.96 \times 10^{-5}$	12.5	41.6
		40	$1.02 \times 10^{-5}$		
0	50	$1.53 \times 10^{-5}$	13.2	39.8	
	40	$7.68 \times 10^{-6}$			

zene with anilines in a medium of acetonitrile have been studied spectrophotometrically by Kavalek and his coworkers<sup>7</sup> and they found that the reaction is base-catalyzed. It means that the bond breaking step is rate determining in acetonitrile rich solvent while the bond formation step is rate determining in methanol rich

solvent.

Tables 2~3 show the kinetic results for the reactions of 2,4-dinitrofluorobenzene and 2,4-dinitrobromobenzene with anilines. The substituent effect of anilines (see also Fig. 2) shows that the bond formation step is important since the electron donating group enhances while

Table 4. Rate ratios,  $k_X/k_I$  ( $X=F, Br, Cl$ ) at 50 °C. F=2,4-Dinitrofluorobenzene, Br=2,4-dinitrobromobenzene, Cl=2,4-dinitrochlorobenzene, I=2,4-dinitroiodobenzene.

Nucleophile	Substrate	Vol. % of MeOH				
		100	75	50	14.3	0
<i>p</i> -Toluidine	F	212	129	88	—	—
	Br	2.7	2.4	2.6	2.5	2.3
	Cl	1.7	1.5	1.6	1.6	2.2
	I	1	1	1	1	1
Aniline	F	160	109	60	—	—
	Br	2.8	2.9	2.4	3.2	1.6
	Cl	1.9	2.1	1.4	1.8	1.3
	I	1	1	1	1	1
<i>p</i> -Chloroaniline	F	79	51	32	—	—
	Br	2.4	2.5	2.7	1.5	0.9
	Cl	1.8	1.9	2.1	2.0	0.5
	I	1	1	1	1	1

electron withdrawing group reduces the rate. But in the reactions between 2,4-dinitrofluorobenzene and anilines in acetonitrile,<sup>7</sup> electron donating group reduces while electron withdrawing group enhances the rate which suggests that the reaction mechanism changes as the solvent is changed from methanol to acetonitrile.

Table 4 shows the reactivity ratios of 2,4-dinitrofluorobenzene, 2,4-dinitrobromobenzene and 2,4-dinitrochlorobenzene in comparison with 2,4-dinitroiodobenzene. The sequence of rate ratios is  $F \gg Br > Cl > I$  in methanol rich solvents. It can be easily expected from the rate decreasing tendencies of 2,4-dinitrofluorobenzene that the relative reactivities of 2,4-dinitrofluorobenzene becomes rapidly smaller as the solvent system changes from methanol rich solvents to acetonitrile rich solvents. Thus from the second criterion the bond formation step is rate determining in methanol rich solvents while the bond breaking step is rate determining in acetonitrile rich solvents for the reactions between 2,4-dinitrofluorobenzene and anilines. This conclusion is in accordance with the kinetic crite-

tion.

The order of reactivities  $F \gg Br > Cl > I$  when the bond formation step is rate determining, can be explained qualitatively in terms of HSAB principle.<sup>8</sup> Aniline is known as borderline base, so that both the acidity (hardness) and polarizability (softness) of the reaction center of 2,4-dinitrohalobenzenes are important factors for aniline displacement reaction on 2,4-dinitrohalobenzenes. The order of hardness is  $F \gg Cl > Br > I$  while the order of softness,  $I > Br > Cl > F$ . So the order of reactivity  $F \gg Br > Cl > I$  seems the result of compromising with both acidity and polarizability. This conclusion may be supported from Bunnett's data<sup>9</sup> on the reactions of 2,4-dinitrohalobenzenes with methoxide and thiophenoxide ion in a medium of methanol. The order of reactivity of methoxide (hard base) is  $F \gg Cl > Br > I$  while that of thiophenoxide (soft base) is  $F > I \sim Br > Cl$ .

Fig. 1 shows the CNDO/2 MO quantities. Without considering the solvent effects in generalized perturbation theory,<sup>10</sup> if the covalent term determines the reactivity (orbital controlled

F	—	<sup>(1)</sup> $\epsilon^{\text{LU}}=0.493$	<sup>(2)</sup> $f_c^{\text{LU}}=0.405$	<sup>(3)</sup> $Z_c=+0.270$
Cl	—	$\epsilon^{\text{LU}}=0.0544$	$f_c^{\text{LU}}=0.444$	$Z_c=+0.102$
<i>p</i> -CH <sub>3</sub>	—	$\epsilon^{\text{HO}}=-11.2$	$f_N^{\text{HO}}=0.596$	$Z_N=-0.266$
<i>p</i> -Cl	—	$\epsilon^{\text{HO}}=-11.5$	$f_N^{\text{HO}}=0.481$	$Z_N=-0.263$
<i>p</i> -H	—	$\epsilon^{\text{HO}}=-11.7$	$f_N^{\text{HO}}=0.751$	$Z_N=-0.266$

Fig. 1. MO quantities of 2,4-dinitrohalo (F, Cl) benzenes and *para* substituted (*p*-CH<sub>3</sub>, *p*-Cl, *p*-H) anilines.

- (1)  $\epsilon^{\text{LU}}$ ,  $\epsilon^{\text{HO}}$ : energy levels of LUMO, HOMO (eV)  
 (2)  $f$ : frontier electron density of the reaction center.  
 (3)  $Z$ : charge density of the reaction center.

reaction) the sequence of rate may be Cl > F because not only the energy of LUMO of 2,4-dinitrofluorobenzene is higher than that of 2,4-dinitrochlorobenzene but also the frontier electron density of 2,4-dinitrofluorobenzene is smaller than that of 2,4-dinitrochlorobenzene. If the electrostatic term determines the reactivity (charge controlled reaction), the order of rates, F > Cl and *p*-toluidine > aniline > *p*-chloroaniline, is predictable from the charge density of reaction sites which is consistent with the experimental results. So the rate constant sequence F > other halogens seems that the reaction is charge controlled.

Fig. 2. shows the correlation between  $\log k$  and mole fraction of methanol for the reactions of 2,4-dinitrohalobenzenes with anilines. The increasing tendencies of rate constants of 2,4-dinitrofluorobenzene are nearly the same as those of 2,4-dinitrochlorobenzene and 2,4-dinitroiodobenzene when the solvent is varied from acetonitrile to methanol. But the curve of 2,4-dinitrofluorobenzene is much steeper relative to other 2,4-dinitrohalobenzenes in methanol rich solvents. We have already pointed out<sup>3,4</sup> that such an increase in reaction rates by methanol is due to the specific solvent effect of methanol, and also alcohols can fulfill the role of bifunctional catalysts, nucleophilic and electrophilic, while acetonitrile can act neither role. The similarity of the slope of  $\log k$  vs.  $X_{\text{MeOH}}$  in

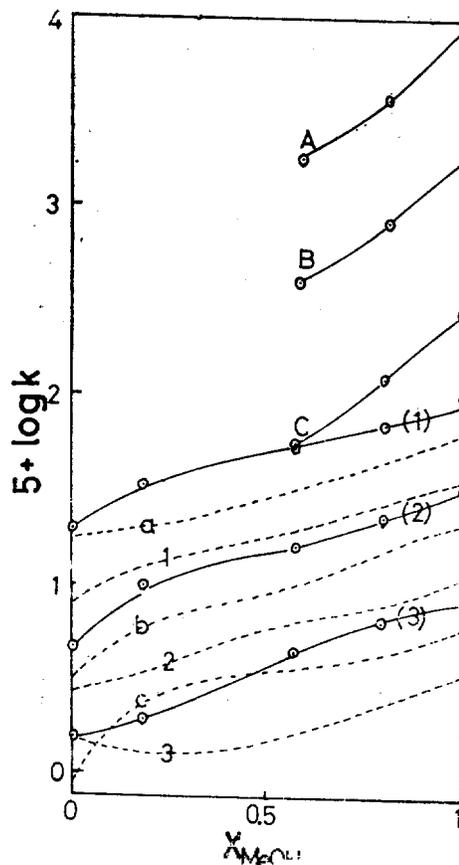
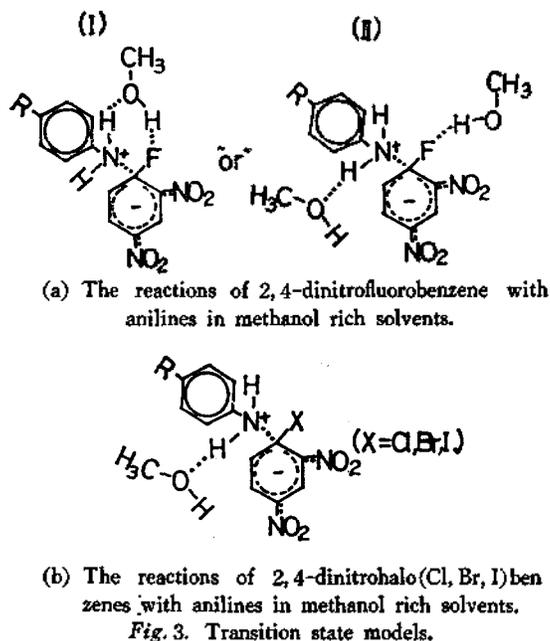


Fig. 2. Dependence of  $\log k$  on mole fraction of methanol in  $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$  binary mixtures in reactions of 2,4-dinitrofluorobenzene with A; *p*-toluidine, B; aniline and C; *p*-chloroaniline, and of 2,4-dinitrochlorobenzene with (1) *p*-toluidine, (2) aniline and (3) *p*-chloroaniline and of 2,4-dinitroiodobenzene<sup>3</sup> with a; *p*-toluidine, b; aniline and c; *p*-chloroaniline and of 2,4-dinitroiodobenzene<sup>4</sup> with 1; *p*-toluidine, 2; aniline and 3; *p*-chloroaniline at 50 °C.

2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene and 2,4-dinitroiodobenzene means that the specific solvent effect of methanol is only due to the nucleophilic catalyst of methanol which can be explained in terms of hydrogen bonding between the hydrogen atom of aniline and alcoholic oxygen atom of methanol by stabilization of the transition state in the rate determining step that results in rate increase when the solvent system changes from acetonitrile to methanol



as mentioned before<sup>4</sup> (see Fig. 3).

The electronegativity of fluorine atom is the largest which means that the hydrogen bonding ability is the largest. The negative charge of fluorine atom in the bond formation step may be larger than that in the initial state and smaller than that in the bonding breaking step. In methanol rich solvent the splitting of the C-F bond can be readily facilitated by formation of hydrogen bond between fluorine atom and alcoholic hydrogen atom so the bond formation step is rate determining. But in acetonitrile rich solvent the absence of acid proton of acetonitrile makes difficult the breaking of the strong C-F bond, so the bond breaking step is rate determining and the reaction is base catalyzed where the leaving group mobility depends on the acid strength of conjugate acid of amine,  $RR'NH_2^+$ . The increase of basicity of nucleophile (*p*-toluidine > aniline > *p*-chloroaniline) reduces the acid strength of conjugate acid of nucleophile, so the reaction rates decrease in the order of *p*-chloroaniline > aniline > *p*-toluidine.<sup>7</sup>

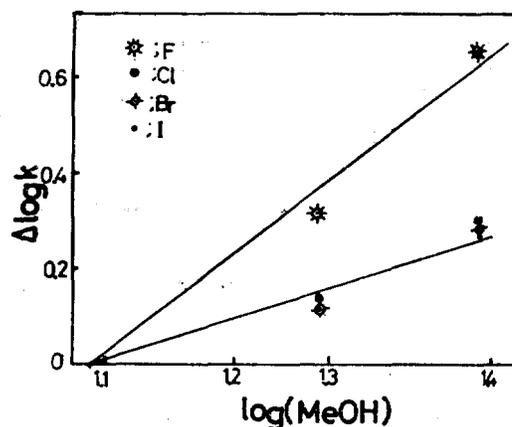


Fig. 4. Reaction order with respect to MeOH for the reaction of 2,4-dinitrohalo(F, Cl, Br, I) benzenes with aniline at 50°C.

A steep slope of 2,4-dinitrofluorobenzene in methanol rich solvents suggests that the specific solvent effect of methanol is different from that of other 2,4-dinitrohalobenzenes. It can be explained by way of bifunctional catalysis of methanol, that is, nucleophilic catalysis of alcoholic oxygen with amine hydrogen and electrophilic catalysis of alcoholic hydrogen with fluorine atom in the rate determining step as shown in Fig. 3.

Fig. 4. shows the correlation between  $\log k$  vs.  $\log (\text{MeOH})$  in methanol rich solvents. The slope is close to 2 for 2,4-dinitrofluorobenzene and 1 for 2,4-dinitrohalo(Br, Cl, I) benzenes. These results probably indicate that two methanol molecules participate in the rate determining step in the reaction of 2,4-dinitrofluorobenzene with anilines and one methanol molecule in the reaction of 2,4-dinitrohalo(Br, Cl, I) benzenes with anilines in methanol rich solvents. Thus in the reactions of 2,4-dinitrofluorobenzene transition state (II) seems more favorable than (I) in Fig. 3.

The activation enthalpy values for the reaction of 2,4-dinitrofluorobenzene with anilines are generally much smaller than those for the re-

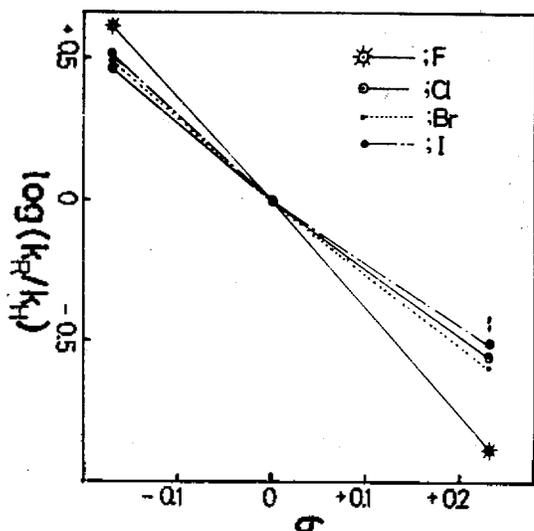


Fig. 5. The plots of  $\log(k_R/k_H)$  vs.  $\sigma$  for the reactions of 2,4-dinitrohalo (F, Cl, Br, I) benzenes with substituted anilines ( $R=p\text{-CH}_3, p\text{-H}, p\text{-Cl}$ ) in pure methanol at  $50^\circ\text{C}$ .

actions of 2,4-dinitrohalo(Br,  $\text{Cl}^3$ ,  $\text{I}^4$ )benzenes with anilines, while the negative activation entropy values of 2,4-dinitrofluorobenzene are larger than those of 2,4-dinitrohalo(Br,  $\text{Cl}^3$ ,  $\text{I}^4$ ) benzenes. The activation enthalpy and entropy values of 2,4-dinitrohalo(Br, Cl, I)benzenes have comparable magnitudes. These are in agreement with our proposed mechanism of rate-determining bond-formation since in a charge controlled reaction 2,4-dinitrofluorobenzene will be the easiest to approach and hence the greatest in reaction rate.

Fig. 5. shows the Hammett plots. The  $\rho$  values obtained in pure methanol are approximately -3.8 for 2,4-dinitrofluorobenzene, -2.7 for 2,4-dinitrobromobenzene, -2.6 for 2,4-dinitrochlorobenzene<sup>3</sup> and -2.6 for 2,4-dinitroiodobenzene<sup>4</sup>. The substituent effect of aniline is largest in 2,4-dinitrofluorobenzene and is nearly

the same in other 2,4-dinitrohalobenzenes. This is again in accord with the  $S_N$ -addition mechanism proposed since the extent of bond formation will be the greatest for 2,4-dinitrofluorobenzene and hence the substituent effect will be the largest. But going to acetonitrile rich solvent, the Hammett plots become concave in all substrates.

#### ACKNOWLEDGEMENT

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