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(Journal of the Korean Chemical Society)
Vol 21, No. 2, 1977
Printed in Republic of Korea

2, 4-이니트로 할로벤젠과 치환된 아닐린의 반응속도에 대한 용매효과 (제 1 보)

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(1977. 1. 22 접수)

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

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(Received Jan. 22, 1977)

요 약. 2,4-이니르로 염화벤젠과 *p*-톨루이딘, 아닐린 및 *p*-염화아닐린간의 반응속도론적인 연구를 메탄올-아세토니트릴 혼합용매에서 실시하였다. 알코올의 수소에 의한 특수용매화로 실험결과를 해석하였으며, 용매의 변화에 따라 반응메카니즘이 변함을 알았다.

ABSTRACT. Kinetic studies on the rates of reactions of 2, 4-dinitrochlorobenzene with *p*-toluidine, aniline and *p*-chloroaniline in CH_3CH-CH_3OH binary solvent mixtures have been carried out. The experimental results have been explained in terms of the specific solvation by alcoholic hydrogen. It has been shown that the bond breaking step is rate determining in the solvent system studied and the energy barrier is getting low as the solvent changes from acetonitrile to methanol.

1. INTRODUCTION

The reactions of nitro activated halobenzenes with nucleophiles in various solvents have been studied extensively.

According to the concept of Hughes and Ingold,[1] an increase in polarity of the medium must increase rates of those reactions for which a larger charge seperation occurs in the activated state than in the initial state. Therefore in the case of reactions of halosubstituted benzenes with neutral bases, it is natural to expect an increase in rate constants upon going from nonpolar solvent to polar protic and dipolar aprotic solvent. In other words, for reactions of neutral or polar molecules in the presense of only electrostatic interaction between the reagent and solvent, log k *vs.* Kirkwood function shows linear correlation. Parker *et al.*[2] have studied the solvent effects on the reaction between aromatic halides and anionic nucleophiles.

According to Parker *et al.*, the solvation of anions in initial state and also in transition state is the most important factor in determining reactivities.

There is no doubt that it is very dangerous to conclude the reaction mechanism and the reactivities without the discussion of solvent effects.

In this work kinetic studies for the reaction

between 2, 4-dinitrochlorobenzene and *p*-toluidine, aniline, *p*-chloroaniline in methanol-acetonitrile binary solvents have been made in order to clarify the mechanism of this reaction.

2. EXPERIMENTAL

Materials. 2, 4-Dinitrochlorobenzene and p-chloroaniline were purified by recrystallization from ethanol and had m. p 51~52 °C and 70~71 °C, respectively. *p*-Toluidine was recrystallized from petroleum ether, had m. p 43~44 °C. Aniline was shaken over KOH and then distilled under reduced pressure. Mg (10g) and iodine (5g) were dissolved in AnalaR methanol (2*l*) which was then refluxed for half an hour and distilled fractionally. Acetonitrile was shaken over KOH, dried with P_2O_5 and then distilled in the fractional distillation column.

Kinetic Procedures. For the the measurement of rate, conductivity method was adopted. Conductance was measured by Leeds and Northrup 4959 electrolytic conductivity bridge. Adjusting the concentration of the salt to about a hundred fold greater than that of the substrate, pseudou-first order rate constant was obtained by the Guggenheim method.[3] Initial concentrations of 2, 4-dinitrochlorobenzene amounted to 0. 0005 ~0. 002 *M* and substituted anilines, 0. 05~0. 2*M*.

3. RESULTS AND DISCUSSION

The rate constants were obtained from the plot of ln $(\lambda_{t+\Delta}-\lambda_t)$ *vs.* *t*. Guggenheim plot in this work showed satisfactory linearities. The typical plot is shown in *Fig.* 1.

The second order rate constants, summarized in *Table* 1, for the reaction in 50 vol. % CH_3CN—CH_3OH mixture at 50 °C, maintaining the 2, 4-dinitrochlorobenzene concentration at 0. 00165 ~ 0. 00170 *M* and varying the *p*-toluidine concentration from 0. 065 to 0. 25 *M*, are nearly independent of the *p*-toluidine concentrations within the accuracy of our measurements.

Base catalysis has been found with many reactions between amines and nitro-activated halobenzenes,[4] that is, the second order rate

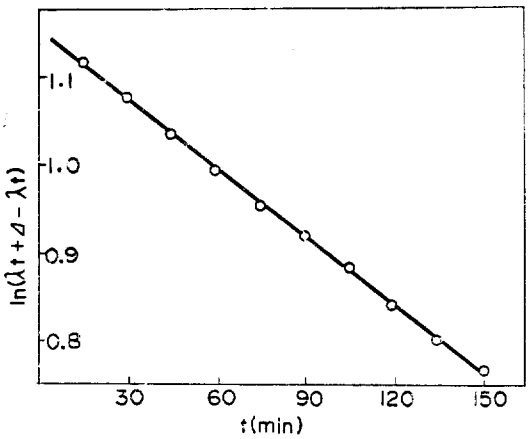

Fig. 1. First order plot for the rate of reaction of *p*-toluidine and 2, 4-dinitrochlorobenzene in 50 vol. % CH_3CN—CH3OH mixture at 50 °C. [Substrate] $=1.65\times10^{-3}M$, [Salt] $=1.31\times10^{-1}M$, $k_1=4.45\times10^{-5}$ sec^{-1}, $k_2=3.40\times10^{-4}$ l/mole·sec.

Table 1. Reaction Rate Constants of 2, 4-dinitrochlorobenzene and *p*-toluidine in 50 vol. % CH_3CN-CH_3OH mixture at 50 °C.

2, 4-Dinitrochlorobenzene (mole/*l*)	*p*-Toluidine (mole/*l*)	$k_1\times10^5$ (sec^{-1})	$k_2\times10^4$ (*l*/mole·sec)
1.65×10^{-3}	0. 0655	2. 18	3. 33
1.65×10^{-3}	0. 133	4. 45	3. 40
1.69×10^{-3}	0. 188	6. 02	3. 20
1.70×10^{-3}	0. 259	8. 16	3. 15
			av. 3. 27

Table 2. Kinetics of the reactions of 2, 4-dinitrochlorobenzene with *p*-toluidine in CH_3CN—CH_3OH mixed solvents. Accuracy of kinetic measurements is ±5 % relative units.

Vol. % of MeOH(D)*	Temp. (°C)	k (l/mole·sec)	$\Delta H^{\neq}$ (kcal)	$-\Delta S^{\neq}$ (e. u.)
0	30	6.17×10^{-5}		
(36. 02)	40	1.03×10^{-4}		
	50	1.74×10^{-4}	9. 5	46. 5
6. 25	30	6.42×10^{-5}		
(36. 01)	40	1.11×10^{-4}		
	50	1.78×10^{-4}	9. 7	45. 9
14. 3	30	6.53×10^{-5}		
(35. 52)	40	1.17×10^{-4}		
	50	2.16×10^{-4}	11. 0	41. 5
25	30	6.91×10^{-5}		
(35. 15)	40	1.29×10^{-4}		
	50	2.35×10^{-4}	11. 1	41. 7
33. 3	30	7.98×10^{-5}		
(34. 76(	40	1.42×10^{-4}		
	50	2.65×10^{-4}	11. 1	40. 7
50	30	9.35×10^{-5}		
(34. 21)	40	1.73×10^{-4}		
	50	3.27×10^{-4}	11. 3	39. 8
75	30	1.44×10^{-4}		
(33. 41)	40	2.50×10^{-4}		
	50	4.50×10^{-4}	10. 5	40. 9
95. 2	30	1.90×10^{-4}		
(32. 75)	40	3.35×10^{-4}		
	50	6.15×10^{-4}	10. 8	40. 0
100	30	2.33×10^{-4}		
(32. 63)	40	3.76×10^{-4}		
	50	6.52×10^{-4}	9. 4	44. 2

*D: Dielectric constant at 25 °C, data from ref. 5.

Table 3. Kinetics of the reactions of 2, 4-dinitrochlorobenzene with aniline in CH_3CN—CH_3OH mixed solvents.

Vol. % of MeOH	Temp. (°C)	k (l/mole·sec)	$\Delta H^{\neq}$ (kcal)	$-\Delta S^{\neq}$ (e. u.)
0	35	1.71×10^{-5}		
	50	3.41×10^{-5}	11. 1	44. 7
14. 3	35	2.54×10^{-5}		
	50	6.11×10^{-5}	11. 0	44. 0
50	35	3.94×10^{-5}		
	50	9.76×10^{-5}	11. 4	41. 8
75	35	6.37×10^{-5}		
	50	1.62×10^{-4}	11. 7	39. 9
100	35	9.18×10^{-5}		
	50	2.21×10^{-4}	11. 0	41. 9

Table 4. Kinetics of the reactions of 2, 4-dinitrochlorobenzene with *p*-chloroaniline in CH_3CN—CH_3OH mixed solvents.

Vol. % of MeOH	Temp. (°C)	k (l/mole·sec)	$\Delta H^{\neq}$ (kcal)	$-\Delta S^{\neq}$ (e. u.)
0	35	3.86×10^{-6}		
	50	8.65×10^{-6}	10.0	50.0
14.3	35	1.15×50^{-5}		
	50	2.54×10^{-5}	9.9	49.1
50	35	1.66×10^{-5}		
	50	3.64×10^{-5}	9.8	48.7
75	35	2.26×10^{-5}		
	50	4.65×10^{-5}	8.9	50.9
100	35	2.94×10^{-5}		
	50	6.28×10^{-5}	9.4	48.8

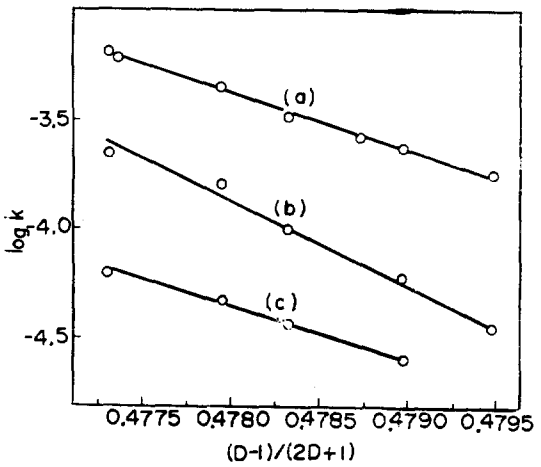

Fig. 2. Dependence of log k on the dielectric constant of the solvent in reactions between 2, 4-dinitro chorobenzene with(a) *p*-toluidine, (b)aniline and (c) *p*-chloroaniline at 50°C.

constant (first order in substrate, first order in amine) has been found to be augmented by increase in amine concentration or by addition of other bases. However the results in *Table* 1 demonstrate that base catalysis is absent or its extent is too small to perturb the rate measurements in our experimental conditions.

The results of kinetics are summarized in *Tables* 2~4.

In contrast to Menschutkin reaction, it can be seen that the dependence of log k on t he Kirkwood function, $(D-1)/(2D+1)$, shows linearities with negative slope (*Fig.* 2).

Even though the difference in dielectric constant between methanol and acetonitrile is very small, such an inverse correlation indicates that specific solvation by alcohol rather than electrostatic interaction is likely to be predominant in the course of reaction. It is in accordance with the conclusions of Schukova and Shein[6]. Since the dielectric constant of methanol is slightly smaller than that of acetonitrile, acetonitrile-methanol binary solvent system can be considered as isodielectrics. The significant differences between these solvent pairs are that acetonitrile is a dipolar aprotic solvent while methanol is a protic solvent. Thus it can be argued that the differences in specific solvation of acetonitrile and methanol would be dependent on their aprotic and protic nature.

From *Fig.* 3 considerable increase in rates of the reactions studied is observed upon going from acetonitrile to methanol. Such an increase in reaction rates by alcohol is uncommon and it is probably associated with the specific solvation of the latter. Since alcohol can display acid properties by way of the hydrogen of the hydroxyl group and is strong base in comparison

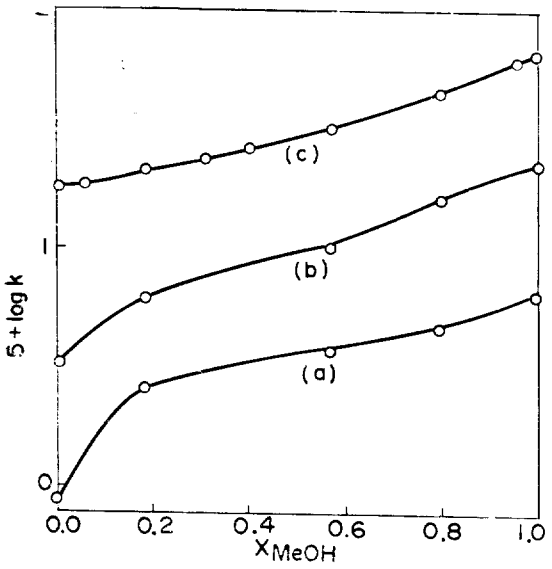

Fig. 3. Dependence of log k on mole fraction of methanol in CH_3CN—CH_3OH binary mixtures in reactions of 2, 4-dinitrochlorobenzene with (a) *p*-chloroaniline, (b) aniline and (c) *p*-toluidine at 50°C.

with acetonitrile.[7] Alcohol molecules may favor solvation around the negatively charged halogen and positively charged nitrogen of amine group compared with acetonitrile in the transition state. Considering the steric hindrance of positive site, the electrophilic specific solvation by alcoholic hydrogen would be more favorable.

It can be confirmed by the fact that the rate ratio of 2, 4-dinitrofluorobenzene with *p*-toluidine to that of 2, 4-dinitrochlorobenzene in 50 vol. % binary solvent at 50 °C is ~140.[8] Such a high reactivity of fluorine compound can partially be attributed to the hydrogen bonding ability of fluorine. However it is also necessary to include the electronegativity effect of fluorine atom attatched to nucleophilic carbon center in discussing relative reactivities.

From *Fig.* 3 and *Tables* 2~4, the order of nucleophilicities of the substituted anilines over whole spectrum of solvent is as follows, *p*-toluidine>aniline>*p*-chloroaniline. This matches with the order of increasing basicity of nitrogen of para substituted anilines, which in turn is the order of easiness of bond formation. On the other hand, bond-breaking is shown to be important as mentioned above through specific solvation of methanol. It is well known that the bimolecular nucleophilic substitution reaction of nitroactivated halobenzenes passes through addition-elimination reaction. Thus we can conclude that not only the elimination step but also the addition step in S_NAr mechanism is important.

Since the degree of solvation of the initial state, that is, neutral polar molecules is nearly same both in methanol and in acetonitrile,[9] transition state solvation determines the reactivity. It is reasonable to assume that the first transition state is bond formation step and the second transition state is bond breaking step. Both the negative charge of leaving atom, chlorine, and positive charge of attacking nitrogen atom become larger in bond breaking step than in bond formation step. Then both sides the second transition state can be more solvated than that of the first transition state

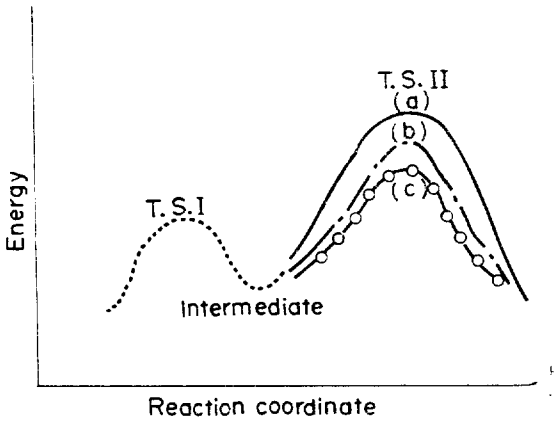

Fig. 4. Approximate energy-reaction coordinate diagram for the reaction of 2, 4-dinitrochlorobenzene with substituted anilines in CH_3CN—CH_3OH binary solvent system. (a) pure CH_3CN, (b) mixture of CH_3CN and CH_3OH, (c) pure CH_3OH.

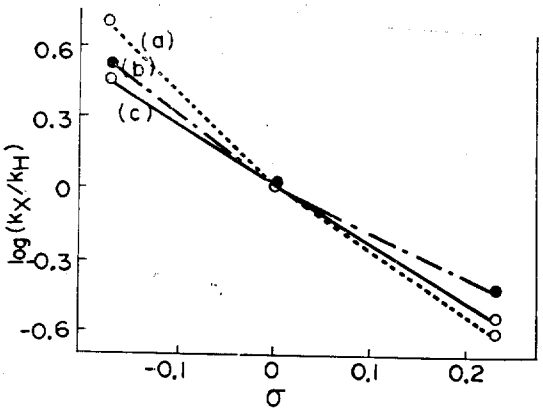

Fig. 5 The plots of $\log(k_X/k_H)$ *vs.* σ for reactions of 2, 4-dinitrochlorobenzene with substituted anilines (X=*p*-CH_3, *p*-H, *p*-Cl) in (a) pure CH_3CN (b) 50 vol. % CH_3CN-CH_3OH mixture (c) pure methanol at 50 °C.

by methanol. It means that the bond breaking step is rate determing in methanol, since addition of methanol increases the rate despite of its low dielectric constant.

Acetonitrile, dipolar aprotic solvent, can hardly sovate the small hard anion, Cl^-, whille methanol, the hard protic solvent, shows great solvation by hydrogen bonding interaction with Cl^-. Thus the rate determining step is bond breaking in the solvent system studied. As the solvent composition changes, the energy profile may change as shown in *Fig.* 4.

Referring to *Fig.* 5 the Hammett plot shows near linearites in methanol but going to acetonitrile rich solvent, the plots become curved. In methanol the reaction constant ρ is about -2.5.

From *Tables* 2∼4, over all ranges of solvent the activation enthalpy values are relatively small, while the entropies of activation show large negative values.

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