

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

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(1977. 11. 7 接受)

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

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(Received Nov. 7 1977)

요 약. 이니트로요오도벤젠과 파라치환체 아닐린과의 반응을 아세토니트릴-메탄올 혼합용매에서 연구하였다. 행해진 반응에서의 반응속도 상수는 메탄올 용매하에서 아세토니트릴 용매에 비해 큰 값을 보였다.

실험 결과로 부터 중간체 생성 과정이 반응속도 결정 단계임을 알았으며 용매효과는 메탄올의 산소 원자와 아닐린의 수소원자 사이의 수소결합에 의한 전이상태 안정화로 설명하였다.

ABSTRACT. The reactions of 2,4-dinitroiodobenzene with para substituted anilines in acetonitrile-methanol binary solvent mixtures have been studied. Rate constants for reactions in methanol rich solvents are greater than for reactions in acetonitrile rich solvents. Kinetic results show that the bond formation step is rate determining in the solvent system studied. The solvent effect can be explained by stabilization of the transition state by formation of hydrogen bond between oxygen atom of methanol and hydrogen atom of aniline.

1. INTRODUCTION

A knowledge of the solvent natures on the rate of chemical reactions is one of the fundamental problems of theoretical organic chemistry. A point of view has been noted according to which the rate of chemical reactions in solution can be affected by two solvent effect types;

nonspecific and specific.

Nonspecific solvent effects mean the electrostatic interaction of the solvent molecules with the dissolved substances, while specific solvent effects mean the chemical interaction due to the presence of electron-donating or electron-accepting centers in the solvent molecules, or both simultaneously.

The qualitative Hughes-Ingold solvent theory¹ predicts that reaction between polar molecules in

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which uncharged reactants pass to products through a transition state in which charge is being developed, will proceed more rapidly when transferred to a more polar solvents.

The aim of this work is to study the influence of solvents on the rate of reaction between polar molecules. In this work the reactions of 2,4-dinitroiodobenzene with *p*-toluidine, aniline, and *p*-chloroaniline are studied in acetonitrile-methanol binary solvent mixtures.

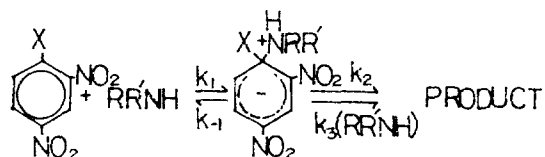
2. EXPERIMENTAL

Materials. 2,4-Dinitroiodobenzene was prepared by halide exchange from 2,4-dinitrochlorobenzene and sodium iodide in dimethylformamide, followed by recrystallization from petroleum ether and identified by m.p (88~90°C)². The purifications of remaining materials have been described elsewhere³.

Kinetic Procedures. Kinetic measurements were done by conductivity method described previously³. Initial concentrations of 2,4-dinitroiodobenzene amounted to 0.001~0.006 *M* and substituted anilines 0.1~0.6 *M*.

3. RESULTS AND DISCUSSION

The broad mechanistic features of nitro activated nucleophilic aromatic substitutions by primary or secondary amines are well established, mainly due to the work of Bunnett⁴. The accepted mechanism is addition-elimination reaction represented as follows,



If the product forming step (bond breaking step) is rate determining, the reaction is base

catalyzed, that is, linear increases of the second order rate constant with increasing amine (or more generally, added base) concentration are observed. If the formation of the intermediate (bond formation step) is rate determining, the reaction is not base catalyzed and so the second order rate constant is not affected by the concentration of amine.

We have found that the reactions between 2,4-dinitroiodobenzene and anilines in all the solvent system studied were first order in both the substrate and nucleophile even at the high base concentrations. Table 1 shows the typical second order rate constant for the reaction in 50 vol. % acetonitrile-methanol mixture at 50°C maintaining the 2,4-dinitroiodobenzene concentration at $2.6 \times 10^{-3} M$ varying the aniline concentration approximately five-fold from 0.12 to 0.52 *M*. The rate constants are nearly independent of the aniline concentration within the accuracy of our measurements. Thus in the reactions of 2,4-dinitroiodobenzene with anilines in the solvent system studied, the bond formation step is rate determining.

Tables 2~4 show the kinetic results of the reactions between 2,4-dinitroiodobenzene and anilines. It can be seen that bond formation is important in this reaction since the electron withdrawing substituent on aniline reduces while electron donating substituent enhances the rate.

Table 1. Reaction rate constants of 2,4-dinitroiodobenzene and aniline in 50 vol. % $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ mixture at 50°C.

2,4-dinitroiodobenzene (mole/l)	aniline (mole/l)	$k_1 \times 10^{-5}$ (sec ⁻¹)	$k_2 \times 10^{-5}$ (l/mole·sec)
2.58×10^{-3}	0.121	0.84	6.94
2.58×10^{-3}	0.250	1.67	6.68
2.61×10^{-3}	0.375	2.58	6.87
2.61×10^{-3}	0.452	3.03	6.71
2.63×10^{-3}	0.516	3.48	6.75
			mean 6.79

Table 2. Kinetics of the reactions of 2,4-dinitroiodobenzene with *p*-toluidine in $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ mixed solvents.

Vol. % of MeOH	Temp. (°C)	k (l/mole·sec)	ΔH^\ddagger (kcal)	$-\Delta S^\ddagger$ (e. u.)
100	50	3.87×10^{-4}	8.80	47.1
	40	2.42×10^{-4}		
75	50	2.87×10^{-4}	12.0	37.7
	40	1.53×10^{-4}		
50	50	2.09×10^{-4}	10.7	42.5
	40	1.19×10^{-4}		
14.3	50	1.34×10^{-4}	11.1	42.0
	40	7.46×10^{-5}		
0	50	8.10×10^{-5}	9.80	47.1
	40	4.82×10^{-5}		

Table 3. Kinetics of the reactions of 2,4-dinitroiodobenzene with aniline in $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ mixed solvents.

Vol. % of MeOH	Temp. (°C)	k (l/mole·sec)	ΔH^\ddagger (kcal)	$-\Delta S^\ddagger$ (e. u.)
100	50	1.18×10^{-4}	9.8	46.4
	40	7.02×10^{-5}		
75	50	7.87×10^{-5}	11.2	42.7
	40	4.36×10^{-5}		
50	50	6.79×10^{-5}	11.4	42.5
	40	3.73×10^{-5}		
14.3	50	3.36×10^{-5}	11.7	43.0
	40	1.82×10^{-5}		
0	50	2.72×10^{-5}	10.7	46.6
	40	1.55×10^{-5}		

Table 4. Kinetics of the reactions of 2,4-dinitroiodobenzene with *p*-chloroaniline in $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ mixed solvents.

Vol. % of MeOH	Temp. (°C)	k (l/mole·sec)	ΔH^\ddagger (kcal)	$-\Delta S^\ddagger$ (e. u.)
100	50	3.58×10^{-5}	14.1	35.4
	40	1.72×10^{-5}		
75	50	2.51×10^{-5}	11.8	43.1
	40	1.35×10^{-5}		
50	50	1.70×10^{-5}	12.4	42.1
	40	8.88×10^{-6}		
14.3	50	1.27×10^{-5}	13.3	39.9
	40	6.36×10^{-6}		
0	50	1.54×10^{-5}	13.9	37.6
	40	7.46×10^{-6}		

The rate constants are greater for 2,4-dinitrochlorobenzene³ than for 2,4-dinitroiodobenzene (Fig. 1). The independence of rate constant upon aniline concentration, (absence of base catalysis) and faster rates for 2,4-dinitrochlorobenzene compared with those for 2,4-dinitroiodobenzene (see, Fig. 1), clearly suggest that the rate of reaction between 2,4-dinitrohalobenzene with aniline is determined by the bond forming step. This is at variance with the view held previously.³

From Hughes-Ingold solvent effect theory, it seems natural to suppose that if both reactants are uncharged in the initial state then because of charge separation during the transition state, the rate constant of this reaction should be nearly same in the solvent system studied since the difference of the dielectric constant between acetonitrile ($D=36.02$) and methanol ($D=32.63$) is very small and acetonitrile-methanol solvent

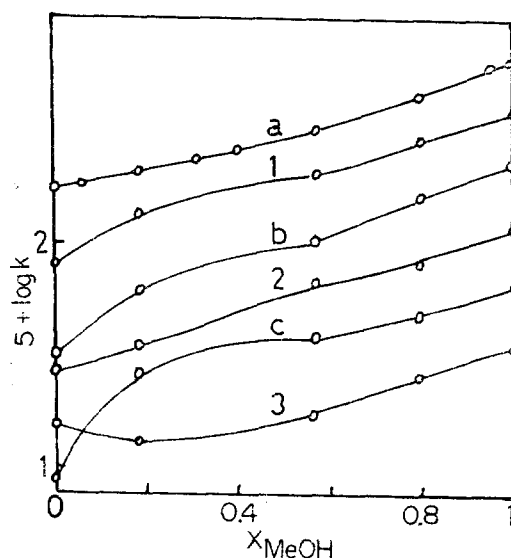


Fig. 1. Dependence of $\log k$ on mole fraction of methanol in $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ binary mixtures in reaction of 2,4-dinitroiodobenzene with (1) *p*-toluidine, (2) aniline and (3) *p*-chloroaniline and 2,4-dinitrochlorobenzene³ with (a) *p*-toluidine, (b) aniline and (c) *p*-chloroaniline at 50 °C.

mixture can be treated as isodielectrics.

Fig. 1 shows the correlation between $\log k$ and mole fraction of methanol. A significant increase in rates of the studied reactions is observed upon going from acetonitrile to methanol. In spite of the fact that the dielectric constant of acetonitrile is slightly larger than that of methanol, such an increase in reaction rates by methanol is uncommon and is probably associated with specific solvation of methanol.

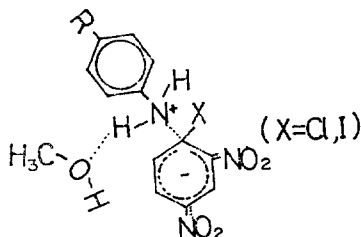
Acetonitrile is a dipolar aprotic while methanol is a protic solvent. It is notable that alcoholic protic solvent has not only hydrogen atom which can make a hydrogen bond but also oxygen atom which can accept hydrogen atom from the other molecules. In other words, alcohols can play the role of electrophilic catalyst by way of hydrogen and nucleophilic catalyst by way of oxygen of the hydroxyl group. It is well known that the basicity of acetonitrile is much weaker than that of methanol⁵, so it can't be expected that acetonitrile shows the nucleophilic catalysis. According to Parker⁶, hard protic solvent, methanol, shows greatest hydrogen bonding interactions with small hard anion, Cl^- , and least hydrogen bonding with large soft anion, I^- , while mutual polarizability is greatest for latter ion with either dipolar aprotic solvents or with polarizable protic solvents.

Fig. 1 shows the increasing tendencies of the rate constants toward increasing the mole fraction of methanol are the same for both substrates, 2,4-dinitrochlorobenzene and 2,4-dinitroiodobenzene. If the chlorine atom is strongly solvated with methanol in the rate determining step in the reaction between 2,4-dinitrochlorobenzene and anilines, the slope of $\log k$ vs. X_{MeOH} of 2,4-dinitrochlorobenzene would be greater than of 2,4-dinitroiodobenzene. The absence of electrophilic catalysis of methanol in the reaction between 2,4-dinitrochlorobenzene and anilines

means that the bond formation step is rate determining. If the bond breaking step is rate determining the electrophilic catalysis of methanol would appear since the negative charge of chlorine atom in the bond breaking step is largely developed in comparison with the bond formation step. Ballistreri *et al.*⁷ studied the reaction of benzyl chloride with aniline in various solvents and the kinetic results were explained in terms of electrophilic catalysis of protic solvent by favoring the displacement of the chloride ion by hydrogen bonding where the breaking of leaving group is rate determining. In the reaction of 2,4-dinitroiodobenzene with anilines, mutual polarizability between iodine atom and acetonitrile may appear in the bond breaking step since the negative charge of iodine atom in the bond breaking step is largely developed in comparison with bond formation step. If mutual polarizability exists between iodine atom and acetonitrile in the rate determining step, the slope of $\log k$ vs. X_{MeOH} for 2,4-dinitroiodobenzene cannot be the same value as that for 2,4-dinitrochlorobenzene. It means that the bond formation step must be the rate determining.

Consequently it seems reasonable that the bond formation step is rate determining and the specific solvent effect of methanol to these reaction systems may be due to the nucleophilic catalysis and the effects of specific solvation are the same for both reactions. The nucleophilic catalysis of methanol can be explained by stabilization of the transition state by formation of hydrogen bonding between the hydrogen atom of aniline and oxygen atom of methanol.

The reactions of benzyl amine⁸ with aryl halides are faster in the presence of dimethylsulfoxide than in pure methanol and the rate increases about 80 fold when the reaction of benzylamine transferred from methanol to 80



vol. % DMSO-methanol. Although the dielectric constant of DMSO-methanol solvent mixtures is higher than that of pure methanol, such a suprisingly large increase of rate may be mainly due to the larger nucleophilic catalysis of DMSO in comparison with methanol, since DMSO is a stronger base and probably a stronger hydrogen bond acceptor from amine than methanol⁹.

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 as in the reaction of 2,4-dinitrochlorobenzene and anilines.

The rate constants measured are correlated with the Hammett σ constants. The value ρ obtained in pure methanol is about -2.6; thus the substituent effect of aniline is nearly the same as in the reactions with 2,4-dinitrochlorobenzene.

ACKNOWLEDGEMENT

We wish to thank the Ministry of Education for the support of this work.

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