

아세톤 용매에서의 Benzyl Arenesulfonate 의 가용매 분해(제 4 보)

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Solvolysis of Benzyl Arenesulfonates in Acetone-Water Mixture(IV)

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要 約. 合成한 benzyl arenesulfonate 의 離脫基의 置換基效果를 研究하기 위하여 10~15 vol. % 아세톤-물 혼합용매속에서 용매분해속도를 電氣傳導法으로 測定하였다.

용매효과, 置換基효과 그리고 물 함량에 따른 速度變化를 檢討한 結果, 물 함량이 적은 部分에서는 p -OCH₃ 는 S_N2 性格이 다소 나타나나, 全置換基를 通해서 대체적으로 S_N1 性格이 支配的인 反應임을 알 수 있었다.

ABSTRACT. Substituent effects of leaving group in benzylarenesulfonates solvolysis have been carried out in 10~50% water-acetone mixtures by electric conductivity method.

Results of solvent effects, substituent effects and variable rate difference of water contents, show that S_N1 character almost predominates through the substituents, though p -MeO favors more or less S_N2 character in low water contents.

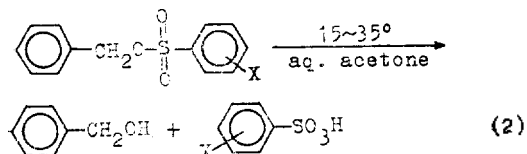
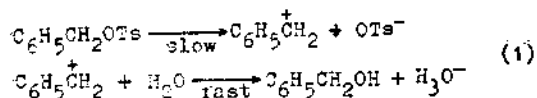
INTRODUCTION

A detailed kinetic study of the solvolysis of benzyl tosylates in solutions of aqueous acetone and aqueous dioxane has been made by Hammond and co-workers¹ (Eq. 1) that has been shown to follow especially, an S_N1 mechanism in electron-donating group.

The substituent effect for the reaction of benzyl benzenesulfonate with pyridines in acetone has been previously studied. Also the S_N2 reaction

was postulated that the O—N bond making and C—O bond breaking occurred simultaneously.²

The present work has been carried out to investigate the solvolysis of benzylarenesulfonates that have the substituent in the leaving groups (Eq. 2). It is very significant to study the leaving group effect. It's rate constant and activation parameter in 10~50 vol. % water-acetone mixtures at 15, 25 and 35° have been determined by an electric conductivity method. The mechanism has also been discussed.



X: p-MeO, p-Me, H, p-Br, p-Cl, p-NO₂, m-NO₂.

EXPERIMENTAL

Materials and Instruments. All reagents in the experiment were of WAKO' extra pure grade.

Acetone was refluxed over KNO_3 for 1 day, distilled, dried with anhydrous potassium carbonate for 3 days, and fractionated by using the 50 cm Widmer distilling column³.

Acetonitrile was distilled after drying over K_2CO_3 for 3 days⁴.

IR is Hitachi EPI-eG Infrared Grating Spectrophotometer, NMR is Varian A-60 Spectrometer, G. C. in Yanakimoto Gas Chromatography SCG-55 type.

Benzyl arenesulfonates were prepared by the prior method.¹

Apparatus and Kinetic Measurements. The kinetics of the solvolysis of the benzyl arenesulfonate with aq.-acetone were examined by an electric conductivity method. The apparatus was composed of water bath, a long necked reaction cell in which two platinum electrodes (round $d=1.0$ cm) were inserted through mercury tubes and an electric conductivity outfit. The conductivity cell was cleaned with acetone, distilled water, ethanol and acetone, and dried in oven before use. The bath temperature was maintained at $\pm 0.01^\circ$.

Pseudo-first order rate constant of the reaction of the benzyl substituted benzenesulfonates

(0.0025 mole) with aq.-acetone (10~50 vol. %) was obtained.

Generally, pseudo-first-order-reaction rate constant was obtained by

$$\ln \frac{a}{a-x} = \ln \frac{\lambda_\infty - \lambda_0}{\lambda_\infty - \lambda_t} = kt \quad (3)$$

where, λ_0 : Initial electric conductivity, λ_∞ : Electric conductivity at the terminal period as the 100 % reaction, λ_t : Electric conductivity at time t .

The reproducibility of the data (λ_∞ and λ_0) was difficult to be determined, so the pseudo first-order rate constant was calculated, from the Guggenheim equation⁶

$$kt + \ln(\lambda - \lambda') = \text{constant} \quad (4)$$

where, λ : Electric conductivity at time t , λ' : Electric conductivity at time, $t + \Delta$: Δ is constant increment (ca. 2~3 times of half-time)

An example of the results obtained by the above procedure is in Table 1. The plot of $\ln(\lambda - \lambda')$ against, time shows good linearity (Fig. 1).

RESULTS AND DISCUSSION

Pseudo-first-order rate constants and activa-

Table 1. The rate of solvolysis of $\text{C}_6\text{H}_5\text{CH}_2\text{OTs}$ in 40% water-acetone mixture at 15° .

t (min)	λ_t	$t + \Delta$ ($\Delta=120$)	$\lambda_{t+\Delta}$	$\ln(\lambda - \lambda')$
39	1.22×10^{-4}	70	1.19×10^{-3}	1.028
40	2.26	71	1.21	0.993
41	3.35	72	1.24	0.956
42	4.31	73	1.25	0.913
43	5.15	74	1.28	0.883
44	5.92	75	1.29	0.843
45	6.64	76	1.30	0.804
46	7.27	77	1.31	0.765
47	7.90	78	1.32	0.724
48	8.44	79	1.33	0.686
49	8.91	80	1.35	0.662

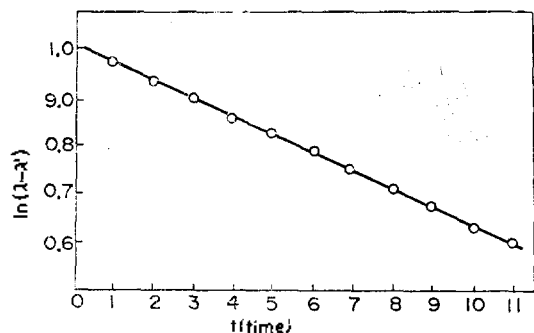


Fig. 1. Plot of $\ln(\lambda-\lambda')$ vs. time for the solvolysis of $C_6H_5CH_2OTS$ in 40% water-acetone mixture at 15° .

tion parameters of solvolysis of benzyl arenesulfonate in various aq.-acetone are given in Table 2. As shown in Table 2, rate constant increased according to the increase of water content. In the same water content, rate constant increased in the order $p-OCH_3 < p-CH_3 < p-H < p-Br < p-Cl < m-NO_2 < p-NO_2$. The electron-donating group suppressed rate constant. Increasing water-content tends to increase the ΔH^\ddagger , and decrease the negativity of ΔS^\ddagger .

Effect of Solvent. Winstein and Grunwald⁷ have shown that the rate constant, k , for the unimolecular solvolysis of alkyl halides, tosylates and brosylates can be correlated with the constitution of the medium by the equation

$$\log k/k_0 = mY \quad (5)$$

This implies a correlation of $\log k$ with the water concentration. Acetone and water mixtures showed good linearities in Fig. 2. Slopes of line, i. e. m were 0.7~1.4, the order being $p-OCH_3 < p-CH_3 < p-H < p-Br < p-Cl < m-NO_2 < p-NO_2$. That is to say, from m values, $p-NO_2$ group was very large in S_N1 character. Moving to $p-OCH_3$ m value decreased, so S_N2 character increased. This implies that the bond-making between water and carbon in $p-OCH_3$ compound is becoming less important compared to carbon-oxygen bond stretching in $p-NO_2$

compound.

Also we can see like tendency in activation parameter. In general, $p-NO_2$ group is large in ΔH^\ddagger , small in $-\Delta S^\ddagger$ compared with $p-OCH_3$. Large ΔH^\ddagger and small $-\Delta S^\ddagger$ is needed to have much progress of bond stretching. Also, in case of $p-OCH_3$ group, ΔH^\ddagger value is comparatively increased and ΔS^\ddagger is decreased. This means that there is a bond-stretching of $p-NO_2$ group in transition state according to increasing water content. Therefore, if there is increasing of the ionizing power of the solvent, bond stretching is increased in the transition state.

Effects of Substituents. It is customary to represent the effect of substituents on the rates and equilibria in aromatic reactions in terms of the Hammett equation⁸

$$\log k_s/k_0 = \rho\sigma \quad (6)$$

Also, Hammett equation is a measure of the extent of bond-making and bond-breaking at the transition state. The value of ρ would be large for those reactions in which bond-breaking occurs prior to bond making (S_N1), while smaller values would be characteristic of bimolecular nucleophilic substitution (S_N2) where the two processes occur together.

The Hammett plot based on the data is shown in Fig. 3. Although high water contents (30, 40, 50 %) show the good linearity, low water content (10, 20 %) show the deviation from the linear in electron-donating group. ρ values in the slope of the linear part is from $\rho = 1.5$ to $\rho = 1.9$ according to the increasing of the water contents (10~50 %). Increasing the water content, ρ value becomes large that shows the predominance of the S_N1 character. So, if ionizing power increases according to increases according to increasing of the water content, the bond-breaking is more important in the transition state. Especially, in electron-dona-

Table 2. Rate constants, ΔH^\ddagger and ΔS^\ddagger for solvolysis of benzyl arenesulfonates in aqueous acetone.

Substituents	Water vol.	Rate consts. $10^4k(\text{sec}^{-1})$			ΔH^\ddagger (Kcal/mol)	$-\Delta S^\ddagger$ (e. u.)
		15°	25°	35°		
<i>p</i> -OCH ₃	10	0.19	0.37	0.76	8.2	34.4
	20	0.92	1.90	3.90	13.3	29.7
	30	3.83	7.59	14.91	17.1	21.5
	40	6.83	13.65	26.73	18.3	19.7
	50	7.62	14.97	29.72	20.8	7.6
<i>p</i> -CH ₃	10	0.27	0.50	0.12	12.7	33.2
	20	2.12	4.36	8.64	15.7	27.2
	30	6.73	13.72	27.43	18.3	20.6
	40	7.81	15.61	31.32	19.0	13.7
	50	8.77	17.43	34.90	21.9	4.9
<i>p</i> -H	10	0.37	0.76	1.54	12.9	32.8
	20	4.75	9.55	19.12	16.3	26.9
	30	7.62	15.20	30.43	19.4	19.4
	40	8.74	17.51	35.02	19.6	12.4
	50	9.97	19.90	39.81	24.5	4.3
<i>p</i> -Br	10	0.64	1.26	2.53	14.3	26.2
	20	6.76	13.51	27.04	17.6	22.3
	30	8.34	16.73	33.47	20.0	14.9
	40	9.87	2.95	39.44	21.2	8.5
	50	11.28	22.53	45.07	25.1	3.2
<i>p</i> -Cl	10	1.01	2.00	4.3	15.2	25.6
	20	7.16	14.31	28.63	19.1	19.9
	30	9.01	18.00	36.12	20.2	12.2
	40	10.62	21.23	42.47	22.8	6.3
	50	12.32	24.65	49.31	26.7	2.2
<i>m</i> -NO ₂	10	2.18	4.37	8.73	16.0	22.3
	20	8.07	16.13	32.27	20.0	15.7
	30	10.47	20.91	41.85	21.4	9.9
	40	12.72	25.21	50.43	26.7	5.7
	50	14.92	29.28	59.65	29.1	1.9
<i>p</i> -NO ₂	10	3.97	7.95	15.81	17.0	20.3
	20	8.91	17.81	35.62	21.1	13.8
	30	11.93	23.84	47.68	21.7	8.6
	40	14.73	29.44	58.78	27.9	4.7
	50	17.73	35.47	70.89	30.3	1.5

ting group of low water content, bond-breaking is less important compared with bond-making, which shows the deviation from the linear line. This is consistent with the results of Swain⁹

which show that the curvature of the Hammett plot is the continuous shift from S_N2 to S_N1 . Continuous change of transition state according to solvent composition is agreeable with Win-

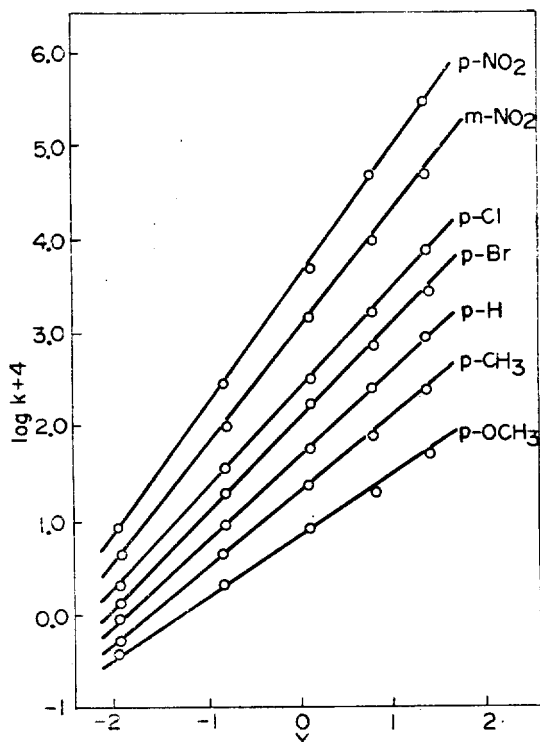


Fig. 2. Grunwald-Winstein plot at 25°C for the solvolysis of benzyl arenesulfonates.

stein.⁷ Although this is S_N1 , electron releasing group gives S_N2 character and will modify the transition state towards a greater degree of bond-making.

Variation of Rate with Molarity of Water in Solvent. It is concluded above that this solvolysis is a S_N1 from the effect of solvent and substituent, but S_N2 character is shown in electron-donating group.

A naive approach to the kinetics of reactions suggests that it is possible to find the number of water molecules involved in the formation of the transition complex from equation (9) by using the gradient of a plot of $\log k_1$ against the logarithm of the molarity of water in the solvent mixture (Fig. 4)

$$\frac{dx}{dt} = k_{obs} [\text{ester}] \quad (7)$$

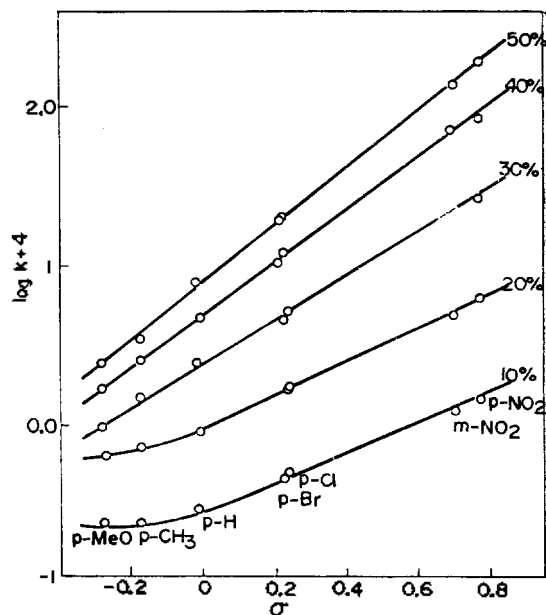


Fig. 3. Hammett plot for the solvolysis of benzyl arenesulfonates₂ in aq. acetone at 25°C.

$$k_{obs} = k[\text{H}_2\text{O}]^n \quad (8)$$

$$\log k_{obs} = \log k + n \log[\text{H}_2\text{O}] \quad (9)$$

where, n is water participation order. Each substituents show a good linearity, n value is from 3.5 to 6.5 the order being $p\text{-OCH}_3 < p\text{-CH}_3 < p\text{-H} < p\text{-Br} < p\text{-Cl} < m\text{-NO}_2 < p\text{-NO}_2$.

Tommila⁴, from a study of solvolysis of tertiary halides and sulphonic esters, suggested that there was a correlation between the value of n obtained from equation (9) and the mechanism of solvolysis: a value of about 2 being indicative of an S_N2 type reaction and a value of about 6 characterizing an S_N1 type solvolysis.

Therefore, from Tommila's results, this solvolysis belongs to the S_N1 mechanism, with a little S_N2 character.

In the former analogous solvolysis of substituted benzyl chlorides, it has been suggested (Archer and Judson¹⁰) that the reaction is of the S_N2 type in aqueous acetone of low water

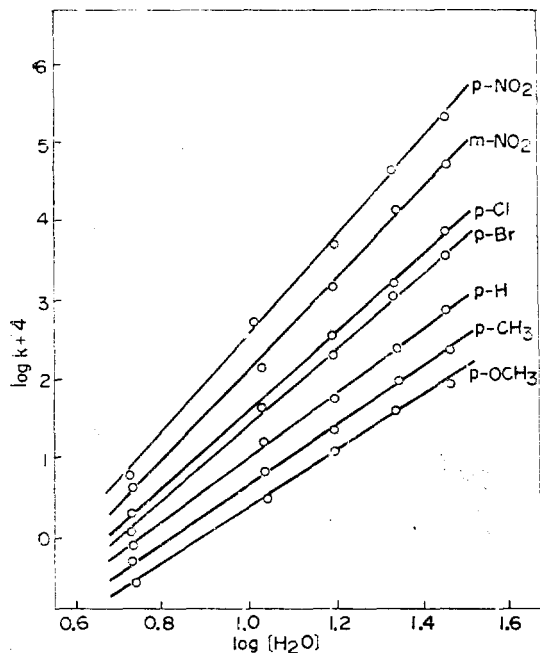


Fig. 4. Plot of $\log k_{\text{obs}}$ vs. $\log [\text{H}_2\text{O}]$ at 25° , for the solvolysis of benzyl arenesulfonates.

content but of the "mixed" S_N2+S_N1 type in high aqueous media. If there is "mixed" S_N2+S_N1 type, we can determine the rate constant k_1 , k_2 of S_N1 , S_N2 respectively.

In S_N1 type:



S_N2 type:



so,

$$\begin{aligned} \frac{dx}{dt} &= k_1(a-x) + k_2(a-x)(b-x) \\ &= [k_1 + k_2(b-x)](a-x) \end{aligned} \quad (12)$$

Here, nucleophile is H_2O , it's concentration is greater compared with substrate.

So,

$$b' = [\text{H}_2\text{O}] \cong (b-x) \quad (13)$$

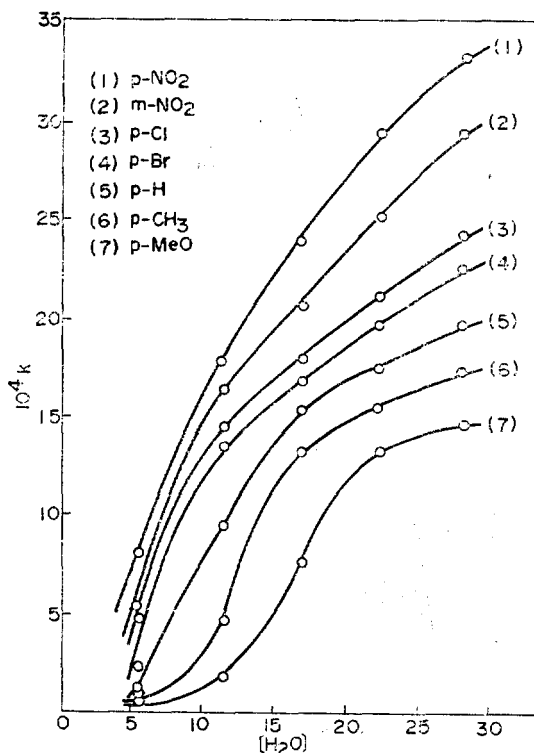


Fig. 5. Plot k vs. $[\text{H}_2\text{O}]$ at 25° , for the solvolysis of benzyl benzylarenesulfonates.

From the Eq. 12,

$$k_{\text{obs}} = k_1 + k_2 [\text{H}_2\text{O}]$$

If there is a linear in plot of $[\text{H}_2\text{O}]$ against k_{obs} , intercept is k_1 which is rate constant of S_N1 type and slope is k_2 , the rate constant of S_N2 type.

The results (Fig. 5) in aqueous acetone solution, which cover a much wider range of $[\text{H}_2\text{O}]$, under conditions where an S_N1 mechanism would be definitely favoured, do not show a linear relationship. Therefore, there is no evidence of "mixed" S_N1+S_N2 type but S_N1 type. These results are consistent with the previous conclusion that bond-breaking is predominant in the transition state in S_N1 type, bond-making is insignificant.

The curvature in Fig. 5 can be expressed in

the mole fraction of water, by equation (15)

$$k_{obs} = k_1 + k_2[H_2O] + k_3[H_2O]^2 \quad (15)$$

Here, water acts as the general base catalyst as well as nucleophile.^{11, 12}

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