

«Original» Halogen Exchange Reactions of Cinnamyl Halides

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Abstract

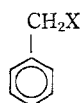
Halogen exchange reactions of trans-cinnamyl chloride and bromide with radioactive chloride, bromide and iodide ions in acetone have been studied. Relative nucleophilicity of halide ions and relative leaving ability have been discussed invoking the principle of HSAB.

요 약

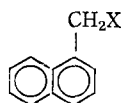
Trans-cinnamyl chloride와 bromide의 방사성 Cl^- , Br^- 및 I^- 와의 교환 반응을 아세톤 용액에서 반응속도론적으로 연구 하였다. 상대적인 할로젠 이온들의 친핵성과 이탈능을 HSAB 원리를 이용하여 논의 하였다.

1. Introduction

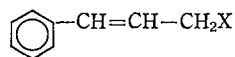
In the previous paper, ⁽¹⁾ we have reported that the relative nucleophilicity of halide ions in benzyl halide (I) exchanges was in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ in acetone for the reaction,



(I)



(II)



(III)

Invoking the principle of hard and soft acids and bases (HSAB) ⁽²⁾ this was rationalized as the order mainly ascribable to the ground state solvation by the soft solvent molecules. ⁽³⁾

On the other hand the rate of halogen exchange in 1-naphthyl methyl halides (II) has been reported ⁽³⁾ to be faster than that for (I) primarily due to the increase in softness of carbon at reaction center. The increase of softness in this case is

thus sufficient to reverse the above order of halide ion reactivity to $\text{I}^- > \text{Br}^- > \text{Cl}^-$, by enhanced soft-soft interactions of the larger halides. ⁽²⁾

We have now conducted a similar series of halide exchange studies on trans-cinnamyl halides (III). Insertion of an ethylene group between C_6H_5- and $-\text{CH}_2\text{X}$ groups will obviously change the degree of softness of the carbon at reaction center as compared with (I), and we may expect the effect of this change reflected in the reactivity and order of nucleophilicity accordingly.

We have assumed in these studies that only the normal $\text{S}_\text{N}2$ substitutions occur since abnormal, $\text{S}_\text{N}2'$, reaction under the condition of these studies may safely be considered to be negligible. ⁽⁴⁾

2. Results and Discussion

Rate constants of halide exchange in trans-cinnamyl halides obtained in this work are sum-

marized in Table I together with representative values for benzyl- and 1-naphthyl methyl halides.^{(1) (3)} For trans-cinnamyl chloride the rate constant is the smallest of the three. Taft's polar substituent constants σ^* for C_6H_5- and $C_6H_5CH=CH-$ groups are +0.60 and +0.41 respectively.⁽⁵⁾ Since the substituent $-H$ has the σ^* value of +0.49,⁽⁵⁾ this means that C_6H_5- substitution in place of $-H$ at methyl carbon will decrease electronegativity of the carbon while $C_6H_5CH=CH-$ substitution will increase electronegativity relative to carbon in a methyl group. In the language of the HSAB principle, C_6H_5- makes the carbon atom softer while $C_6H_5CH=CH-$ makes it less soft.⁽²⁾ Thus SN2 reactivity of trans-cinnamyl halide for halide ions is expected to be less than that of benzyl halide as found for trans-cinnamyl chloride. Although no σ^* value is available for 1-naphthyl group, judging from the higher rate, it is not difficult to accept a greater positive value for the 1-naphthyl-group.

Table I. Summary of Rate Constants (a)
for the Reaction $\phi CH=CHCH_2X + Y^- \longrightarrow \phi CH=CHCH_2Y + X^-$ in Acetone.

X	Temp oc	k [l mole ⁻¹ sec ⁻¹]		
		Cl	Br	I
Cl	15° (e)	1.52 × 10 ⁻³		
	25°	2.75 × 10 ⁻³	5.55 × 10 ⁻⁴	9.77 × 10 ⁻⁴
		(b) 2.83 × 10 ⁻³	18.0 × 10 ⁻⁴	16.2 × 10 ⁻⁴
		(c) 4.29 × 10 ⁻³	30.1 × 10 ⁻⁴	35.8 × 10 ⁻⁴
35°	4.32 × 10 ⁻³	9.62 × 10 ⁻⁴	1.38 × 10 ⁻³	
Br	-10°	(d) 4.25 × 10 ⁻²	4.59 × 10 ⁻³	6.43 × 10 ⁻²
	0°	1.14 × 10 ⁻¹	1.25 × 10 ⁻¹	1.53 × 10 ⁻¹
			(b) 6.33 × 10 ⁻²	3.30 × 10 ⁻²
			(c) 1.48 × 10 ⁻¹	1.43 × 10 ⁻¹

- (a) Averages of more than two determinations. Reproducibilities were better than $\pm 5\%$.
 (b) This row contains values for benzyl halides.
 (c) This row contains values for 1-naphthyl methyl halides.
 (d) Value at -11.0°C .
 (e) Temperature control was better than to $\pm 0.05^\circ\text{C}$.

Table II Relative Nucleophilicity of Halde ion (k_Y/k_{Cl})

for the Reaction; $\phi CH=CH-CH_2X + Y^- \longrightarrow \phi CH=CH-CH_2Y + X^-$.

X		Y		
		Cl	Br	I
Cl	25°	1.0	0.20	0.36
	35°	1.0	0.22	0.32
Br	-10°	1.0	1.08	1.51
	0°	1.0	1.10	1.34

The nucleophilicity of halide ions for chloride system of (III) is in the order $Cl^- > I^- > Br^-$ as seen from Table II. The normal order expected in aprotic media is $Cl^- > Br^- > I^-$ as reported previously,⁽¹⁾ while the degree of symbiosis is in exactly the reverse order.^{(1) (2)} Therefore for chloride system it may be said that ground state solvation effect of halide ions is more important than the symbiotic stabilization effect at the transition state. Activation parameters (Table III) reveal that activation process is quite disentropy when compared with benzyl and 1-naphthyl-methyl chlorides. This may indicate the low degree of solvation of the trans-cinnamyl chloride at the initial state,

Table III. Summary of Activation Parameters
for $\phi CH=CHCH_2X + Y^- \longrightarrow \phi CH=CHCH_2Y + X^-$.

(a) Activation Enthalpies, ΔH^\ddagger (Kcal).

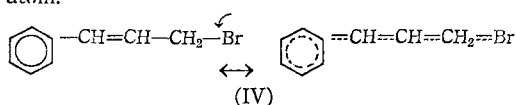
Y	X	
	Cl (25°)	Br (0°)
Cl	7.6	12.2
Br	9.4	13.8
I	6.6	11.9

(b) Activation Entropies, ΔS^\ddagger (e.u.).

Y	X	
	Cl	Br
Cl	-31.8	-3.8
Br	-32.7	-2.8
I	-40.9	-9.6

whereas high degree of solvation is attained at the transition state.

For bromide system of (III), there is a drastic change in relative rates and activation parameters. This is striking when considered with the fact there is only leaving group change from chloride to bromide. The rate constants are now generally greater than those for benzyl bromide and smaller than 1-naphthyl methyl bromide, and the order of nucleophilicity has changed to $I^- > Br^- \geq Cl^-$. This clearly indicates that symbiotic effect is prevailing over ground state solvation effect. ΔH^\ddagger values for trans-cinnamyl bromide exchanges are similar to those for both benzyl⁽¹⁾ and 1-naphthylmethyl⁽²⁾ bromides, while ΔS^\ddagger values are significantly less negative for the former. If the large enhancement of rate in this case is chiefly due to symbiotic stabilization of the transition state as concluded from the relative nucleophilicity, less negative ΔS^\ddagger value implies that ground state of trans-cinnamyl bromide is also stabilized by high degree of solvation. This is an exact opposite of chloride system. In short, trans-cinnamyl bromide is much softer than-chloride and result in high degree of solvation by soft solvent molecule. An increased stability (or softness) conferred by bromine in place of chlorine atom on the initial state of (III) is in fact larger than the same on the initial state of (I), as judged by the general increase of exchange reactivity of (III) compared to (I) as leaving group in changed from Cl to Br. De la Mare and Hughes⁽⁶⁾ explained the increased stability due to bromine substitution with the high polarizability of bromine atom. The fact that mere exchange of $-Cl$ with $-Br$ for (III) gave large increase in molar absorption coefficient at 265 $m\mu$ peak⁽⁷⁾ may also be connected with the considerable increase in conjugation, probably of the butadiene-like structure (IV), brought about in cinnamyl system by bromine atom.



The extra increase in softness due to this enhanced

conjugation will bring increased solvation by soft solvent molecule, which is evident from much less negative ΔS^\ddagger values for -bromide compared with -chloride system.

Table IV Relative Leaving Ability of Halogen (k_x/k_{cl})

for the Reaction; $\phi CH=CH-CH_2X + Y^- \longrightarrow \phi CH=CH-CH_2Y + X^-$.

X	Y		
	Cl	Br	I
Cl	1.0	1.0	1.0
Br	41.4	226	157

The relative leaving ability is shown in Table IV. The difference in leaving ability between $-Cl$ and $-Br$ is the greatest for (III) among the three systems, i.e., (I), (II) and (III). This is again due to the specific stabilization effect of $-Br$ by increased conjugation and hence softness in (III). This effect will be the smallest, if not entirely lacking, for Cl^- and the largest for Br^- . Of course this type of extra stabilization is lacking in other systems, i.e., (I) and (II).

3. Experimental

Materials:

Trans-cinnamyl alcohol was prepared from trans-cinnamaldehyde by the standard method.⁽⁸⁾ m.p. 33°, yield: 90%.

Trans-cinnamyl chloride and bromide were prepared from trans-cinnamyl alcohol and thionyl chloride respectively using the standard methods.⁽⁹⁾

trans-cinnamyl chloride: b.p. 94°/2mmHg.

hydrolyzable Cl, 23.3%

trans-cinnamyl bromide: m.p., 34°

hydrolyzable Br, 40.8%.

Anhydrous acetone was prepared as reported previously.⁽¹⁰⁾

Kinetic Runs:

Kinetic runs were conducted as described before.

⁽¹⁾ In case of chloride ion exchange, activities

were measured in a Beckman LS-100 Liquid Scintillation Counter and quenching corrections were applied as before. ¹¹

Determination of Rate Constants:

Rate constants were calculated using equation (1). ¹²

$$\left(\frac{c-b}{a-b}\right) \log(1-F) = \frac{-Dkt}{2.303} \dots \dots \dots (1)$$

where a and b are the initial concentrations of trans-cinnamyl halides ($\approx 10^{-2}M$) and salts ($\approx 10^{-4}M$), respectively, $c = \frac{1}{2}(D + \frac{D^2}{K})$, =K ion pair dissociation constants in acetone, $D = \sqrt{K^2 + 4Kb}$, and F is the fraction reacted. In case of isotopic exchange reaction, i.e., when X=Y, equation (1) was modified to,

$$\left(\frac{1}{a+b}\right) \log(1-F) = \frac{-\alpha kt}{2.303} \dots \dots \dots (2)$$

where α is the degree of dissociation of salt. Ion pair dissociation constants, K, in acetone were taken from the literature. ¹³

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