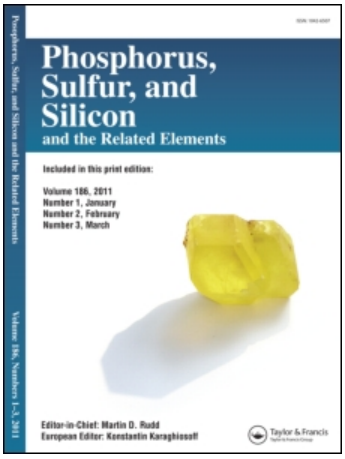

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KINETIC STUDIES ON THE ADDITION OF *p*-TOLUENESULFINIC ACID TO BENZYLIDENEACETOPHENONES

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KINETIC STUDIES ON THE ADDITION OF *p*-TOLUENESULFINIC ACID TO BENZYLIDENEACETOPHENONES

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Kinetics of the addition of *p*-toluenesulfinic acid to *p*-substituted benzylideneacetophenones has been investigated. The reaction was second order, first order each in the concentration of sulfinic acid and chalcone. Effects of the *p*-substituents on the reaction rate were small (rho = 0.4). The reaction was strongly acid catalyzed.

INTRODUCTION

Sulfinic acid has an unique feature to add easily to the unsaturated bonds such as carbonyl, azo, and nitroso group. The addition of sulfinic acids to α,β-unsaturated carbonyl compounds to afford Michael type products are also well known reaction and used for preparation of ketosulfones. Since this addition takes place under acidic conditions, reaction may proceed with the formation of a conjugate acid of the enone in the first step followed by the combination with a sulfinate anion. Or attack of a sulfinate anion to the β-carbon atom of the enone may precede, due to the high nucleophilicity of the sulfinate anion, followed by a protonation. Since there is no report on the kinetics of this reaction except the study on a similar reaction between p-benzoquinone and benzenesulfinic acid,[1] we have carried out kinetic studies on the addition of p-toluenesulfinic acid (1) to several p-substituted benzylideneacetophenones (2) (chalcones) and results will be described in this paper.

$$\underset{\textbf{(1)}}{p\text{-}CH_3C_6H_4SO_2H} + \underset{\textbf{(2)}}{p\text{-}XC_6H_4CH{=}CHCOPh} \rightarrow \underset{\textbf{(3)}}{\begin{matrix} p\text{-}XC_6H_4CH\text{—}CH_2COPh \\ | \\ p\text{-}CH_3C_6H_4SO_2 \end{matrix}}$$

RESULTS AND DISCUSSION

Addition of sulfinic acids to chalcones was not observed under basic conditions, and elimination of sulfinic acid from β-ketosulfones (**3**) was induced with strong bases. Therefore, the rate studies were carried out under acidic conditions below pH 6.7. An ethanol-water (50-50 vol%) mixture was used as solvent throughout.

Since chalcones have strong UV absorption in the 300–430 nm region while there is no absorption above the 300 nm region in the UV spectra of sulfinic acid

1 and adducts **3**, the reaction rate was followed by measuring the decrease of the absorption intensities in the region of UV maximum of chalcones.

Reaction Order

Since reaction rate was influenced by pH as described later, reaction order and substituent effects were investigated at constant pH.

Reaction order was found to be second order, first order each in the concentration of sulfinic acid and chalcones at any given pH. Initial concentration of sulfinic acid and chalcones were varied between $2.5 \times 10^{-3} - 5.0 \times 10^{-4}$ M and 2.5×10^{-3} to 5.0×10^{-5} M, respectively. Typical examples of the effects of the variation of the initial concentrations of both reactants on the rate constants are shown in Table I.

Activation Parameters

At pH 2.60, dependence of the rate on the reaction temperature was investigated in the reaction between 1 and benzylideneacetophenone (**2a**). Effects of temperature was small as shown in Table II.

Activation parameters estimated from these figures are $E_a = 21.3\ \text{kJmol}^{-1}$, $H^{\neq} = 18.8\ \text{kJmol}^{-1}$, and $S^{\neq} = -242\ \text{JK}^{-1}\,\text{mol}^{-1}$. The large negative entropy of activation suggests a strained transition state for the rate determining step, probably the step to form an adduct of the sulfinate anion to the enone.

Substituent Effects

Effects of *p*-substituents (X) of benzylideneacetophenones (**2a–2f**) on the reaction rates were investigated at pH 2.60 ($T = 30.1$°C). (Table III).

Except for *p*-dimethylaminochalcone **2c**, Hammett plot of these figures gave a straight line against Hammett sigma, and rho value was estimated as 0.40. Positive rho value suggests the attack of anionic species (probably sulfinate anion) to the substrate in the transition state.

Reaction rate constant for *p*-dimethylamino derivative **2c** was far larger than the value expected from the Hammett plot. This fact can be explained by N-protonation of **2c** in the reaction mixture. In 50% ethanol solution, **2c** has UV absorption maximum at 430 nm. In the diluted sulfuric acid solution, this

TABLE I

Effects of the initial concentration of the reactants on the rate constants

$[1]_0$/mol l^{-1}	$[2]_0$/mol l^{-1}	2nd order rate constant $k \times 10^4$/l mol^{-1} s^{-1}
5.0×10^{-4}	5.0×10^{-5}	8.71
2.50×10^{-3}	5.0×10^{-5}	8.85
5.0×10^{-3}	5.0×10^{-4}	8.70
2.50×10^{-2}	2.5×10^{-3}	8.35
($T = 30.1$°C)		

TABLE II

Temperature effects on the rate constants

T/K	$k \times 10^4/1\,mol^{-1}\,s^{-1}$
293.3	6.268
298.3	7.823
303.1	8.348

Initial concentration: $[1]_0 = 2.5 \times 10^{-2}$ M; $[2a]_0 = 2.5 \times 10^{-3}$ M; pH 2.60.)

absorption disappeared and new absorption maximum was observed in the 300 nm region, which was coincided with the absorption maximum of **2a**. This fact indicated that **2c** was protonated in acid solution to form **2g**.

$$(CH_3)_2N^+—C_6H_4CH{=}CHCOPh$$
2g

From the pH of the sulfuric acid solution and the decrease of the intensity of 430 nm absorption, pK_a of **2c** was estimated as 2.78 using following equation.

$$pK_a = \log[B^+H]/[B] + pH$$

From this pK_a, extent of the N-protonation of **2c** at pH 2.60 was estimated around 60%. By calibrating with this protonation, true rate of **2g** was estimated as $18.8 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$.

Effects of pH

As mentioned before, the rate was influenced by pH of the reaction medium substantially. Variation of the apparent rate constants with the pH was examined by changing the hydronium ion concentration with buffer solution. Results are shown in Table IV.

As seen from the figures in Table IV, reaction rate increases with the increase of the acidity of the reaction medium, but is not proportional to pH. Variation of the apparent rate constant may be expressed by following equation:

$$v = k_0[AH][B] + k_h[AH][B][H_3O^+]^n$$

where AH = *p*-toluenesulfinic acid
B = benzylideneacetophenone

TABLE III

Substituent Effects on the Rate Constants

X	Substrate	$k_{obs} \times 10^4/1\,mol^{-1}\,s^{-1}$ (30.1°C)
H	**2a**	8.348
CH_3O	**2b**	6.848
$(CH_3)_2N$	**2c**	11.73
Cl	**2d**	8.377
CN	**2e**	16.27
NO_2	**2f**	16.66

TABLE IV

Effects of pH on the reaction rates

pH	$k_{obs} \times 10^4$ ($1\,mol^{-1}\,s^{-1}$)	pH	$k_{obs} \times 10^4$ ($1\,mol^{-1}\,s^{-1}$)
6.7	0.8027	3.30	8.216
5.6	2.574	2.02	10.398
5.1	2.735	1.72	15.933
3.95	4.805	1.40	20.258

For pH 6.7–3.30, buffer solution was prepared with acetic acid–sodium acetate; for pH 2.02–1.40, buffer solution was made with perchloric acid. Initial concentration: $[1]_0 = 3.0 \times 10^{-2}$ M; $[2a]_0 = 3.0 \times 10^{-3}$ M. $T = 30.1$°C.

Assuming $k_{obs} = k_0$ at pH = 6.7, a plot of $\log(k_{obs} - k_0)$ versus pH gave a straight line with slope $n = 0.25$. From this plot, $k_h = (k_{obs} - k_0)$ at pH = 0 and k_0 could be estimated as 3.80×10^{-3} and $0.80 \times 10^{-4}\,l\,mol^{-1}\,s^{-1}$ respectively. This means that the reaction is acid catalyzed through all pH region investigated.

Reaction Mechanism

Validity of a mechanism involving the formation of a conjugate acid of chalcone by the protonation in the first step was examined in the first place.

$$B + [H_3O^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [B^+H] + H_2O$$

$$[BH^+] + A^- \xrightarrow{k_2} [ABH]$$

where $B = C_6H_5CH{=}CHCOPh$

$BH^+ = C_6H_5{-}CH{=}CH{-}C(OH){-}Ph$ (+)

From the pK_a (−5.6) of benzylideneacetophenone,[2] the extent of the formation of the conjugate acid $[BH^+]/[B]$ was estimated to be 6×10^{-9} at pH 2.60. Assuming a steady state concentration for $[BH^+]$, following rate equation can be derived.

$$v = k_2[BH^+][A^-] = \frac{k_1 k_2[B][H_3O^+][A^-]}{k_{-1}[H_2O] + k_2[A^-]}$$

If $k_2[A^-] \gg k_{-1}[H_2O]$, namely first step is the rate determining, the rate should not depend on the concentration of sulfinic acid. This contradicts with the experimental fact.

If $k_2[A^-] \ll k_{-1}[H_2O]$, the second step will be the rate determining and the rate should depend on the hydronium ion concentration linearly. This also contradicts with the experimental fact.

Considering the facts that (1) reaction is first order in sulfinic acid and also benzylideneacetophenones, (2) Hammett's rho is positive, (3) reaction is acid

catalyzed but rate is not first order in hydronium ion, (4) activation entropy is large and negative, and (5) *p*-toluenesulfinic acid is rather strong acid (pK_a = 1.24),[3] and (6) the UV spectrum of a 10^{-4} M solution of *p*-toluenesulfinic acid in 50% ethanol exhibited the absorption maxima at 223 and 260 nm, which coincided with the UV maxima of the *p*-toluenesulfinate anion,[4] showing a complete dissociation of sulfinic acid in a reaction mixture, following mechanism seems to be plausible:

$$A^- + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB^- \quad (1)$$

$$AB^- + H_3O^+ \xrightarrow{k_2} ABH + H_2O \quad (2)$$

where $A^- = p\text{-}CH_3C_6H_4SO_2^-$

$B = C_6H_5CH{=}CHCOPh$

$AB^- = C_6H_5CHCH^-COPh$ (with $p\text{-}CH_3C_6H_4SO_2$ on the CH)

ABH = (3)

Assuming a steady state concentration for $[AB^-]$, following rate equation is derived.

$$v = \frac{k_1 k_2 [A^-][B][H_3O^+]}{k_{-1} + k_2[H_3O^+]}$$

The fact that reaction is acid catalyzed suggests that the second step plays an important role in rate controlling. But, the reaction rate is not first order in pH, showing the overall reaction is composite of the first and second reaction rates. The small value of the apparent rho value observed (0.40) may be understood in terms of opposing substituent effects. The first step is addition of the sulfinate anion to the vinylic carbon atom next to phenyl group which will be accelerated by an electrophilic substituent on the benzene ring (positive rho), while in the second step the substituent of the same type will decrease (negative rho) the rate of protonation of the intermediate carbanion.

EXPERIMENTAL

All compounds used in this study were known compounds and prepared according to the literature. UV spectra were recorded on Hitachi 220A spectrophotometer.

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