

## Solvent and Substituent Effect on Acetophenone-Phenylhydrazone Formation

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The kinetics of acetophenone-phenylhydrazine reaction has been studied spectrophotometrically in different solvents and solvent compositions. The effect of various substituents on acetophenone and the effect of changing dielectric constant on the rate of the reaction have been studied by employing different dipolar and aprotic solvents. The rate data were fitted into the extended linear free energy relationship (LFER) equation and the inductive-resonance substituent constants have been evaluated. It was inferred that higher the polarity of the medium in each of the solvents employed, the magnitudes of substituent constants increased and saved the resonance contribution of substituted acetophenones.

**Key Words:** Kinetics, Acetophenone, Phenylhydrazine, Dipolar, Aprotic, Linear free energy relationship, Hammett equation.

### INTRODUCTION

The dielectric constant of a solvent has an important effect on its ability to accommodate separation of charge<sup>1</sup>. An important property of the solvent molecules with regard to reactions is the way in which the solvent molecules interact with the changes in charge distribution that accompanies many reactions.

Similarly the structural modifications of a reactant molecule may in principle influence the rate or equilibrium constants of a reaction through polar, resonance or steric effects<sup>2</sup>. Linear free energy relationships, notably the Hammett equation is applied to a series of chemical equilibrium involving a family of aromatic compounds with different substituents but a common reaction site<sup>3</sup>. Rate constants for hydrated proton catalysis for *p*-substituted benzaldehyde-phenylhydrazone formation were well-correlated by a dual Hammett substituent parameter treatment<sup>4</sup>.

### EXPERIMENTAL

Acetophenone (AP) and phenylhydrazine (PH), of AR grade (Merck) were used for all the reactions. The purity of the chemicals has been checked from their boiling points (phenylhydrazine 242 °C and acetophenone 201 °C). Phenylhydrazine solutions

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were prepared freshly just prior to use. All the solvents used were of AR grade (Qualigens) and the purity has been checked by comparing their boiling points. Double distilled water was used and the products formed have been characterized with the parent/substituted acetophenone-phenylhydrazones prepared by the traditional method. Kinetics of the reaction was carried out spectrophotometrically at 30 °C with the aid of UV-visible spectrophotometer (Chemito 2600). The dielectric constant values of different solvent compositions used in the reactions have been measured using a digital dielectric meter (Shimadzu).

The specific rate constants were calculated from the integrated rate equation.

$$k = \frac{2.303}{t} \log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$$

where  $A_0$  is the absorbance of the product initially,  $A_t$  is the absorbance of the product at time  $t$  and  $A_{\infty}$  is the absorbance of the product at infinity. The initial concentration of acetophenone was kept at  $2 \times 10^{-4}$  M and in all cases a sufficient excess of nucleophilic reagent (phenylhydrazine) was employed so that pseudo first order rate behaviour was observed.

## RESULTS AND DISCUSSION

The rates of the reactions were monitored in the presence of 100 and 80 % (remaining 20 % water) solvent media of acetic acid (AcOH), dichloro acetic acid (DCA), dioxane and dimethyl sulfoxide (DMSO). The order with respect to phenylhydrazine was found to be unity irrespective of the nature or composition of all the solvent systems studied. The order of acetophenone was evaluated by determining the rate of the reaction in different solvent compositions by varying the concentration of acetophenone [AP] at fixed phenylhydrazine concentration [PH]. The slope of the  $\log k_1$  vs.  $\log [AP]$  plots were calculated by the linear regression and the data are presented in Table-1.

TABLE-1  
CHANGE IN ORDER OF ACETOPHENONE WITH SOLVENT MEDIUM AND  
COMPOSITION IN PHENYLHYDRAZINE-ACETOPHENONE REACTION  
[PH] =  $2 \times 10^{-2}$  M, [AP] =  $2 \times 10^{-4}$  M, Temperature = 30 °C

Solvent medium/ composition		[AP] $\times 10^4$ s <sup>-1</sup>					order
		1.0	1.5	2.0	2.25	2.5	
AcOH	100 %	6.470	4.65	3.38	3.10	2.62	-1
	80 %	0.430	0.60	0.87	0.95	0.97	+1
DCA	100 %	12.56	8.33	6.25	5.63	5.08	-1
	80 %	2.420	3.68	4.93	5.36	6.14	+1
Dioxane	100 %	5.910	4.13	3.00	2.62	2.34	-1
	80 %	6.420	6.21	5.93	5.86	5.68	0
DMSO	100 %	9.620	9.60	9.66	9.63	9.61	0
	80 %	7.600	7.52	7.49	7.55	7.52	0

The effect of substituents in acetophenone on the rate of phenylhydrazine-acetophenone reaction was studied by varying the solvent composition at fixed concentration of *p*-substituted acetophenone (XAP) and phenylhydrazine (PH). The data are presented in Table-2. [x = methoxy (–OCH<sub>3</sub>), methyl (–CH<sub>3</sub>), fluoro (–F), chloro (–Cl) and nitro (–NO<sub>2</sub>).

TABLE-2  
SUBSTITUENT EFFECT IN PHENYLHYDRAZINE-ACETOPHENONE  
REACTION IN DIFFERENT SOLVENTS  
[PH] = 2 × 10<sup>-2</sup> M, [XAP] = 2 × 10<sup>-4</sup> M, Temperature = 30 °C

Solvent	Rate constants (k <sub>1</sub> × 10 <sup>4</sup> s <sup>-1</sup> )					
	<i>p</i> -OCH <sub>3</sub> AP	<i>p</i> -CH <sub>3</sub> AP	AP	<i>p</i> -FAP	<i>p</i> -ClAP	<i>p</i> -NO <sub>2</sub> AP
100 % Dioxane	2.69	2.81	3.00	3.01	2.90	5.150
100 % DMSO	9.67	9.61	9.66	9.62	9.64	9.790
100 % AcOH	0.83	2.18	3.38	6.16	6.25	15.56
100 % DCA	5.63	5.63	6.25	7.03	7.09	20.09
80 % Dioxane	4.81	5.01	5.93	5.98	6.00	11.41
80 % DMSO	7.45	7.45	7.49	7.53	7.55	11.16
80 % AcOH	0.54	0.71	0.87	3.65	3.81	12.03
80 % DCA	2.38	2.38	4.93	6.43	6.68	16.32

The rate data in different solvent compositions have been fitted into the extended LFER equation,

$$\log \frac{k_x}{K_0} = \rho_I \sigma_I + \rho_R \sigma_R$$

where  $\rho_I$  and  $\rho_R$  values were evaluated and presented in Table-3.

TABLE-3  
 $\rho_I$  AND  $\rho_R$  VALUES FOR THE SUBSTITUTED ACETOPHENONE-  
PHENYLHYDRAZINE REACTION IN DIFFERENT ORGANIC-AQUEOUS MEDIA

Medium	$\rho_I$	$\rho_R$
100 % Dioxane	0.230	0.260
100 % DMSO	0.005	0.007
100 % AcOH	0.800	0.820
100 % DCA	0.560	0.530
80 % Dioxane	0.290	0.340
80 % DMSO	0.170	0.160
80 % AcOH	1.470	0.620
80 % DCA	0.610	0.660

It was inferred from the above table that the electronic effects-*i.e.*, induction and resonance are marginally enhanced when the solvent composition of dioxane and dichloroacetic acid switched over from 100 to 80 %. However, a similar change of solvent medium is accompanied by a pronounced change in both the  $\rho_I$  and  $\rho_R$

magnitudes. It was worthy to note that the higher the polarity of the medium in each of the solvents employed, the magnitudes of  $\rho_I$  and  $\rho_R$  increased and saved the resonance contribution of substituted acetophenones in acetic acid. Thus, it underscores the significance of factors other than a simple alteration of the dielectric constant and polarity of the medium, such as the nature and the actual species of the solvent molecules while considering the solvent influence.

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