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Effect of Ionic Strength on the rate of Acetophenone-Phenylhydrazine reaction

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Abstract: *The effect of ionic strength on the rate of Acetophenone-Phenylhydrazine reaction has been studied by determining the rate in the presence of added neutral salts $NaNO_3$ and NaCl. The kinetics were also carried out for substituted acetophenones with phenylhydrazine in the presence of $NaNO_3$ and NaCl. The rate constants were determined and fitted into extended LFER equation and ρ_I/ρ_R were determined.*

I. Introduction

Phenylhydrazone formation by carbonyl compounds are well known in organic chemistry and are being used to identify the functional groups. Phenylhydrazones show efficient fungicidal activity and are important intermediates in the synthesis of carbazoles, triazoles and some pesticides. Though reports are abundantly available on different methodologies of synthesizing phenylhydrazones, the kinetic details are few and far.

Structural modifications of a reactant molecule may in principle influence the rate or equilibrium constants of a reaction through polar, resonance or steric effects[1]. Linear free energy relationships, notably the Hammett equation, are very important tools for structure-activity correlation[2].

The solvent effect[3]and micellar effect[4]on acetophenone-phenylhydrazine reaction have been studied.

Experimental

Phenylhydrazine and Acetophenones of AR grade (Merck) were used in all the reactions. 80% acetic acid – 20% water solvent media was used throughout the reactions. Phenylhydrazine [PH] of concentration 2 x 10^{-2}M and substituted acetophenones [XAP] of concentration 2 x 10^{-4}M were prepared. Reactions were carried out at 30^{o}C. The kinetics of phenylhydrazine and substituted acetophenones was followed at various concentrations of $NaNO_3$ and NaCl using UV-Visible spectrophotometer (Chemito 2600) at 360nm, which is the characteristic wavelength of corresponding phenylhydrazone product. The initial concentration of acetophenone was fixed at 2 x 10^{-4}M and a sufficient excess of nucleophilic reagent (phenylhydrazine) was employed, so that pseudo first-order rate behaviour was observed. The specific rate constants were calculated from the integrated rate equation:

$$k = \frac{2.303}{t} \log \frac{A\alpha - A_0}{A\alpha - A_t}$$

Where A_0 is the absorbance of the product initially at time (t) = 0 seconds. A_t is the absorbance of the product at time *t* and Aα is the absorbance of the product at α.

II. Results And Discussions

Table – 1

Rate constants (k_1 x 10^4 S^{-1}) for the XAP-PH reaction in the presence of $NaNO_3$

[PH] = 2 x 10^{-2}M Solvent = 80% Acetic acid – 20% Water

[XAP] = 2 x 10^{-4}M Temperature = 30^{o}C.

$NaNO_3$	*p*-OCH_3AP	*p*-CH_3AP	AP	*p*-FAP	*p*-ClAP	*p*-NO_2AP
Nil	0.57	0.71	0.87	3.65	3.81	12.76
0.01	2.25	2.23	2.26	1.36	1.28	8.18
0.02	2.36	2.48	2.30	1.23	1.14	8.08
0.10	2.47	2.52	2.42	1.20	0.89	7.61
0.20	2.50	2.57	2.48	1.15	0.72	7.20

[*p*-OCH $_3$AP - para methoxy acetophenone, *p*-CH_3AP - para methyl acetophenone , parent acetophenone, *p*-FAP para-fluoro acetophenone, *p*-ClAP – para chloro acetophenone, and *p*-NO_2AP – para nitroacetophenone respectively]

The data suggests that the added $NaNO_3$ exhibited a dual behavior – viz with increase in its concentration, increases the rate for electron donating substituents on acetophenone but resulting in a perceptible reduction in rate for reactions with electron withdrawing substituents on acetophenone. The data in Table – 1 have been fitted into the extended LFER equation

$$\log \frac{kx}{k_O} = \rho_I\sigma_I + \rho_R\sigma_R$$

Where kx and k_O are the observed rate constants for the substituted and parent acetophenone respectively, σ_I & σ_R are the respective substituent constants for the inductive and resonance contribution; the ρ_I & ρ_R are the inductive and resonance reaction constant contributions for the overall reaction.

From LFER equation, ρ_I & ρ_R are determined.

Table – 2

ρ_I & ρ_R values for XAP –PH reaction in the presence of $NaNO_3$

[PH] = 2 x 10^{-2}M Solvent = 80% Acetic acid – 20% Water

[XAP] = 2 x 10^{-4}M Temperature = 30^oC.

$NaNO_3$	ρ_I	ρ_R
0.00	1.47	0.62
0.01	0.42	0.73
0.02	0.38	0.76
0.10	0.28	0.81
0.20	0.24	0.87

The trend in the ρ_I & ρ_R in the above table suggests that with increase in [$NaNO_3$], the resonance contribution of the substituent groups moderately increases while their inductive contribution suffers drastically.

The same reactions were repeated in the presence of NaCl and the data was subjected to LFER fit.

Table – 3

ρ_I & ρ_R values for the XAP –PH reaction in the presence of NaCl

[PH] = 2 x 10^{-2}M Solvent = 80% Acetic acid – 20% Water

[XAP] = 2 x 10^{-4}M Temperature = 30^oC.

NaCl	ρ_I	ρ_R
0.00	1.47	0.62
0.10	0.30	0.97
0.20	0.21	1.00

It was observed that an enhanced resonance contribution by the substituents in the presence of NaCl and a dramatic reduction in their inductive contribution, similar to the one observed in the presence of $NaNO_3$.

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