Pergamon

*Tetrahedron*, Vol. 52, No. 10, pp. 3669-3682, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/96 $15.00 + 0.00

S0040-4020(96)00043-9

# Kinetics and Mechanism of Vilsmeier-Haack Synthesis of 3-Formyl Chromones Derived from o-Hydroxy Aryl Alkyl Ketones : A Structure Reactivity Study

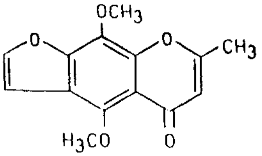
K.C. Rajanna[a*], Florence Solomon[a], Mir Moazzam Ali[a], P.K. Saiprakash[b]

[a]O.U.P.G.School in Applied Chemistry,
Mirzapur (SGD) - 502 249, A.P., (INDIA)

[b]Department of Chemistry, Osmania University,
Hyderabad-500 007 (INDIA)

**Abstract:** Kinetics of Vilsmeier-Haack reaction with o-hydroxy acetophenones (OHAP) have been investigated in different solvent systems comprising either a single component viz., dichloromethane (DCM), dichloroethane (DCE), acetonitrile (ACN), benzene or binary solvent mixtures of benzene and acetonitrile. The study revealed a total second order kinetics with a first order dependence on each of the [reactant] namely, [VH adduct] and [OHAP]. Increase in the dielectric constant (D) of the medium altered the rate of the reaction non linearly. The data did not fit into either Amis or Kirkwood's theories. These results were interpreted in terms of solvent-solute and solvent-cosolvent interactions. Structure-reactivity correlations have been explained by Hammett's equation.

## INTRODUCTION



(I) Khellin

Khellin[1] (Plate I) is the principal constituent of Ammi Visnaga L. It is a 2-methylchromone with a linearly fused furan ring system and has been found to be a potent coronary vasodilator in bronchial action on bronchial muscle, gall bladder and bileduct. Additionally, it has also been used as an anti-spasmodic agent[1-4]. The remarkable physiological activity of khellin prompted several groups of workers to synthesize a large variety of 2- or 3- substituted chromones and other chromone derivatives to study their physiological activity[5-14]. Many of these compounds were also found to exhibit antiallergic, antispasmodic, antiasthmatic, spasmolytic and coronary dilatory activity. In particular acetylchromones and 3-formyl chromones, upon oxidation, have yielded physiologically active 3-hydroxy chromones[5]. It has been previously reported that 3-formylchromones can be synthesised from o-hydroxy arylalkyl ketones by Claisen condensation[5,6,11], in the presence of propionic acid. The intermediate product thus obtained can be cyclised in the presence of triethoxy methane and acetic acid, to give 3-formylchromone.

3-Formylchromones and 3-methyl chromones can be prepared from o-hydroxy acetophenones by Vilsmeier-Haack reaction[15-17] more conveniently than by other existing methods. However, no kinetic study of this reaction has been accomplished so far. This prompted us to take up a detailed kinetic study of Vilsmeier-Haack synthesis of 3-formylchromones from o-hydroxy acetophenones (OHAP) with a view to understanding the mechanistic aspects. Reaction kinetics have been undertaken in variety of solvents with varied dielectric constants (D) viz., dichloromethane, dichloroethane, acetonitrile benzene etc. The study has also been extended with a variety substituted o-hydroxy acetophenones (comprising either electron-releasing alkyl, alkoxy or electron-withdrawing nitro groups) in order to get insight into the nature of reaction.

## RESULTS AND DISCUSSION

### a) Order of the reaction

Kinetics of VH reaction of o-hydroxy phenones revealed first order in [OHAP] as well as [VH adduct] (fig.1). The kinetics of VH-adduct formation[18], however, has earlier been determined and found to exhibit a first order dependence on [DMF] and [$POCl_3$]. The rate of formation of chromone has been found to decrease with a decrease in the dielectric constant (D) of the medium. The rate of the reaction increased significantly with an increase in the percentage of binary solvent mixture (Fig.2 and Tables 1,2).

### b) Reaction species and mechanism

Infrared spectroscopic studies of Arnold and Holy together with electronic spectroscopic results of Marino and Martin's $^{31}P$ nmr studies on VH adducts revealed that a number of covalent and ionic species of VH-adduct exist in solution[18-27] as indicated in structures I-VI.

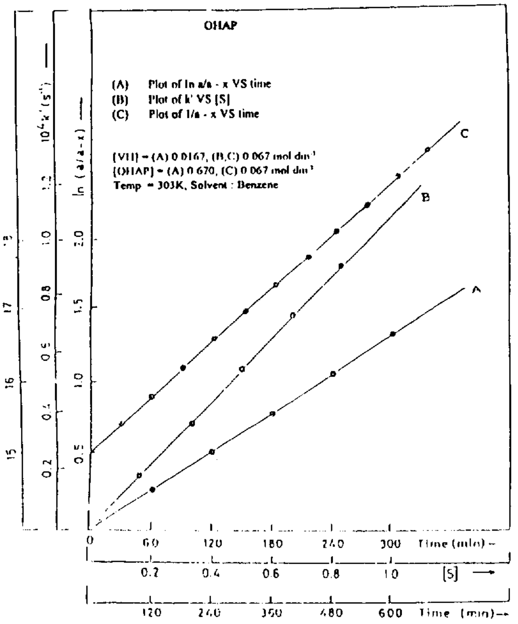
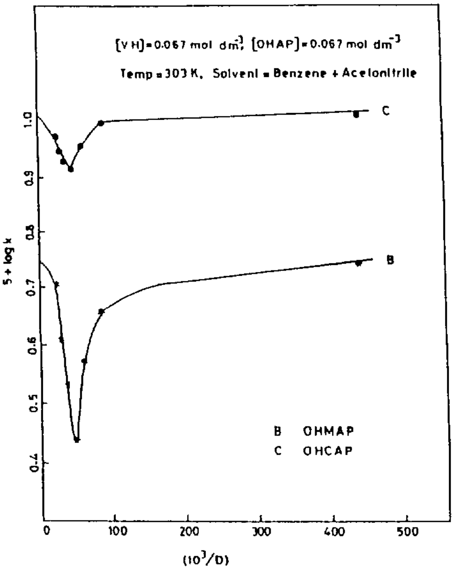


Fig. I

Fig. II Amis' Plots



Plot of log k vs (10³/D)

**Table-1. Second Order Rate Constants and Activation Parameters of VH Reaction with OHAP Compounds**

[VH Reagent] = 0.067 mol dm$^{-3}$, [OHAP] = 0.067 mol dm$^{-3}$,
Solvent Composition (% V/V),
Temp.(K): (A) = 303, (B) = 318, (C) = 333.

| OHAP | $10^4k$ dm$^3$ mol$^{-1}$ s$^{-1}$ | | | $\Delta H^{\#}$ | $\Delta G^{\#}$ | $-\Delta S^{\#}$ |
|---|---|---|---|---|---|---|
| | (A) | (B) | (C) | kJ mol$^{-1}$ | | JK$^{-1}$mol$^{-1}$ |
| Benzene = 15; ACN = 85 | | | | | | |
| p-methoxy | 1.320 | 2.870 | 5.830 | 39.1 | 96.8 | 190 |
| p-methyl | 1.050 | 2.280 | 4.620 | 38.8 | 97.3 | 193 |
| H | 0.818 | 1.720 | 3.430 | 38.0 | 98.0 | 198 |
| m-methyl | 0.877 | 1.890 | 3.850 | 38.7 | 97.8 | 195 |
| m-ethyl | 0.955 | 2.070 | 4.160 | 37.7 | 97.6 | 198 |
| m-chloro | 0.410 | 0.869 | 1.720 | 37.7 | 99.7 | 205 |
| m-nitro | 0.233 | 0.493 | 0.978 | 37.6 | 101.0 | 209 |
| Benzene = 30; ACN = 70 | | | | | | |
| p-methoxy | 1.260 | 2.790 | 5.780 | 40.2 | 96.9 | 187 |
| p-methyl | 0.977 | 2.150 | 4.400 | 39.6 | 97.5 | 191 |
| H | 0.719 | 1.600 | 3.330 | 40.4 | 98.3 | 191 |
| m-methyl | 0.841 | 1.870 | 3.840 | 39.7 | 97.9 | 192 |
| m-ethyl | 0.891 | 1.970 | 4.060 | 39.9 | 97.8 | 191 |
| m-chloro | 0.343 | 0.750 | 1.530 | 39.4 | 100.0 | 200 |
| m-nitro | 0.155 | 0.331 | 0.689 | 39.3 | 102.0 | 207 |
| Benzene = 45; ACN = 55 | | | | | | |
| p-methoxy | 1.200 | 2.610 | 5.310 | 39.0 | 97.0 | 191 |
| p-methyl | 0.933 | 2.020 | 4.090 | 38.9 | 97.9 | 195 |
| H | 0.574 | 1.240 | 2.510 | 38.8 | 98.9 | 198 |
| m-methyl | 0.811 | 1.760 | 3.570 | 38.9 | 98.0 | 195 |
| m-ethyl | 0.849 | 1.840 | 3.740 | 39.0 | 97.9 | 194 |
| m-chloro | 0.274 | 0.590 | 1.190 | 38.7 | 101.0 | 206 |
| m-nitro | 0.110 | 0.237 | 0.478 | 38.5 | 103.0 | 213 |
| Benzene = 60; ACN = 40 | | | | | | |
| p-methoxy | 1.500 | 3.300 | 6.780 | 39.7 | 96.4 | 187 |
| p-methyl | 1.220 | 2.690 | 5.500 | 39.7 | 97.0 | 189 |
| H | 0.870 | 1.930 | 3.980 | 40.0 | 97.8 | 191 |
| m-methyl | 0.918 | 2.040 | 4.210 | 40.1 | 97.7 | 190 |
| m-ethyl | 0.977 | 2.170 | 4.470 | 40.1 | 97.5 | 191 |
| m-chloro | 0.378 | 0.828 | 1.690 | 39.5 | 99.9 | 199 |
| m-nitro | 0.174 | 0.380 | 0.776 | 39.4 | 102.0 | 207 |
| Benzene = 75; ACN = 25 | | | | | | |
| p-methoxy | 1.570 | 3.510 | 7.330 | 40.7 | 96.3 | 183 |
| p-methyl | 1.320 | 2.920 | 5.930 | 40.0 | 96.8 | 188 |
| H | 0.967 | 2.130 | 4.380 | 39.8 | 97.6 | 190 |
| m-methyl | 0.993 | 2.190 | 4.470 | 39.9 | 97.5 | 190 |
| m-ethyl | 1.050 | 2.320 | 4.480 | 40.0 | 97.3 | 189 |
| m-chloro | 0.457 | 1.000 | 2.050 | 39.5 | 99.4 | 198 |
| m-nitro | 0.275 | 0.601 | 1.230 | 39.3 | 101.0 | 204 |

**Table-2. Second Order rate Constants and Activation Parameters of VH Reaction with OHAP Compounds**

[VH Reagent] = 0.067 mol $dm^{-3}$, [OHAP] = 0.067 mol $dm^{-3}$,
Temp.(K): (A) = 303, (B) = 318, (C) = 333.

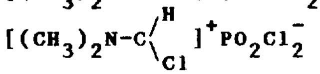
| OHAP | $10^4 k$ $dm^3$ $mol^{-1}$ $s^{-1}$ | | | $\Delta H^{\#}$ | $\Delta G^{\#}$ | $-\Delta S^{\#}$ |
|---|---|---|---|---|---|---|
| | (A) | (B) | (C) | kJ $mol^{-1}$ | | $JK^{-1} mol^{-1}$ |
| Solvent : | Benzene | | | | | |
| p-methoxy | 1.740 | 4.220 | 9.480 | 45.0 | 96.1 | 169 |
| p-methyl | 1.510 | 3.640 | 8.090 | 44.4 | 96.4 | 172 |
| H | 1.080 | 2.560 | 5.600 | 43.4 | 97.3 | 178 |
| m-methyl | 1.180 | 2.830 | 6.320 | 44.6 | 97.1 | 173 |
| m-ethyl | 1.260 | 3.030 | 6.870 | 45.0 | 96.9 | 191 |
| m-chloro | 0.560 | 1.300 | 2.810 | 42.7 | 98.9 | 185 |
| m-nitro | 0.348 | 0.792 | 1.680 | 41.5 | 100.0 | 193 |
| Solvent : | Acetonitrile medium | | | | | |
| p-methoxy | 1.390 | 3.220 | 6.950 | 42.6 | 96.6 | 178 |
| p-methyl | 1.150 | 2.570 | 5.360 | 40.6 | 97.1 | 186 |
| H | 0.832 | 1.830 | 3.740 | 39.6 | 97.9 | 192 |
| m-methyl | 0.933 | 2.060 | 4.230 | 39.8 | 97.6 | 191 |
| m-ethyl | 0.982 | 2.170 | 4.480 | 40.0 | 97.5 | 190 |
| m-chloro | 0.507 | 1.110 | 2.280 | 39.5 | 99.2 | 197 |
| m-nitro | 0.316 | 0.690 | 1.400 | 39.2 | 100.0 | 200 |
| Solvent : | Dichloromethane medium | | | | | |
| p-methoxy | 1.180 | 2.600 | - | 39.0 | 97.0 | 191 |
| p-methyl | 0.923 | 2.020 | - | 38.9 | 97.9 | 195 |
| H | 0.574 | 1.230 | - | 38.8 | 98.9 | 198 |
| m-methyl | 0.810 | 1.740 | - | 38.9 | 98.0 | 195 |
| m-ethyl | 0.842 | 1.820 | - | 39.0 | 97.9 | 194 |
| m-chloro | 0.270 | 0.590 | - | 38.7 | 101.0 | 206 |
| m-nitro | 0.110 | 0.235 | - | 38.5 | 103.0 | 213 |
| Solvent : | Dichloroethane medium | | | | | |
| p-methoxy | 1.250 | 2.790 | 5.780 | 39.1 | 96.8 | 190 |
| p-methyl | 0.970 | 2.150 | 4.400 | 38.8 | 97.3 | 193 |
| H | 0.719 | 1.600 | 3.330 | 38.0 | 98.0 | 198 |
| m-methyl | 0.845 | 1.870 | 3.840 | 38.7 | 97.8 | 195 |
| m-ethyl | 0.890 | 1.970 | 4.660 | 37.7 | 97.8 | 195 |
| m-chloro | 0.340 | 0.750 | 1.530 | 37.7 | 99.7 | 205 |
| m-nitro | 0.150 | 0.331 | 0.689 | 37.6 | 101.0 | 209 |

(I) $[(CH_3)_2N\text{-}CHClOPOCl_2]$

(II) $[(CH_3)_2N\text{=}CHCl]^+[OPOCl_2]^-$

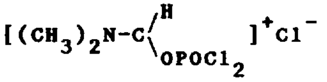
(III) $[(CH_3)_2N\text{=}CH\text{-}OPOCl_2]^+Cl^-$

(IV)



$[(CH_3)_2N\text{-}C\begin{matrix}H\\ Cl\end{matrix}]^+PO_2Cl_2^-$

(V)



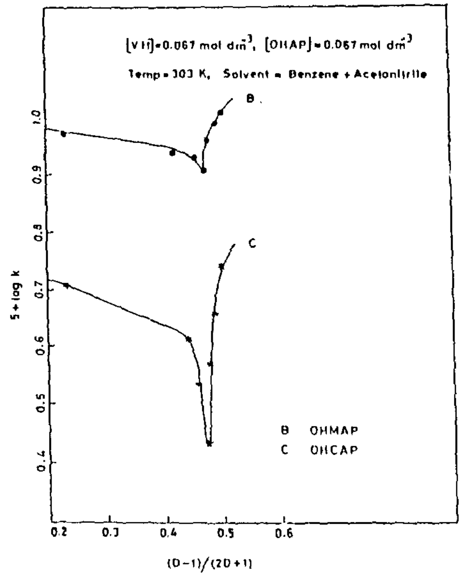
$[(CH_3)_2N\text{-}C\begin{matrix}H\\ OPOCl_2\end{matrix}]^+Cl^-$

(VI) $[(CH_3)_2N\text{-}C^+HCl]$

Solvent effect studies of the present investigation, however, reveal that the second order rate constants decrease gradually with an increase in the percentage composition (V/V and W/W) of benzene (in binary solvent mixtures of benzene and acetonitrile) upto 45% benzene composition and gradually increases. It is also interesting to note that the second order rate constants indicated such a non-linear trend even in pure organic solvents. The order of reactivity has been depicted as : benzene > acetonitrile > dichloroethane > dichloromethane.

The plots of log-rate constant (log k) as a function of composition of benzene (% V/V or % W/W), mole fraction of benzene ($n_x$), 1/D, (D-1)/(2D+1) have been found to be non-linear[28-33] (Figs. 3,4). The log k - percentage composition (V/V, W/W) plots pass through a minimum and have indicated concave (or V-shape) shape curves, while the log k vs 1/D, (log k vs $n_x$) and log k vs [(D-1)/(2D+1)] profiles have depicted typical non-linear curves with steep troughs and crests. Such non-linear plots may probably point to a change in the nature of the reactive species on passing from highly polar acetonitrile solvent to less polar benzene via the binary solvent mixtures. A similar explanation can be offered in pure solvents of different dielectric media passing from acetonitrile to benzene. It is of interest to note that the rate constants in dichloromethane and dichloroethane are entirely different with those in similar isodielectric media (the isodielectric media representing DCM and DCE are obtained by the binary compositions of benzene and acetonitrile). Such descrepancies may probably indicate that solvent-solute or solvent-cosolvent interactions to be operative in the present study apart from the influence of dielectric constant of medium. Mixed aquo-organic solvent effects on organic reactions have often been examined in terms of changes in the activation parameters viz., $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$. The $\Delta H^{\#}$ - $n_x$ and/or $\Delta S^{\#}$ - $n_x$ profiles pass through certain inflexion points and yield non-linear curves as depicted in Fig.5. The data presented in Tables 1,2 also indicate that $\Delta S^{\#}$ values are negative. On the basis of relative magnitudes of $\Delta S^{\#}$ it can be interpreted that the transition state is more structured and the reorganisation of transition state appears to take place with a gradual increase in the composition of

Fig. III Kirkwoods' Plots



Plot of log k vs (D-1)/(2D+1)

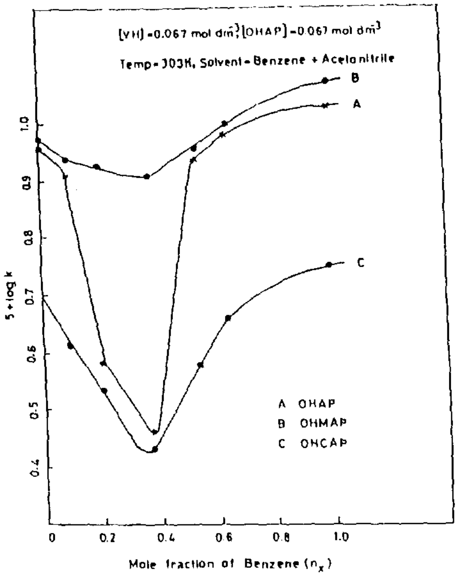


Fig. IV Plot of log k vs mole fraction of Benzene ($n_x$)

non-polar component. The linearity of Leffler and Exner's plots indicate a similar type of mechanism to be operative in all the solvent media at all temperatures[34-38].

However, due to the lack of relevant thermodynamic functions of transfer, detailed analysis of interaction mechanisms between the reactants and transition state and the solvent mixture is not possible. With the available data of activation parameters and their dependence on various physical parameters such as $n_x$, dielectric constant (D) coupled with Hepler's isokinetic plots[39-41], it can be concluded that solvent-solute interaction, solvent structure as well as electrostatic parameters are also important in controlling the reaction[42,43].

The foregoing discussion coupled with the kinetic features of the present study substantiate the participation of either covalent (I) or ion-pair forms (II to V) of VH adduct and OHAP in the high dielectric media. Among the covalent (I) and ion-pair species (II-V) of VH-adducts, ion-pir (V) was supported by Marino etal[18] on the basis spectroscopic and thermodynamic evidence[19,26]. Hence, in high dielectric media, participation of ion-pair species of VH adduct (V) and OHAP with the elimination of HCl has been proposed in the slow step to give phosphorous oxychloro methyliminium intermediate (B). However, in low dielectric media, participation of cationic form of VH adduct (VI) and OHAP with the elimination of $H^+$ and to give chloromethyliminium intermediate (A), has been proposed. The intermediate species (A or B) thus obtained in path A or B, upon hydrolysis (when the reaction mixture is transferred into water) yield end products. A detailed mechanism is given in Scheme-1.

For the mechanism given in Scheme-1, the rate law is

$$\frac{-d[\text{OHAP}]}{dt} = k\,[\text{VH adduct}]\,[\text{OHAP}] = kK[\text{DMF}][\text{POCl}_3][\text{OHAP}]$$

c) Structure reactivity study

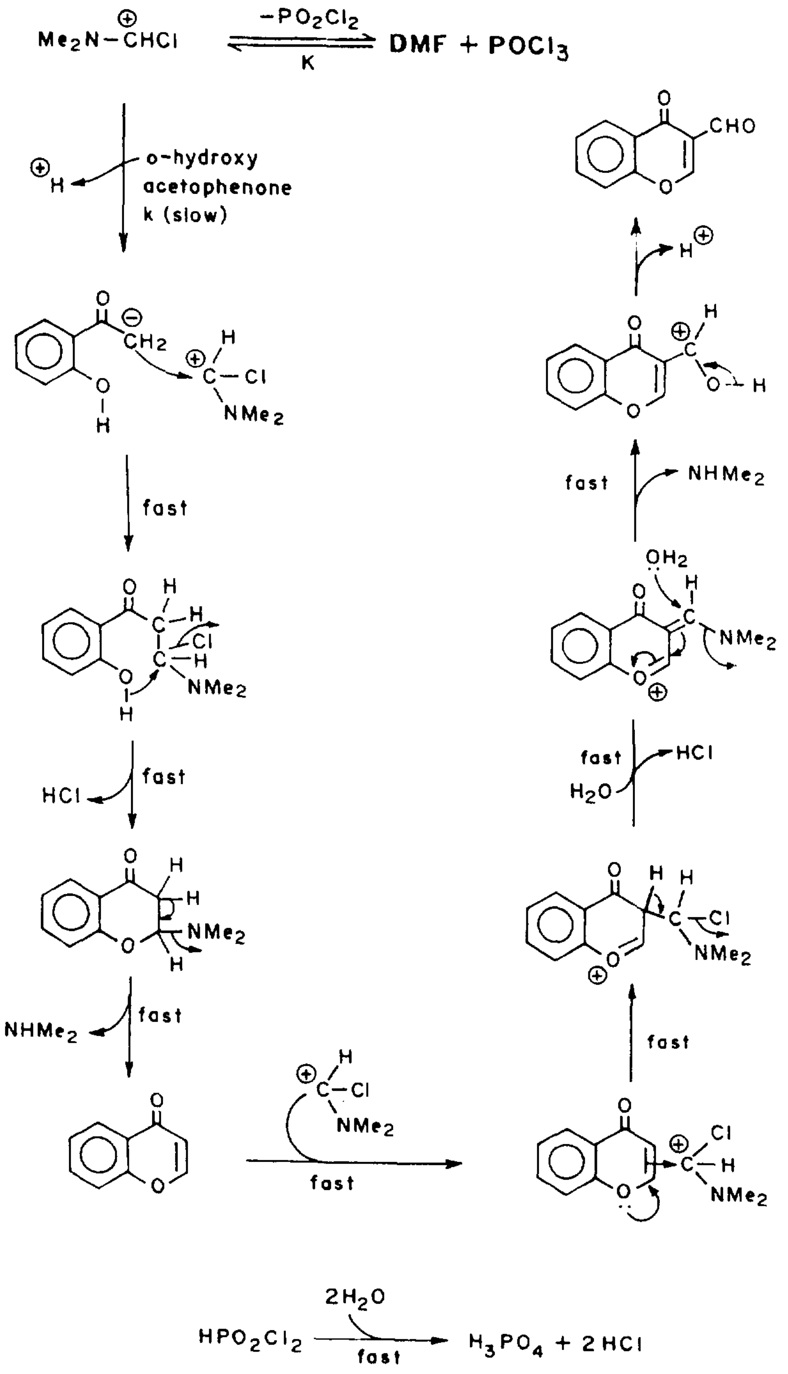
In order to understand the effect of structure on the reactivity of OHAP, the study has been done with five different OHAP compounds. Reactivity of OHAP compounds indicated that the rates are accelerated by electron-donating groups and decelerated by withdrawing groups.

Plots of $\log(k/k_o)$ Vs Hammett's $\sigma$ yielded a good correlation in all the solvent media (Table 3). The $\rho$ values obtained are in accordance with the electrophilic substitution reactions[34].

d) Activation parameters

In order to have a better understanding about the controlling factors of reaction viz., enthalpy or entropy, the thermodynamic data have been

SCHEME - 1 PATH A



**SCHEME 1 PATH B**

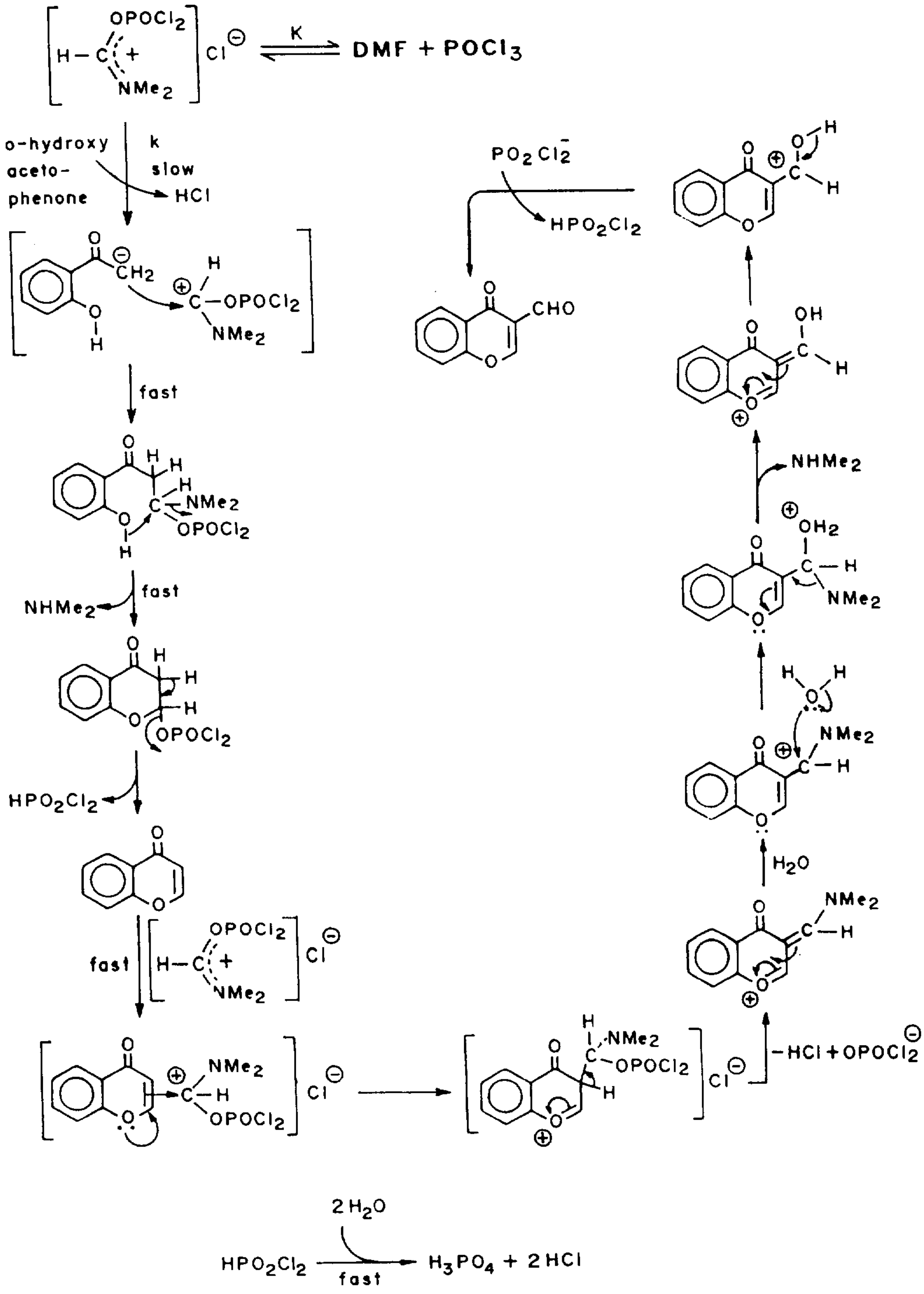


Fig. V Solvent effects on activation parameters of OHAP.

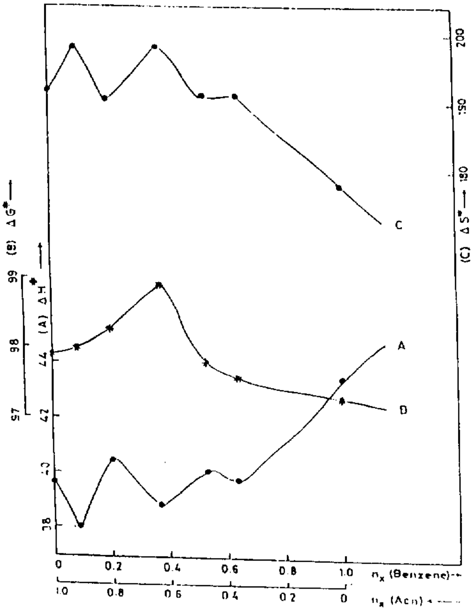


Table-3. Variation of Reaction Constant for VH Reaction of O-Hydroxy Acetophenones

| Solvent Composition (%) | | Temperature (K) | |
|---|---|---|---|
| ACN | Ben | 303 | 333 |
| 100 | 0 | - 0.576 | - 0.600 |
| 85 | 15 | - 0.791 | - 0.769 |
| 70 | 30 | - 0.877 | - 0.963 |
| 55 | 45 | - 0.858 | - 1.015 |
| 40 | 60 | - 0.973 | - 1.000 |
| 25 | 75 | - 0.903 | - 0.778 |
| 0 | 100 | - 0.863 | - 0.737 |
| DCM (only) | - | - 0.860 | - 1.020 |
| DCE (only) | - | - 0.800 | - 0.768 |

Table -4. Iso Kinetic Temperature

| Solvent Composition (%V/V) | | Leffler | Exner |
|---|---|---|---|
| ACN | Ben | | |
| 85 | 15 | 75.00 | 78.00 |
| 40 | 60 | 215.00 | 216.00 |
| Nil | 100 | 155.00 | 160.00 |
| 100 | Nil | 110.00 | 105.00 |
| DCM (only) | - | 185.00 | 180.00 |
| DCE (only) | - | 160.00 | 158.00 |

tested by Leffler's relationship[35]. According to this relationship, plot of $\Delta H^{\#}$ Vs $\Delta S^{\#}$ should be linear with a slope equal to isokinetic temperature ($\beta$). The values obtained by this method are confirmed by Exner's treatment. By-and-large, the $\beta$-values agree with one another (Table 4). Since the $\beta$-values are much below the experimental temperature range, it appears that reactions are entropy controlled.

Further, linearity of Exner's plots[36], log k at $T_1$ versus logk at $T_2$, indicate a similar type of mechanism to be operative in all the systems at different temperatures.

## EXPERIMENTAL DETAILS

*o*-Hydroxy acetophenones were prepared either according to standard procedures or procured from Aldrich/Fluka-AG. The liquid reactants are distilled and solids are recrystallised before use.

Dichloromethane (DCM), dichloroethane (DCE), acetonitrile (ACN), dimethylformamide (DMF) and benzene were either HPLC grade or were distilled according to standard literature procedures[44]. Phosphorus oxychloride (Fluka-AG) was also distilled according to literature procedures[45]. The Vilsmeier-Haack reagent (VHA) was always prepared fresh just before use and the content checked by acid-base titrations according to literature reports[18-22].

Progress of the reaction was followed by estimating the unreacted [VHA] at regular intervals. Aliquots of the reaction mixture were transferred to 25 $cm^3$ of hot distilled water. VHA ($DMF/POCl_3$) hydrolysis to give a mixture of phosphoric and hydrochloric acid. Acid content, thus obtained, was estimated by standard alkali using phenolphthalein as indicator[20-25].

## CONCLUSIONS

Vilsmeier-Haack reaction with *o*-hydroxy arylketones (OHAK) in non-aqueous solvents has exhibited first order in [VHA] and [OHAK]. Reactions have been found to be in the increasing order : benzene > acetonitrile > dichloro ethane > dichloro methane. Rate limiting steps with the participation of $[(CH_3)_2N\text{-}CHCl]^+$, OHAK in low dielectric media and $[(CH_3)_2N\text{-}CH(OPOCl_2)]^+[Cl^-]$, OHAK in high dielectric media, have been proposed to explain the kinetic behaviour.

*Acknowledgements*. The authors thank University Grants Commission, New Delhi, for financial support. The authors are grateful to Prof. T. Navaneeth Rao, former Vice-Chancellor, Osmania University, Hyderabad, for constant encouragement.

## REFERENCES

1. Spath, E. and Grumber, W., Ber, 1938, 71, 106.
2. Geissmann, T.A. and Halshall, T.G., J. Am. Chem. Soc., 1968, 73, 1280.
3. Clarke, J.R. and Robertson, A., J. Chem. Soc., 1949, 302
4. Murthy, V.V.S. and Sheshadri, T.R., J. Scient. Ind. Res., 1949, 8B, 112.
5. Chandra Prakash Reddy, K., "Studies on synthetic and natural hetero- cyclics of physiological interest", Ph.D. thesis, Osmania University, Hyderabad, (1983).
6. Ellis, G.P., "Chromones, Chromanones and Chromenes", John Wiley and Sons, New York, 1977.
7. Schonberg, A. and Sinha, A., J. Am. Chem. Soc., 1950, 72, 1611.
8. Fitzmaurice, C. and Wragg, A.H., Chem. Abstr., 1966, 65, 3844.
9. Clarke, F.H., "Annual reports in medicinal chemistry", Academic Press, New York, 1967, 3; 1970, 12; 1981, 16.
10. Darbarwar, M., Murthy, V.S. and Subba Rao, N.V., Indian J. Chem., 1973, 11, 850.
11. Moznigo, R., Organic Synthesis, 1955, 3, 387.
12. Kostanecki, S.V. and Rozycki, A., Ber., 1901, 34, 102, 2942.
13. Vonstrandfmann, M., Kluchlo, S., Coher, M.P. and Shavel, J., J. Heterocyclic Chem., 1972, 9, 171; 1974, 11, 183.
14. Dorofenko, G.N. and Mezheritskii, V.V., J. Org. Chem., (U.S.S.R.), 1968, 4, 1260.
15. Harnish, V.H. and Liebigs, M., Ann. Chem., 1972, 765, 8.
16. Nohara, A., Umetani, T. and Sanno, Y., Tetrahedron Lett., 1973, 1995.
17. Bass, R.J., J. Chem. Soc. (C), 1976, 78.
18. Marino, G., Alunni, S., Linda, P., Santini, S. and Savelli, S., J. Chem. Soc., Perkin Trans II, 1972, 2070.
19. Martin, G.J., Poignant, S., Filleux, M.L. and Quemeneur, M.T., Tetrahedron Lett., 1970, 58, 5061.
20. Arnold, Z. and Holy, A., Collect. Czech. Chem. Commn., 1962, 27, 2886 and references therein.
21. Smith, T.D., J. Chem. Soc. (A), 1966, 841.
22. Anderson Jr., A.G., Owen, N.E.T., Franon, F.J. and Ereckson, D., Synthesis, 1966, 398.
23. Linda, P., Luccarelli, A., Marine, G. and Savelli; J. Chem. Soc., Perkin Trans.II, 1972, 1610 and references therein.

24. Martin, G.J. and Poignant, S., J. Chem. Soc., Perkin Trans.II, 1972, *11*, 1964.
25. Marino, G., Adv. Heterocyclic Chem., 1971, *13*, 235.
26. Filleux-Blanchard, M.I., Quemeneur, M.T. and Martin, G.J., Chem. Comm., 1968, 836.
27. Taylor, E.C., "Advances in Organic Chemistry", (Part I and II), John Wiley and Sons Inc., New York (1979).
28. Amis, E.S., "Solvent effects on reaction rates and mechanisms", Academic Press, London (1966).
29. Kirkwood, J.G., J. Chem. Phys., 1934, *2*, 351.
30. Ingold, C.K., "Structure and Mechanism in Organic Chemistry", Bell, London, 1953, 324.
31. Irving, H. and Rossetti, H., Acta Chem. Scand., 1956, *10*, 72.
32. Brown, D.A. and Hudson, R.F., J. Chem. Soc., 1953, 883, 3352.
33. Born, M., *Z. Physic*., 1920, *1*, 45.
34. Hammett, L.P., "Physical Organic Chemistry", McGraw Hill, Kogakusa Ltd., Tokyo, (1970).
35. Leffler, J., J. Org. Chem., 1955, *20*, 1202.
36. Exner, O., Collect. Czech. Chem. Commn., 1972, *37*, 1425.
37. Peterson, P.C., J. Org. Chem., 1964, *29*, 3133.
38. Blackadder, D.A. and Hinshelwood, C.N., J. Chem. Soc., 1958, 2720, 2728.
39. Hepler, L.G., J. Am. Chem. Soc., 1963, *85*, 3089.
40. Laidler, K.J., Trans. Faraday Soc., 1959, *55*, 1725.
41. Ritchie, G.D. and Sagar, W.F., Prog. Phys. Org. Chem., 1964, *2*, 223.
42. Helmi Neuvonon, J. Chem. Soc., Perkin Trans II, 1987, 1723 and references therein.
43. Harned, H.S. and Owen, B.B., "The Physical Chemistry of electrolytic solutions", Reinhold publications corpn., New York (1950).
44. Riddik, J.A. and Berger, W.B., "Technique of Organic Chemistry", Vol.II (Organic Solvents), Wiley Interscience, New York (1970).
45. Vogel, A.I., "A Text Book of Practical Organic Chemistry", 4th ed., Longman Group Ltd., London, (1978).

(*Received in UK* 19 *September* 1995; *revised* 10 *January* 1996; *accepted* 11 *January* 1996)