A Kinetic and Synthetic Approach of Surfactants Accelerated by Vilsmeier-Haack Acetylation and Formylation with Anisole

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Abstract

Introduction: Vilsmeier-Haack (VH) reactions are mostly too slow even at higher temperatures. However, quick and easy transformation was observed in micellar media even at moderate temperatures. **Materials and Methods:** Different types of surfactants (anionic – sodium dodecyl sulfate, cationic – cetyltrimethyl ammonium bromide, and non-ionic – T X-100) are used as micelle forming compounds. **Results and Discussion:** Micellar-mediated reactions exhibited dramatic rate accelerations and improvements in the yield of end products. The VH reactions pursued pseudo-first- and second-order kinetics. **Conclusion:** This study with anisole is the first such report demonstrating a feasible, controllable, non-toxic, and easy methodology for the synthesis of formylated and acetylated derivatives and a study of their kinetic behavior.

Key words: Vilsmeier-haack reaction, anisole, kinetics, acetylation, surfactants

INTRODUCTION

The well-known Vilsmeier-Haack (VH) reaction is a versatile tool for the introduction of formyl or equivalent groups onto a diverse group of organic substrates such as heterocyclic compounds, alkene derivatives, aldehydes and ketones, carboxylic acids, amides, lactams, lactones, nitriles, benzylic, methyl, and methylene groups.[1-9] Micelles are supramolecular aggregates of colloidal size, which possess a hydrophobic non-polar head and hydrophilic polar group. The hydrophobic non-polar group has alkyl hydrocarbon chain, which occupies the interior of surfactant whereas hydrophilic polar group occupies the surface. Micellization of surfactants varies in polar and non-polar solvents due to solute-solute, solvent-solvent, and solute-solvent interactions.[10,11] In non-aqueous solvents, surfactant reverse their character, that is, polar head protrude into the interior part and the hydrocarbon chain diverts toward the micelle-solvent interface.

Several reports on micellar-mediated reactions are known but kinetics and mechanistic studies under VH conditions appeared to be scanty. For the past two decades, our group is actively involved in the studies of VH reactions[12] and micellar-mediated organic transformations.[13] Recently, Shetty *et al.* reported the kinetics analysis and reaction mechanism for anisole over zirconia-supported molybdenum oxide.[14]

Anisole is widely used in the manufacturing of fragrant, human and veterinary medicines, and phenol-formaldehyde

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resins and related materials and as a feedstock for industrial organic synthesis.[15] Kirichenko *et al.* employed some oxide catalysts and zeolites to study the vapor-phase alkylation of phenol with methanol to produce anisole.[16] The synthesis of anisole by vapor-phase methylation of phenol with methanol overactivated alumina-supported catalysts was investigated in a fixed bed reactor. KH_2PO_4/Alumina gave the best performance among the eight tested catalysts.[17] The author has taken up VH reactions with DMF/$POCl_3$ and DMA/$POCl_3$ adduct in non-aqueous solvent media such as acetonitrile (ACN) and dichloroethane (DCE) with and without cationic surfactant cetyltrimethyl ammonium bromide (CTAB), anionic surfactant sodium dodecyl sulfate (SDS), and non-ionic surfactant (Triton-X 100 and TX-100). The study is also aimed to examine kinetic and mechanistic features in addition to synthetic features of activated and deactivated anisoles. The author herein reports one such attempt made to explore the trends observed in controlling the rate of reaction. Anisole and substituted anisoles were chosen as substrates due to their active role as lead compound in pharmaceutical manufacturing.

MATERIALS AND METHODS

Experimental

KH_2PO_4 (S.D. Fine, India), Alumina (S.D. Fine, India), DMF (Sigma-Aldrich, Germany), $POCl_3$ (Sigma-Aldrich, Germany), DMA (Sigma-Aldrich, Germany), ACN (SRL, India, 99.9%), DCE (SRL, India, 99%), CTAB (BDH, UK, 99%), SDS (Sigma, USA, 99%), and Triton-X 100 or Tx-100 (Fluka, Switzerland, 99%).

RESULTS AND DISCUSSION

Salient features of the kinetic study

The interesting feature of these reactions is that they follow both second-order and pseudo-first-order kinetics. Second-order kinetics was followed when $[\text{VH reagent}]_o = [\text{substrate}]_o$ and pseudo-first-order kinetics under the conditions $[\text{Substrate}]_o >> [\text{VH reagent}]_{o,}$ typical plots 1/Vt versus time are given for VH formylation and acetylation which are straight line having a positive slope and definite intercept indicate overall second-order kinetics. On the contrary, Figures 3 and 4 are pseudo-first-order plots $\ln(V_o/V_t)$ versus time, which are linear with positive slope (k pseudo-first-order rate constant values), passing through origin depicting first-order dependence on [VH reagent].

Reaction rates were generally increased with an increase in temperature. Activation parameters such as enthalpy of activation ($\Delta H^\#$) and entropy of activation ($\Delta S^\#$) were obtained from Eyring plots of ln(k/T) versus temperature, as shown in Figures 5 and 6. Free energy of activation was calculated using Gibbs-Helmholtz equation. Data pertaining to activation parameters are compiled in Tables 1 and 2. Cipciani *et al.* obtained acetyl derivatives during their study on VH reaction with indoles and carbazoles. The observed rate data were processed with semi-quantitative theories developed by Amis, Kirkwood, Irving, and Rossetti[18] to ascertain the type of reactive species. Eyring plots of ln (k/T) versus temperature were used to determine the enthalpy of activation ($\Delta H^\#$) and entropy of activation ($\Delta S^\#$). The rate constant k_ψ was plotted as a function of [surfactant] or (C_D). Experimental results revealed different types of

Table 1: Temperature dependent rate constants and activation parameters for VH formylation reactions with anisoles

1	2	$10^4 k$ ($dm^3\ mol^{-1}s^{-1}$)			$\Delta H^\#$	$\Delta G^\#$	$\Delta S^\#$	Solvent
		313 K	323 K	333 K	(JK^{-1}/mol)	(kJ/mol)	(JK^{-1}/mol)	
1a	2a	1.45	2.24	3.45	52.3	97	−142	ACN
1b	2b	1.62	2.08	2.71	39.6	101	−196	ACN
1c	2c	3.33	5.59	5.80	54.2	97	−138	ACN
1d	2d	1.76	4.82	12.42	85.6	101	−50	ACN
1e	2e	0.46	1.78	6.35	22.5	97	−237	ACN
1f	2f	2.16	3.92	6.84	97.7	100	−10	ACN
1a	2a	1.28	2.49	4.43	92.6	102	−32	DCE
1b	2b	3.13	4.56	6.47	37.1	99	−196	DCE
1c	2c	3.31	6.32	1.16	32.5	100	−215	DCE
1d	2d	3.81	5.10	6.71	93.8	100	−21	DCE
1e	2e	3.63	5.86	9.1	82.9	99	−54	DCE
1f	2f	4.43	6.02	8.07	73.6	98	−77	DCE

ACN: Acetonitrile, DCE: Dichloroethane

profiles sigmoid curves, bell type, valley type, straight lines with positive or negative slopes, or wavy type curves in many cases. These profiles could be conveniently treated with Piszkiewicz's cooperativity approach[19] to evaluate the aggregation (index) numbers. In the present study, five types of k_{Ψ}-C_D profiles were observed Type A, B, C, D, and E [Figures 7-14]. All the figures are provided in the supplementary information.

Mechanistic aspects

A significant feature of the current study is the remarkable acceleration in rates of micellar mediated acetylation and formylation. The reaction time is reduced from 6 h to 60 min in presence of micelles under thermal conditions. The reaction times and yield (%) of the products for micellar catalyzed and uncatalyzed reactions are presented in Tables 3 and 4. According to literature reports by Louis Hammett,[20] VH adduct exists as covalent, ion pair, and ionic species. This trend was observed for SDS, CTAB, and TX-100 micellar media. It was proposed that the rate enhancements could be due to reactions occurring in polar cavity. An orderly constant arrangement of monomer-dimer-trimer in contradiction to the monomer ↔ n-mer equilibria could also be considered in non-aqueous media which were generally observed in aqueous micellar system as reported by Fendler.[21] Micelle

Table 2: Temperature-dependent rate constants and activation parameters for VH acetylation reactions with anisoles

1	2	10^4k (dm^3 mol^{-1}s^{-1})			ΔH$^{\#}$	ΔG$^{\#}$	ΔS$^{\#}$	Solvent
		313 K	323 K	333 K	(JK^{-1}/mol)	(kJ/mol)	(JK^{-1}/mol)	
1a	3a	4.11	7.86	14.7	34.6	99	−208	ACN
1b	3b	2.84	9.08	1.05	36.8	98	−196	ACN
1c	3c	0.40	1.43	4.74	19.4	99	−255	ACN
1d	3d	0.76	2.17	5.86	81.7	99	−55	ACN
1e	3e	4.25	5.78	7.67	110	102	−25	CAN
1f	3f	0.90	2.98	9.23	46.9	98	−165	ACN
1a	3a	0.43	1.35	3.96	50.6	100	−157	DCE
1b	3b	1.33	2.03	3.01	50.9	97	−146	DCE
1c	3c	2.69	10.05	37.73	28.5	98	−221	DCE
1d	3d	1.10	3.48	10.28	21.7	97	−241	DCE
1e	3e	1.39	3.87	10.05	36.8	97	−235	DCE
1f	3f	2.36	5.89	13.85	23.2	97	−235	DCE

ACN: Acetonitrile, DCE: Dichloroethane

Table 3: Yield of VH formylation with anisoles[a]

1	2	Uncatalyzed (6 h)	SDS (1.5 h)	CTAB (1.5 h)	Tx-100 (1.5 h)	Solvent
		Yield[ab] %	Yield[ab] %	Yield[ab] %	Yield[ab] %	
1a	2a	27	51	40	71	ACN
1b	2b	30	46	57	63	ACN
1c	2c	40	49	61	65	ACN
1d	2d	22	49	46	50	ACN
1e	2e	20	35	49	41	ACN
1f	2f	42	56	60	75	ACN
1a	2a	40	61	51	63	DCE
1b	2b	30	64	46	60	DCE
1c	2c	40	49	69	76	DCE
1d	2d	22	58	68	75	DCE
1e	2e	20	64	80	70	DCE
1f	2f	44	54	67	72	DCE

[a]All products are characterized by comparison of their m.p., IR, 1 H NMR, and mass spectra. [b]Isolated yields after column chromatography on silica gel. ACN: Acetonitrile, DCE: Dichloroethane, CTAB: Cetyltrimethyl ammonium bromide, SDS: Sodium dodecyl sulfate

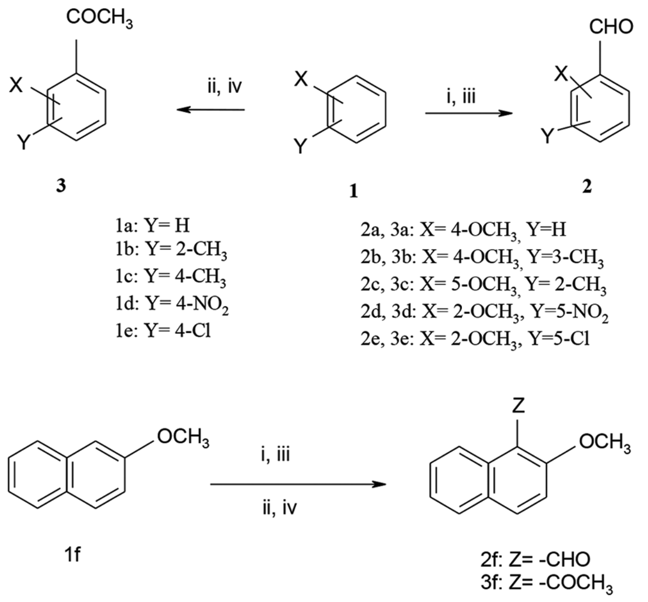
Table 4: Yield of VH acetylation with anisoles[a]

1	3	Uncatalyzed (6 h)	SDS (1.5 h)	CTAB (1.5 h)	Tx-100 (1.5 h)	Solvent
		Yield[ab] %	Yield[ab] %	Yield[ab] %	Yield[ab] %	
1a	3a	21	57	61	60	ACN
1b	3b	36	48	73	63	ACN
1c	3c	20	43	62	58	ACN
1d	3d	19	52	65	71	ACN
1e	3e	20	59	43	65	ACN
1f	3f	33	72	78	74	ACN
1a	3a	19	36	51	57	DCE
1b	3b	36	63	48	56	DCE
1c	3c	20	58	56	60	DCE
1d	3d	19	65	33	49	DCE
1e	3e	20	85	57	65	DCE
1f	3f	43	58	50	54	DCE

[a]All reactions were carried out at room temperature. [b]Isolated yields after column chromatography on silica gel. ACN: Acetonitrile, DCE: Dichloroethane, CTAB: Cetyltrimethyl ammonium bromide, SDS: Sodium dodecyl sulfate

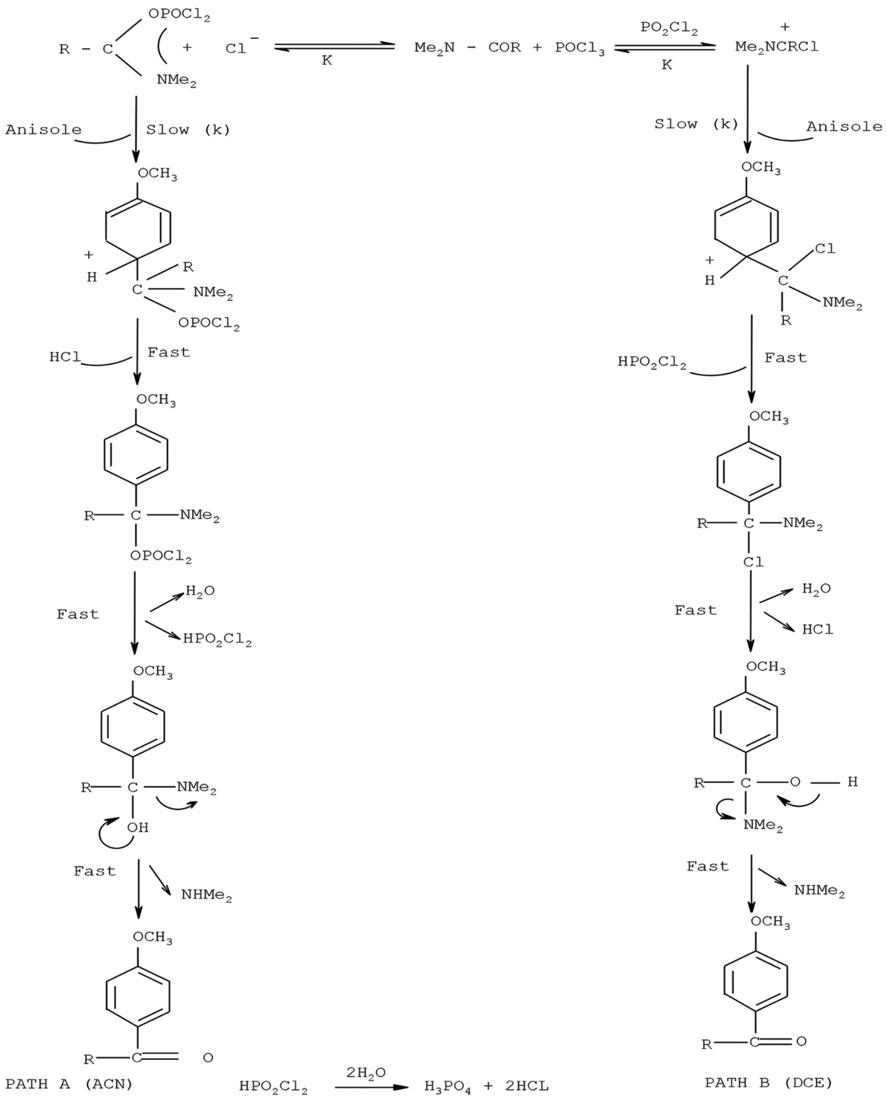
formation takes place only if there is disparity in solubility, that is, when one ion is soluble and its counter ion insoluble in organic solvent. On the contrary, equilibrium of hydrophobic-lipophilic groups is an important factor in determining the micellization of non-ionic surfactants. Interactions between hydrophobic groups assist formation of reversed micelles while hindrance in micellization is produced due to synergy among the polar part of the surfactant and the solvent. Therefore, similar contentions were made regarding mechanistic aspects in this part of the study, as shown in Scheme 1.

It was also observed that lower concentration range of k_ψ versus C_D profile indicates the rate enhancement even though the profiles are wavy at higher concentrations. In view of this, lower concentration of surfactant is used in synthetic studies. The wavy nature of the k_ψ-C_D profiles in a number of reactions may be due to the (1) formation of more than 1 micelle with different critical micellar concentration values and with different aggregation number, (2) due to the formation of rod or thread-like unsymmetrical or non-spherical structures of micelles in which interior part is polar and exterior is non-polar, and (3) also due be to the formation of cationic as well as dipolar VH species with substrate in the rate-determining step as proposed by a detailed mechanism in Scheme 2.



Scheme 1: Reagents and conditions (1) DMF/$POCl_3$ (1 equivalent), 6 h, rt; (ii) DMA/$POCl_3$ (1 equivalent), 6 h, rt; (iii) DMF/$POCl_3$ (1 equivalent), cetyltrimethyl ammonium bromide (CTAB) or sodium dodecyl sulfate (SDS) or Tx-100, 1 h, rt; (iv) DMA/$POCl_3$ (1 equivalent), CTAB or SDS or Tx-100, 1 h, rt

A detailed study has also been taken up in mixed micellar media under varied conditions to gain an insight into the factors affecting the reaction rates. It was found that the kinetic features of VH transformations were similar to those in single surfactant media. Representative data are presented in Tables 5 and 6. A perusal of the kinetic results in mixed micellar media reveals that the reaction rates are generally less in mixed micellar media compared to those in a medium of single surfactant. The kinetic study was also taken up in binary solvent mixtures of DCE and ACN solvents to gain an insight into the nature of reactive substrate and VH adduct species. Variation in composition of binary solvent mixture resulted in the variation of dielectric constant (D) of the medium [Table 7]. Remaining provided in supplementary information.



Scheme 2: Proposed mechanism of Vilsmeier-Haack reactions for anisoles

Table 5: Effect of simultaneous variation of surfactants in mixed micellar VH* transformations

S. No.	10^3 [SDS] 10^3[Tx] (mol dm^3) VHF		10^4 k^3 (dm^3/mol/s)		10^3 [Tx] 10^3[CTAB] (mol dm^3)VHF (moldm^3)		10^4 k^3 (dm^3/mol/s)	
			VHF	(mol dm^3)			VHF	(mol dm^3)
1a	1.25	11.25	0.76	3.68	1.25	11.25	2.04	2.27
	2.50	10.0	0.60	1.40	2.50	10.0	1.19	2.69
	5.00	7.50	1.52	1.52	5.00	7.50	1.06	2.22
	7.50	5.00	1.28	1.18	7.50	5.00	1.59	2.43
	10.0	2.50	0.96	0.81	10.0	2.50	1.06	2.72
	11.25	1.25	0.41	0.68	11.25	1.25	1.15	1.97
1c	1.25	11.25	0.90	1.07	1.25	11.25	4.38	0.35
	2.50	10.0	0.67	1.89	2.50	10.0	2.55	0.60
	5.00	7.50	0.21	3.93	5.00	7.50	2.23	0.39
	7.50	5.00	0.22	2.17	7.50	5.00	0.85	0.54
	10.0	2.50	0.183	2.17	10.0	2.50	1.63	0.48
	11.25	1.25	0.28	1.27	11.25	1.25	2.12	0.41

*[VHR] = 0.10 mol dm^3 ; [substrate] = 0.10 mol dm^3; solvent=DCE ; Temp=323 K. DCE: Dichloroethane, CTAB: Cetyltrimethyl ammonium bromide, SDS: Sodium dodecyl sulfate

Table 6: Effect of second [surfactant] in mixed micellar media
[VHR]=[DMF/$POCl_3$]=0.01 mol dm^3; [substrate]=0.10 ml dm^3; [solvent]=DCE; Temp=323 K

S. No.	(A) [CTAB] = 2.5 mM				(B) [SDS] = 2.5 mM				(C) [Tx] = 2.5 mM			
	[SDS] 10^4 k_Ψ [Tx] $10^4 k_\Psi$ (mM) (mM)				[Tx] 10^4 k_Ψ [CTAB] $10^4 k_\Psi$ (mM) (mM)				[CTAB] 10^4 k_Ψ [SDS] $10^4 k_\Psi$ (mM) (mM)			
1a	1.25	2.55	1.25	0.12	1.25	0.76	1.25	4.01	1.25	1.18	1.25	3.68
	2.50	1.77	2.50	1.38	2.50	0.60	2.50	3.66	2.50	1.38	2.50	1.40
	6.25	3.43	6.25	0.83	6.25	1.52	6.25	5.03	6.25	1.20	6.25	1.18
	12.5	1.56	12.5	1.26	12.5	1.28	12.5	3.60	12.5	1.07	12.5	0.81
1c	1.25	7.69	1.25	4.38	1.25	5.42	1.25	0.10	1.25	4.38	1.25	0.90
	2.50	2.14	2.50	2.55	2.50	1.37	2.50	0.16	2.50	2.55	2.50	0.66
	6.25	0.27	6.25	2.23	6.25	1.19	6.25	0.17	6.25	2.23	6.25	0.21
	12.5	0.52	12.5	2.12	12.5	1.21	12.5	0.16	12.5	2.12	12.5	0.28

mM=10^{-3} mol dm^{-3}; units of k_ψ: dm^3/mol/s. DCE: Dichloroethane, CTAB: Cetyltrimethyl ammonium bromide, SDS: Sodium dodecyl sulfate

Table 7: Effect of variation of solvent composition on the rate of VH reactions*

% composition (V/V)		10^4 k (dm3/mol/s)			
ACN	DCE	1b	1c	1d	1e
(A) VHR= [DMF+$POCl_3$] (1:1)					
0.0	100.0	21.6	11.8	3.70	4.91
20.0	80.0	18.5	11.2	1.98	4.97
40.0	60.0	8.17	11.3	1.13	1.24
60.0	40.0	4.69	0.26	4.35	1.05
80.0	20.0	2.77	2.13	4.85	6.09
100.0	0.0	3.04	0.46	4.80	6.02
(B) VHR = [DMA+$POCl_3$] (1:1)					
0.0	100.0	3.32	5.43	0.83	0.82
20.0	80.0	1.64	1.70	0.99	0.75
40.0	60.0	1.01	2.40	0.87	0.52
60.0	40.0	1.15	0.90	0.19	0.61
80.0	20.0	0.65	0.73	0.28	0.55
100.0	0.0	0.42	0.07	0.14	0.65

*[VHR] =0.100 mol dm^{-3}; [Sub] = 0.100 mol dm^{-3}; Temp = 323 K

CONCLUSION

It has been investigated that the Vilsmeier-Haack acetylation and formylation can be efficiently executed under micellar catalyzed system. A complete elaborate study was performed embroiling reaction time (t), temperature (T), solvent (DCE/ACN), VH reagent (DMF+$POCl_3$ and DMA+$POCl_3$), and micelles (CTAB, SDS, and TX-100) as framework. There was acceleration in micellar-mediated reactions from several hours to 60 min under thermal conditions. Successful acetylation and formylation of several substituted anisoles were also demonstrated favorably well and it can be concluded that apart from electrostatic and non-electrostatic factors, solvent-solute interactions, solvent-structure, and solvent-cosolvent interactions were also important.

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