Vilsmeier–Haack Formylation of Coumarin Derivatives. A Solvent Dependent Kinetic Study

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ABSTRACT

A kinetic study of the reaction of coumarin derivatives with Vilsmeier–Haack (VH) reagent (1:1 DMF-POCl₃) in various solvent media revealed second-order kinetics with a first-order in [Substrate] and first-order in [VH reagent]. The reaction rates altered nonlinearly with an increase in the dielectric constant of the medium and the data did not fit completely well with either Amis or Kirkwood's theories of ion–dipole and dipole–dipole type reactions. On the basis of kinetic and spectroscopic results, participation of VH-adduct and coumarin molecule in the rate limiting step, has been proposed. Kinetic and activation parameters have been evaluated and discussed in terms of isokinetic relationship and as a function of solvent compositions. Linearity of Leffler's and Exner's plots indicate a similar type of mechanism to be operative in different dielectric media at all temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Coumarin, with the accepted nomenclature benzo-pyrone, 2H-benzo[b]pyran-2-one, 2H-chromen-2-one, 2-oxo-1,2-benzopyran, or 2H-1-benzopyran-2-one, is the structural unit present in a large number of oxygen heterocycles isolated from plants [1], animals [2,3], and microbes. In recent times, 2H-1-benzopyran-2-ones are extensively used as lasing materials [4], fabric dyes [5], fluorescent brighteners [5], photosensitizers [6], analytical reagents [7], pH indicators [8], as intermediates for dyes, pesticides and pharmaceuticals [9], perfume formulations [10,11], electrophotography reagents [12], for electro deposition of metals [13], and as biological probes in enzymology [14]. Owing to such a broad spectrum of applications in several fields, considerable attention has been paid towards synthesis, spectral characterization and physiological activity of coumarin derivatives. A perusal of literature also revealed that formyl derivatives of coumarin serve as good source material for the synthesis of dyes such as coumaral green coumaral rhodamine. It is interesting to note that coumaral dyes produce beautiful bluish green and

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bluish violet shades on silk, wool, and surpass the dyes derived from benzaldehydes. It is also reported earlier that formylation can be achieved more conveniently by Vilsmeier-Haack reaction than Reimer-Tiemann, Gattermann-Koch, and Duff's methods of formylations [15-21]. These striking features prompted the authors to take up the present study in various solvent media, viz., dichloro methane (DCM), dichloro ethane (DCE), acetonitrile (ACN), benzene, and, also, in binary composition of benzene and acetonitrile (ACN), with a view to explore the kinetic methods for understanding the mechanistic aspects.

EXPERIMENTAL DETAILS

Coumarin (COUM), 4-hydroxy coumarin (FHCOUM) are B.D.H. (England) samples. The other Coumarin derivatives, such as 7-hydroxy coumarin (SHCOUM), 3-acetyl-7-hydroxy coumarin (AHCOUM), 4-methyl-7-hydroxy coumarin (MHCOUM), and 4,8-dimethyl-7-hydroxy coumarin (DMHCOUM) were prepared according to literature procedures and recrystallized before use [19-22]. The solvents used in this study, viz., benzene, acetonitrile (ACN), dichloro methane (DCM), and dichloro ethane (DCE) were either HPLC grade or purified according to standard literature reports [23].

VH Reagents

Flasks containing dialkyl amide (DMF) dissolved in a suitable solvent (generally DCM, DCE, ACN, or benzene) and POCl₃ were cooled and thermally equilibrated for about half-an-hour at -5° C by keeping in an ultra cryostat or in a benzene trough chilled from outside with the help of ice and common salt. Requisite amounts of solvent and amide were transferred into a 100 ml volumetric flask and POCl₃ was added dropwise, at -5° C with constant stirring. The resultant reagent mixture was kept aside for about an hour in oder to ensure complete formation of Vilsmeier-Haack (VH) adduct. Its concentration was checked by acid-base titrations at phenolphthalein end point according to literature reports [24-31].

Kinetic Method

Thermostat (Toshniwal, India) was adjusted to desired reaction temperature. Two different flasks, one containing known amount of Vilsmeier-Haack reagent in a suitable solvent and the other with the substrate solution, were taken and clamped in the thermostatic bath for about half-an-hour. Reaction was initiated by adding requisite amount of substrate solution to the reaction vessel containing the other contents of the reaction mixture. The entire reaction mixture was stirred till the end of the reaction. Aliquots of the reaction mixture were withdrawn into a conical flask, containing considerable (known) amount of hot distilled water, at regular time intervals. The unreacted VH adduct underwent hydrolysis and gave a mixture of hydrochloric and phosphoric acids. The acid content was estimated against standard NaOH solution to phenolphthalein end point [29–31].

Products of the reaction were isolated under kinetic conditions. To the Vilsmeier-Haack complex prepared from DMF and POCI, (0.02 moles each) in DCE (100 ml), 0.02 moles of coumarin were added with constant stirring. The reaction mixture was refluxed for 4 to 5 h and left aside over night. The solution was poured into ice cold water with vigorous stirring and kept aside for about 2 h. The resultant solution was neutralized by sodium hydrogen carbonate. Organic phase was extracted with DCE and dried (with $MgSO_4$) and the solvent evaporated. TLC pure coumarin derivative was characterized by spectroscopic methods. The products were found to be formyl coumarin derivatives. 4-hydroxy coumarin afforded 3-formyl derivative. 7-hydroxy and 4-methyl 7-hydroxy coumarins yielded 8-formyl derivatives while 4,8-dimethyl 7-hydroxy coumarin gave 6-formyl derivative. The melting points were determined on Mettler FP 51 (Neo Pharma Instrument Corp.) and are not corrected. The ¹H NMR spectra were recorded on a Jeol FX-90A instrument in chloroform-d using TMS as internal standard. The mass spectra were recorded on a VG micromass 70-70H spectrometer. The IR were recorded on a Nicolet 740 FT-IR spectrometer. The UV were recorded on Shimadzu-240 UV-Visible spectrophotometer. As a specific case data are given for 3-formyl 4-hydroxy coumarin. Melting point was found to be 139-140°C. 1R (Nujol) 1710 cm⁻¹ (formyl C==O), 1620 (pyrone C=O); PMR (CDCl₂) δ 17.7 (1H, b, -OH); δ 7.3-8.0 (3H, m, H-5, H-6, H-7); δ 8.35 (1H, q, H-8); μ v in 95% ethanol 235 nm (ϵ 1500), 300 nm $(\epsilon 14250)$; and Mass: (m/z) 190(50), 162(100), 121(50), 120(70), 92(30).

RESULTS AND DISCUSSION

Salient Kinetic Features of the Kinetic Study

Under the pseudo-first-order conditions, viz., [VH adduct] << [coumarin], plot of log [a/(a-x)] vs.



Figure 1 (A) Plot of $\ln a/a - x$ vs. time, (VH) = 0.0167 mol dm⁻³ (COUM) = 0.670 mol dm⁻³, Temp = 303 K, Solvent = Benzene; (B) Plot of 1/a - x vs. time, (VH) = 0.067 mol dm⁻³ (COUM) = 0.067 mol dm⁻³, other conditions are same as in A; and (C) Plot of K' vs. (S); (VH) = 0.067 mol dm⁻³, other conditions same as in (A).

time have been found to be linear passing through origin indicating first-order with respect to [VH reagent [Fig. 1(A)]. From the slopes of the plots k'values were calculated. However, the plots of 1/(a-x)vs. time have been found to be linear with positive slopes and an intercept on ordinate when [VH reagent] = [Coumarin] indicating an over all secondorder reaction [Fig. 1(B)]. First-order kinetics in [coumarin] was also confirmed from the plots of k'vs. [4-OH Coumarin] which were linear passing through origin [Fig. 1(C)]. Rates of reaction varied significantly in different solvents with varied dielectric constants (Tables I-III) with the trend Benzene \geq ACN > DCE > DCM. Such studies were also taken up in binary solvent mixtures of benzene and acn with varied compositions of each component (Tables I and III). The data presented in Tables I-III indicated an irregular trend with a regular variation of dielectric constant (D). These observations may suggest the possibility of a change in the reactive species passing from higher dielectric aceto nitrile to low dielectric benzene medium. Rate of formylation has been found to follow the trend: 7-OH > 7-OH > 4,8-dimethyl4 - OH < 4 - methyl7-OH > Coumarin < 3-acetyl7-OH Coumarin (Tables I and II).

Reactive Species and Mechanism of the Reaction

A number of studies have been devoted to indicate the nature of the VH complex since its discovery and a variety of reactive species have been formulated possessing covalent, ionic, and ion-pair structures (I to VI) on the basis of ir, electronic, and ³¹P nmr spectroscopic studies [24–31].

$$[(CH_3), N = CHCl]^+[OPOCl_2]^-$$
(I)

$$[(CH_3)_2N = CH - OPOCl_2]^+Cl^-$$
(II)

$$[(CH_1)_2 N - CHClOPOCl_2]$$
(III)

$$[(CH_{3})_{2}N = C^{+}HCl]$$
 (IV)

$$[(CH_3)_2N - C \bigvee_{OPOCl_2}^{H}]^+ Cl^-$$
(V)

$$[(CH_3)_2N - C \land H]^+ PO_2Cl_2^-$$
(VI)

In 2H-1-benzopyran-2-one, the carbonyl is in 2-position, the olefinic bond between C-3 and C-4 positions and pyrone oxygen in 1-position present the centers of reactivity. Though the pyrone ring of coumarin is an essentially aliphatic system, it shows some aromatic character in its pattern of reactivity. The electron density values of various carbons of coumarin have been calculated by Chatterji et al. [32] (Chart A)



and the crystal structure reveals that it belongs to the ortho rhombic system. Since the present study is an electrophilic substitution reaction such as halogenation, nitration, sulfonation, formylation, chloromethylation, and mercuration, the substituent could be introduced in 3, 6 and 8 positions of coumarin in the order of availability. It has also been reported [20] that Coumarin with a hydroxyl group at position 4 differs considerably from other hydroxy coumarins in their reactivity. Because of the presence of highly enolisable β -ketoester systems 4-hydroxy coumarin is highly acidic. The $[-C^3H=C^4(OH)-]$ moiety of 4-hydroxy coumarin is mainly responsible for its chemical reactivity. Hydroxy group at C-4 enhances the electrophilic activity of the pyron ring. Elec-

Table ISecond-Order Rate Constants and Activation Parameters of VH Reaction with Coumarins in Binary SolventMixtures of Benzene and ACN [VH reagent] = $0.067 \text{ mol dm}^{-3}$; [Coumarin] = $0.067 \text{ mol dm}^{-3}$; Temperature (K):(A) = 303, (B) = 313, (C) = 323, and (D) = 333

Substrate		$10^4 k dm^3$	mol ⁻¹ s ⁻¹	ΔH^*	ΔG^{*}	$-\Delta S^{*}$	
	(A)	(B)	(C)	(D)	kJ r	nol ⁻¹	JK ⁻¹ mol ⁻¹
Solvent compositi	ion (%V/V): Ber	zene = 15, AC	N = 85	· · · · · · · · · · · · · · · · · · ·			
COUM	0.127	0.169	0.198	0.242	15.5	103.0	289
AHCOUM	0.375	0.472	0.586	0.717	15.7	100.0	278
SHCOUM	0.508	0.627	0.762	0.917	14.0	99.2	281
MHCOUM	0.767	0.977	1.230	1.520	16.7	98.2	269
DMHCOUM	0.250	0.315	0.389	0.475	15.5	101.0	282
FHCOUM	0.641	0.803	0.992	1.210	15.3	97.5	271
Solvent compositi	ion (%V/V): Ber	zene = 30, ACI	N = 70				
COUM	0.115	0.144	0.177	0.215	15.0	103.0	290
AHCOUM	0.342	0.431	0.536	0.658	15.8	100.0	278
SHCOUM	0.458	0.573	0.734	0.858	15.0	99.5	279
MHCOUM	0.687	0.877	1.110	1.390	17.2	98.4	268
DMHCOUM	0.225	0.285	0.352	0.433	15.8	101.0	281
FHCOUM	0.575	0.718	0.886	1.080	15.2	98.9	276
Solvent compositi	on (%V/V): Ber	zene = 45, ACI	N = 55				
COUM	0.103	0.129	0.157	0.191	14.8	103.0	291
AHCOUM	0.317	0.390	0.472	0.567	13.7	100.0	285
SHCOUM	0.417	0.513	0.624	0.750	13.9	99.7	283
MHCOUM	0.622	0.798	1.000	1.250	17.0	98.7	270
DMHCOUM	0.208	0.257	0.312	0.375	14.0	101.0	287
FHCOUM	0.517	0.643	0.789	0.958	14.8	99.1	278
Solvent compositi	on (%V/V): Ber	zene = 60, ACI	N = 40				
COUM	0.120	0.151	0.188	0.230	15.7	103.0	288
AHCOUM	0.358	0.450	0.553	0.675	15.2	101.0	283
SHCOUM	0.475	0.596	0.736	0.900	15.3	99.4	278
MHCOUM	0.717	0.933	1.170	1.460	17.4	98.3	267
DMHCOUM	0.233	0.295	0.366	0.450	15.9	101.0	287
FHCOUM	0.600	0.755	0.938	1.150	15.7	98.8	274
Solvent compositi	on (%V/V): Ber	zene = 75, ACN	N = 25				
COUM	0.144	0.184	0.231	0.287	16.8	102.0	281
AHCOUM	0.392	0.521	0.676	0.867	19.7	99.8	274
SHCOUM	0.517	0.688	0.900	1.160	20.1	99.1	261
MHCOUM	0.867	1.130	1.440	1.820	18.2	97.8	263
DMHCOUM	0.258	0.344	0.447	0.575	14.7	98.8	278
FHCOUM	0.717	0.916	1.150	1.430	16.8	98.3	269

trophilic substitutions take place at 3-position of 4hydroxy coumarin, because of the powerful orientating influence of 4-hydroxyl group creating a center of high electron density at 3-position [20,21]. This point lends support to the relatively higher reactivity of 4-OH coumarin over the parent compound during formylation in this study (Tables I--III). It has also been earlier reported [20] that the substitution takes place preferably at 8th position in the case of 7-OH hydroxy derivatives, although substitutions can be expected either at 6th or 8th position. When C-3 is substituted by acetyl moiety in 7-OH (hydroxy) coumarin rate of formylation is not affected much by suggesting that substitution occurs at either 6th or 8th position. However, when C-4 is substituted in 7-hydroxy coumarin rate of formylation is increased quite significantly. When the 8th position of 4-methyl-7hydroxy Coumarin is substituted by another methyl group, rate of formylation has decreased significantly (Tables I and II). This accounts for the higher activity of 4-methyl derivative over 4,8-dimethyl 7-hydroxy derivatives and strengthens the idea that substitution takes place at 8th position in the case of 7-hydroxy coumarins.

Although a variety of covalent, ion-pair, and cationic species of VH adduct are known to be pres-

Table II Second-Order Rate Constants and Activation Parameters of VH Reaction with Coumarins in Various Organic Solvents [VH reagent] = $0.067 \text{ mol dm}^{-3}$; [Substrate] = $0.067 \text{ mol dm}^{-3}$; Temperature (K): (A) = 303, (B) = 313, (C) = 323, and (D) = 333

Solvent	Substrate	$10^4 k \mathrm{dm^3 mol^{-1} s^{-1}}$				ΔH^{*}	ΔG^{*}	$-\Delta S^*$
		(A)	(B)	(C)	(D)	kJ mol ⁻¹		JK^{-1} mol ⁻¹
BENZENE	COUM	0.380	0.382	0.464	0.560	14.2	104.0	296
	AHCOUM	0.900	1.120	1.380	1.670	14.8	9 7.0	274
	SHCOUM	1.200	1.480	1.810	2.180	14.2	9 7.0	273
	MHCOUM	1.850	2.300	2.820	3.420	14.7	95.6	268
	DMHCOUM	0.600	0.748	0.915	1.100	14.7	98.8	278
	FHCOUM	0.940	1.900	2.310	2.780	14.0	96.4	272
ACN	COUM	0.217	0.272	0.334	0.408	15.1	101.0	283
	AHCOUM	0.658	0.818	1.000	1.220	14.8	98.5	276
	SHCOUM	0.867	1.080	1.340	1.630	15.1	97.8	276
	MHCOUM	1.300	1.710	2.090	2.530	14.5	96.8	271
	DMHCOUM	0.433	0.541	0.664	0.808	15.0	99.6	279
	FHCOUM	1.080	1.360	1.680	2.050	15.5	97.3	269
DCE	COUM	0.138	0.173	_	0.213	15.3	102.0	286
	AHCOUM	0.492	0.617	_	0.759	15.0	99.8	280
	SHCOUM	0.650	0.807	_	0.990	14.6	98.6	277
	MHCOUM	0.880	1.100	_	1.391	16.2	97.8	269
	DMHCOUM	0.317	0.398	-	0.491	15.3	100.0	283
	FHCOUM	0.697	0.860	_	1.050	14.2	98.4	278
DCM	COUM	0.132	0.165	_	0.203	15.1	102.0	287
	AHCOUM	0.400	0.501	_	0.615	15.0	99.8	280
	SHCOUM	0.525	0.651	_	0.795	14.4	99.1	280
	MHCOUM	0.792	0.991	_	1.230	15.2	98.1	273
	DMHCOUM	0.267	0.334	-	0.411	15.1	101.0	283
	FHCOUM	0.660	0.813	_	0.992	14.1	98.5	279

ent [24-31], it appears rather difficult to propose suitable reactive species on the basis of dielectric constant effect studies. The rate data were cast into various semiquantitative expressions involving dielectric constant (D), volume %, weight %, and mole fraction (n_x) [33-35]. However, in the present study plots of either Amis, Laidler-Eyring [33], ie., [log k vs. (1/D)] or Kirkwood [34], ie., log k' vs. (D-1)/(2D + 1)] or Irving-Rossotti [35], ie., [log k vs. v%, wt%, or n_x] were found to be nonlinear for all the systems. By using the data given in Table III, representative plots are depicted in Figure 2. (plot of k vs. volume % Benzene curve A; log k vs. Weight % Benzene curve-B and log k vs. molefraction of Ben-

Table IIIEffect of Variation of Solvent on VH Reaction with 4-Methyl 7-Hydroxy Coumarinat 303 K [VH reagent] = $0.067 \text{ mol dm}^{-3}$; [MHC] = $0.067 \text{ mol dm}^{-3}$

Composition of benzene						1046
(%V/V)	(%W/W)	n _x	D	(10 ³ /D)	(D-1)/(2D + 1)	$(dm^3 mol^{-1} s^{-1})$
15	16.4	0.092	32.60	30.70	0.477	0.767
30	32.3	0.200	27.20	36.80	0.473	0.687
45	47.6	0.369	22.60	45.50	0.467	0.622
60	62.5	0.532	16.80	59.50	0.457	0.717
75	76.9	0.637	11.60	86.20	0.438	0.867
100	_	_	2,28	438.00	0.230	1.85
Acn	_	_	37.50	26.70	0.480	1.30
DCE	_	_	9.08	110.00	0.422	0.880
DCM	-	_	10.40	96.20	0.431	0.792



Figure 2 Conditions are mentioned in the "inset" of figure. (A) Plot of Log K vs. % Benzene (V/V); (B) Plot of Log K vs. % Benzene (W/W); and (C) Plot of Log K vs. Mole fraction of Benzene (nx).

zene- n_x curve-C) for 4-methyl 7-hydroxy coumarin (MHC) system. The plots were nonlinear. Such nonlinear curves could also be obtained by plotting $\log k$ as a function of (1/D) or (D - 1)/(2D + 1). These nonlinear plots, however, may point out that apart from dielectric constant (D) other solvent parameters such as solvent-solute, solvent-cosolvent are also important in governing rates of the present reactions. This contention can be supported from the findings of Robinson and Stokes [36], Brown and Hudson [37], and several others [38,39]. Robinson and Stokes [36] stated that the bulk dielectric constant is entirely different from internal dielectric constant. Brown and Hudson [37] noticed that the rate of hydrolysis of acid chlorides is almost equal in 95% ethanol and 95% dioxane although the dielectric constant is different for these solvents. In another report [38], it was stated that the curvature noticed in the plot of $\log k$ vs. (D - 1)/(2D + 1) could be explained due to solvation of the reactive species in high dielectric media for the reaction between triethylamine and ethyliodide. Some of the recent reports published on linear solvent energy relationships by Abraham et al. [39] revealed that rate of the reaction depends on several other properties such as viscosity, surface tension, refractive index, etc., apart from dielectric constant, solvent-solute interactions, and solvation energies. On the basis of the above points it may be at best proposed the participation of coumarin and an ion-pair type VH adduct as reactive species in high dielectric media (the solvent mixture from zero to 45% benzene) while cation type of VH adduct and coumarin in low dielectric media (above 45% benzene) were considered as reactive species in the rate determining step. The most plausible mechanistic path is shown in Scheme I. A general reaction sequence is also shown in the following steps.

DMF + POCl₃
$$\stackrel{\text{fast}}{\leftarrow}$$
 Adduct (C₁)
(C₁) + Coumarin $\stackrel{k_1}{\leftarrow}$ Intermediate

Intermediate $\xrightarrow{\text{fast}}$ Formylated Product + H_3PO_4 + HCl

For the above mechanism, the rate law comes out as,

$$\frac{-d[\text{Coumarin}]}{dt} = k [\text{VH adduct}][\text{Coumarin}]$$

where [VH adduct = K [DMF][POCl₃].

Kinetic and activation parameters have been evaluated and interpreted suitably.





Figure 3 (A) Plot of $\Delta H^{\#}$ vs. n_x ; (B) Plot of $\Delta G^{\#}$ vs. n_x ; and (C) Plot of $-\Delta S^{\#}$ vs. n_x .

In the reactions occurring in mixed organic solvents efforts have been put to interpret rate trends in terms of activation parameters ($\Delta H^{\#}$ or $\Delta S^{\#}$) as a function of solvent parameter. The plots of $\Delta H^{\#}$ vs. n_x and/or $-\Delta S^{\#}$ vs. n_x pass through inflexion points at $n_x =$ corresponding to 45% benzene and 55% acn, respectively, (Fig. 3). This observation coupled with the data presented (Table I) substantiate that solvent reorganization takes place in the transition state passing from relatively high polar acetonitrile to less polar benzene solvent media [39,40]. Further, linearity of Exner's plot [41]; log k at T_1 vs. log k at T_2 indicate a similar type of mechanism to be operative in all the systems at different temperatures. The isokinetic temperature (β) values (Table IV) obtained from the

Table IV Iso-Kinetic Temperature

Solvent compo (% V/V)	osition				
Acn	Ben	Leffler	Exner		
85	15	140.00	145.00		
40	60	230.00	232.00		
Nil	100	248.00	252.00		
100	Nil	146.00	150.00		
DCM (only)		276.00	270.00		
DCE (only)		60.50	62.50		

slopes of these plots indicate that the reactions are controlled by entropy factors.

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