International Journal of Scientific Research & Engineering Trends
Volume 12, Issue 1, Jan-Feb-2026, ISSN (Online): 2395-566X

Role of Secondary Alcohol in Affecting the Kinetics and Thermodynamic Extensive Properties of Catalysed Solvolysis of the Substituted Aliphatic Formate

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Abstract - Role of a secondary alcohol (Propan-2-ol) in affecting the kinetics and the thermodynamic extensive properties of the acid catalysed solvolysis of iso-butyl formate has been highlighted by studying the kinetics of the reaction in different aquo-propan-2-ol reaction media having 20 to 80% (v/v) of propan-2-ol and at five different temperatures rising from 20 to 40°C at interval of 5°C It was found that with increase in Jemperature of the reaction from 20 to 40°C from 0.172 to 1.344 molecules of water are associated with the activated complex and from this, it is inferred that mechanistic path followed by the reaction in presence of propan-2-ol is changed from bimolecular to unimolecular. The depletion and enhancement observed respectively in iso-composition and iso-dielectric activation energies reveal that the transition state is solvated and initial state is desolvated with addition of propan-2-ol in reaction media. Almost unity value of the slope of the plots of log k values against log [H^+] values shows that the reaction follows A_{AC}^2 mechanism. From the values of iso-kinetic temperature, which comes to be 287, it may be concluded that in water-propan-2-ol reaction media, the reaction follows Barclay-Butler rule and there is weak but acceptable interaction between solvent and solute in aquo-propan-2-ol reaction media

Keywords - Secondary alkohol, Substituted formate, Extensive Thermodynamic Properties, Iso-dielectric, Iso-Kinetic Specific solvation, Leffler's rule, Desolvation. Solvent solute Interaction, Barclay-Butler Rule

INTRODUCTION

Various kineticists[1-5] have reported in their researches on the solvent effect of dipolar aprotic solvents like DMSO, DMF, Acetone on the on the alkali and acid catalysed hydrolysis of differnt esters, but the studies on the solvent effect of the dipolar protic solvent like a secondary alcohol on the catalysed hydrolysis of substituted aliphatic formate has not been reported till date.

Hence it is thought essential to study the effect of a dipolar protic solvent, propan-2-ol on the acid catalysed hydrolysis of Iso-butyl formate, as its biochemical use as flavouring agent seems to be very useful in the food technology and also in manufacturing of soft drinks.

Experimental & Calculation:
Export quality of Iso-butyl formate of Fluka grade packed in Switzerland and Merck grade of propan-2-ol of high purity were usod. The kinetics of the reaction was studied by adding 0.65 ml of ester through a German make graduated syringe pipette into 50 ml of 0.5 M solution of HCl. The reaction was found to obey evaluated tabulated the first order kinetic equation and the values of specific rate constants have been recorded in Table-1. The variation of log k values with mol% of propan-2-ol have been in Table-II and variation of log k with log [H_2O] of the reaction media are recorded in Table-III. From the slope of the plots of log k versus log [H_2O], the number of water molecules associated with the transition state of the reaction have been evaluated and are placed in Table - IV. The values of both the iso-composition and iso-dielectric activation energies have been enlisted in Table-V and Table-VI respectively. The numerical values of thermodynamic activation parameters were calculated using Wynne-Jones and Eyring equation and are synchronised in Table-VII. Effect of change in [H^+] ion concentration of the reaction media on the specific rate constants of the reaction has been shown in Table-VIII.

Results and Discussion
From Table-1, it is obvious that the specific rate constants of the reaction decrease with increasing proportion of propan-2-ol

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in the reaction media. On plotting log k values against mol% of propan-2-ol (from recorded values in Table-II) as shown in Fig.-1, it is obvious that up to 21.75 mol% of propan-2-ol in the reaction media, the rate of the reaction falls rapidly but beyond (above) 21.75 mol % of propan-2-ol, the depletion in the rate follows the slow path. From Fig. 1, it is also apparant that with increase in temperature of the reaction, the rate of reaction decreases more sharply. The decreasing trend in the values of the specific rate constants needs to be discussed in the light of Hughes and Ingold[7]

predictions according to which an increase in the dielectric constant values of the reaction medin causes an increase in the rate when there is concentration or constructions of charges on the transition stage and causes a decrease in the rate when there is diffusion or destruction of charges on the transition stage.

The values of dielectric constants of the reaction media go on decreasing with gradual addition of propan-2-ol. So the findings are fully in accordance with the qualitative prediction of Hughes and Ingold[7]. However, these findings and their interpretations are fully in agreement with the qualitative prediction of Laidler and Landskroener[8] and also with the earlier reported views of Kumari & Singh et al[9], Singh & Perween et al[10]. and recently published reports of Raghaw & Singh et al[11]. and Singh, R. T.[12] who predicted that the rate of ion dipol type of reactions decrease with decrease in the dielectric constant values of the reaction media.

Evaluation of number of water molecules involved in the formation of activated complex of the reaction and mechanism of the reaction:

Robertson[13] has derived an equation, which is as:

$$\log K = \log K' + n \log [H_2O]$$

where 'n' is the solvation number ie. the number of water molecules associated with the transition state of the reaction and is evaluated from the slopes of the plots of log k versus log $[H_2O]$,

'n' for unimolecular reactions is fairly high while Robertson et al[14]. suggested that value of that of bimolecular reactions, it will be low.

From the recorded values of log k and log $[H_2O]$ in Table - III, the log k values were plotted against log $[H_2O]$ as shown in Fig-2 and the evaluated values of the slopes of the straight lines have been enlisted in Table-IV.

From Fig-2 it is clear that at each temperature two intersecting straight lines are obtained at log $[H_2O]$ value 1.427 which corresponds to 48.10% of water concentration (v/v) in aquo-propan-2-ol reaction media.

From the recorded values of the slopes of the plots of log k versus log $[H_2O]$ in Table -III, it is clear that below or before log $[H_2O]$ value 1.427, which corresponds to 48.10% of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.172 to 0.748 with increase in temperature of the reaction from 20 to 40°C. Similarly, for above 48.10% water concentration in the reaction media, the number of water molecules involved in the formation of the activated complex increase from 0.418 to 1.314 with rise in temperature from 20 to 40°C.

Overall, it is concluded that number of water molecules associated with the activated complex increase from 0.172 to 1.314 with rise in temperature from 20 to 40°C and from this trend, in the light of the guidelines of Robertson et al. it is inferred that the mechanistic pathway of the reaction is changed from bimolecular to unimolecular with increase in water concentration or with decrease in propan-2-ol content of the reaction media and also with increase in the temperature of the reaction.

From the enhancing trend of number of water molecules involved in the formation of the activated complex, it is also inferred that on addition of propan-2-ol in the reaction media, the equilibrium of water is shifted from its dense form to bulky form.

$$(H_2O)_d \rightleftharpoons (H_2O)_b$$

Similar observations and theit inter-pretations have also been reported recently by Singh & Singh et al[15]. and Kumar & Singh et al[16].

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Solvent effect on Iso-composition Activation energy (E_c)of the reaction:

From the slopes of Arrehenius plots of log k versus 10/T as shown in Fig. -3, the values reaction have been evaluated and are tabulated of iso-composition activation energy (E_c) of the in Table-V. From Table-V, it is obvious that E_c values go on decreasing from 93.23 to 56.23 kJ/mol with increasing the concentration of propan-2-ol from 20 to 80% (v/v) in reaction media. This trend is probably due to solvation changes taking place either at initial state level or at the transition state level or at the level of both the initial and transition states as reported earlier by Elsemongy et al[17]. in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for decrease in E_c values with gradual addition of propan-2-ol in the reaction media:-

- The transition state is solvated and the initial state is desolvated,
- The transition state is desolvated less than the initial state, and
- The transition state is solvated more than the initial state.

The transition state being large cation (ester+H^+) is available more for solvation by propan-2-ol molecule than the initial state, so the first factor seems to be operative in this case and it is also supported by the decrease in entropy of activation (ΔS^*) of the reaction as shown in Table-VII. So situation third is the more plausible explanation for decrease in E_c, values of the reaction as recorded in Table - V.

It is, therefore, concluded that E values of the reaction go on decreasing due to solvation of the transition state and desolvation of initial state. Similar interpretations have also been communicated earlier by Singh & Singh et al[18]. and recently by Dubey & Singh et al[19].,

Effect of Solvent on the Iso-dielectric Activation Energy (E_d) of the Reaction:

In order to minimise the dielectric effect, the iso-dielectric activation energy was evaluated from the slopes of the Arrhenius plots of log K_D values (Obtained from interpolation of the plots of log k values against D values of the reaction media) against 1/T. The value thus obtained have been tabulated in Table-VI. From the Table-VI. it is found that E, values go on increasing from 66.83 to 94.56 kJ/mol with increase in D values from D-30 to D-60. This trend of increase in E_c values is quite in agreement with changes (decrease) in E_c values of this reaction and also with the findings of Wolford[20] and with the earlier reports of Singh & Singh et al[21,22] However. Pathak & Singh et al[23]. and Kumari & Singh et al[24]. have also reported recently similar interpretations for the changes in Iso-dielectric Activation energy of the solvolysis reactions.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:

The three thermodynamic activation parameters namely enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and entropy of activation (ΔS^*) of the reaction were evaluated using Wynne-Jones and Eyring equation[6] and have been mentioned in Table - VII. From the values enlisted in Table - VII, it is clear that ΔG^* values of the reaction go on increasing with simultaneous decrease in both the ΔH^* and ΔS^* values of the reaction.

In order to study the variation in these thermodynamic parameters more clearly, these were plotted against the mol% of propan-2-ol which have been shown in Fig. 4, 5 and 6 for ΔH^*, ΔG^* and ΔS^* respectively. From Fig. -4, 5 and 6, it is clear that ΔH^*, ΔG^* and ΔS^* vary non-linearly to the considerable extent with the increasing concentration (mol%) of propan-2-ol and thisis the indication of specific solvation taking place in the reaction media according to Saville and Hudson[25].

The ΔH^* and ΔS^* are complimentary to each other as the resulting net property of ΔG Table-VII is a well behaved function. From tise values of ΔG^* in Table-VII and also from the F 5, it is clear that ΔG^* is being little affected by the solvent composition (mol%). However, there considerable enhancement (from 82.53 10 84.65 kJ/mol at 30°C) in ΔG^* values.

From Table - VII, it is also clear that ΔG^* values are found to increase simultaneously with depletion in both the ΔH^* and ΔS^* values.

From the thermodynamic relation-

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

it is apparant that enhancement in ΔG^* values with simultaneous decrease in both of ΔH^* and ΔS^* values of the

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reaction is only possible when the extent of depletion in ΔS^* values is greater than in ΔH^* values. From these findings, it is concluded that the acid catalysed hydrolysis of Iso-butyl formate in aquo-propan-2-ol media is entropy controlled but enthalpy dominating reaction.

Such observations and interpretations have also been reported earlier by Akanksha & Singh et al[26]. and recently by Choubey & Singh et al[27] and Singh & Lal et al[28].

Solvent Effect on Solvent-Solute Interaction in the aquo-propan-2-ol Reaction media:

For highlighting solvent-solute interaction for a solvolysis reaction, Barclay and Butler have correlated the enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) by means of the relationship-

$$\delta m\ (\Delta H^*) = \beta\ \delta m\ (\Delta S^*)$$

where B is a constant called iso-kinetic plotserature and it is evaluated fr temperature it is from the slope of

From the recorded values of ΔH* and ΔS* in Table - VII, AH values were plotted against ΔS* (at 30°C) which is shown in Fig.-7. The plot consists of a straight line whose slope value has been evaluated to be 287.44≈287.0 which is less than 300. On the guidelines of Leffler[30] it is concluded that there is weak but considerable solvent-solute interaction for acid catalysed hydrolysis of Iso-butyl formate in aquo-propan-2-ol reaction media.

Such interpretations for weak solvent-solute interaction have also been reported recently by Singh & Hafizee et al.[31].

Effect of change of [H+] in concentration of the reaction media on the Mechanism of the Reaction:

In order to investigate the effect of change in acid concentration of relation media (H* in concentration) on the specific rate constants of the acid catalysed hydrolysis of Iso-butyl formate in aquo-propan-2-ol media, experiments were performed to study the kinetics at various concentrations of HCl (from 0.1M to 0.8 M). keeping the temperature, solvent composition and ionic strength of the reaction media constant. The reactions were carried out at 30°C in the reaction media having 20% (v/v) concentration of propan-2-ol and the evaluated values of specific rate constants have been tabulated in Table-VIII. From the tabulated values of log k and log $[H^+]$ in Table - VIII, log k values were plotted against log $[H^+]$ and has been shown ih Fig. 8. From Fig. 8, it is clear that the plot is an excellent straight line showing linear dependence of rate of reaction on $[H^+]$ ion concentration. The slope of the log k versus log $[H^+]$ plot is evaluated to be 1.003 which is almost equal to unity. From this value of slope (unity), it may be inferred on the basis of the hypothesis of Zucker and Hammett[32] that acid catalysed hydrolysis of Iso-butyl formate in aquo-propan-2-ol media follows A_{AC}^2 mechanism.

Similar conclusions have also been reported in recent years by Singh & Singh et al.[33].

Table - I

Specific rate constant values of Acid catalysed hydrolysis of Iso-butyl formate in water-Propan-2-ol media

$k \times 10^3$ in $(dm)^3\ mol^{-1}\ min^{-1}$

Temp in °C	% of Propan-2-ol (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20° C	63.89	59.27	56.77	53.69	51.44	49.00	45.56
25° C	119.70	108.04	99.45	90.80	83.33	76.09	66.13
30° C	225.53	198.52	173.74	153.67	135.27	119.34	97.07
35° C	407.56	348.42	293.83	251.07	213.07	182.43	138.71
40° C	741.14	614.89	496.94	407.47	332.89	276.18	198.43

Table - II

Variation of log k values of the reaction at different temperatures with mol % of Propan-2-ol in water-Propan-2-ol media.

% of Propan-2-ol (v/v)	Mol % of Propan-2-ol	3 + log k values				
		20°C	25°C	30°C	35°C	40°C
20%	5.50	1.8054	2.0781	2.3532	2.6102	2.8699
30%	9.22	1.7729	2.0335	2.2800	2.5421	2.7887
40%	13.64	1.7541	1.9977	2.2399	2.4681	2.6963
50%	19.16	1.7299	1.9580	2.1865	2.3990	2.6100
60%	26.23	1.7113	1.9208	2.1312	2.3280	2.5223
70%	35.61	1.6901	1.8813	2.0767	2.2611	2.4412
80%	48.67	1.6585	1.8204	1.9870	2.1421	2.2976

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International Journal of Scientific Research & Engineering Trends
Volume 12, Issue 1, Jan-Feb-2026, ISSN (Online): 2395-566X

Table - III

Variation of log k values of the reaction with log [H_2O] values of water - Propan-2-ol system (media) at different temperatures

% of Propan-2-ol (v/v)	% of H_2O	log [H_2O]	3 + log k values				
			20°C	25°C	30°C	35°C	40°C
20%	80%	1.6478	1.8054	2.0781	2.3532	2.6102	2.8699
30%	70%	1.5898	1.7729	2.0335	2.2800	2.5421	2.7887
40%	60%	1.5229	1.7541	1.9977	2.2399	2.4681	2.6963
50%	50%	1.4437	1.7299	1.9580	2.1865	2.3990	2.6100
60%	40%	1.3468	1.7113	1.9208	2.1312	2.3280	2.5223
70%	30%	1.2218	1.6901	1.8813	2.0767	2.2611	2.4412
80%	20%	1.0458	1.6585	1.8204	1.9870	2.1421	2.2976

Table - IV

Values of the slopes of the plots of log k versus log [H_2O] values at different temperatures

Temperature in °C	Slope - I where log[H_2O] value is below 1.427	Slope - II where log[H_2O] value is above 1.427
20°C	0.172	0.418
25°C	0.307	0.597
30°C	0.468	0.815
35°C	0.598	1.053
40°C	0.748	1.314

Table - VIII

Effect of [H^+] on the Specific rate constant values of Acid Catalysed Hydrolysis of Iso-butyl formate in water-Propan-2-ol media at constant ionic strength (μ = 0.9)

Concentration of Propan-2-ol = 20% Temp. - 30°C

[H^+] (v/v)	[KCl]	μ	k x 10^4 in min^{-1}	2 log[H^+]	4 + log k	value of the slope of the plot of log k versus log [H^+]
0.10	0.80	0.90	44.92	1.0000	1.6524	
0.15	0.75	0.90	67.27	1.1761	1.8278	
0.20	0.70	0.90	89.50	1.3010	1.9518	
0.25	0.65	0.90	112.80	1.3979	2.0523	
0.30	0.60	0.90	133.91	1.4771	2.1268	1.003
0.40	0.50	0.90	178.81	1.6021	2.2524	
0.50	0.40	0.90	225.53	1.6990	2.3532	
0.60	0.30	0.90	270.27	1.7782	2.4318	
0.70	0.20	0.90	314.85	1.8451	2.4981	
0.80	0.10	0.90	364.00	1.9030	2.5611	

Table - V

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-Propan-2-ol media.

% of Propan-2-ol (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c value in kJ/mol	93.23	90.41	84.24	77.51	72.56	66.91	56.23

Table - VI

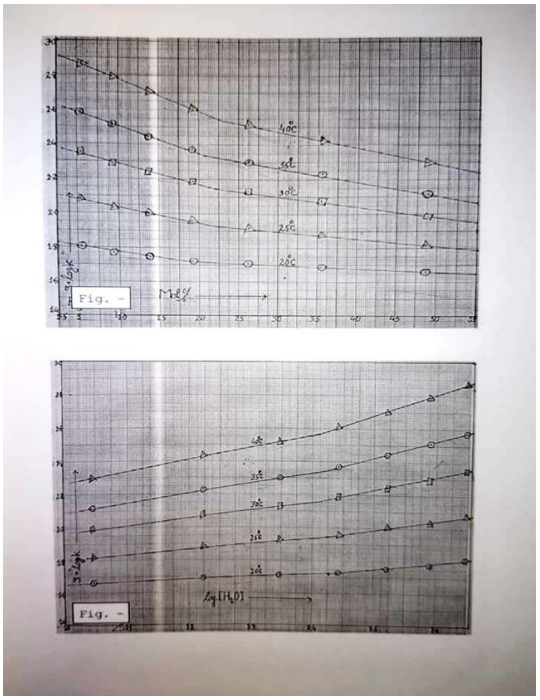
Evaluated Values of Iso-Dielectric Activation Energy (E_D) of the reaction at desired D values of water-Propan-2-ol media.

D values	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55	D = 60
E_D values in kJ/mol	66.83	71.90	76.10	82.06	85.66	91.15	94.56

Table - VII

Variation of log k/T values of the reaction with 10^3/T value in water-Propan-2-ol media.

Temp. °C	10^3/T	5 + log k/T value at different % (v/v) of Propan-2-ol						
		20%	30%	40%	50%	60%	70%	80%
20°C	3.413	1.3386	1.3060	1.2873	1.2630	1.2444	1.2233	1.1917
25°C	3.356	1.6039	1.5594	1.5234	1.4839	1.4466	1.4071	1.3462
30°C	3.300	1.8718	1.8164	1.7585	1.7051	1.6498	1.5953	1.5056
35°C	3.247	2.1216	2.0576	1.9795	1.9112	1.8403	1.7720	1.6537
40°C	3.195	2.3744	2.2933	2.2008	2.1146	2.0268	1.9456	1.8021



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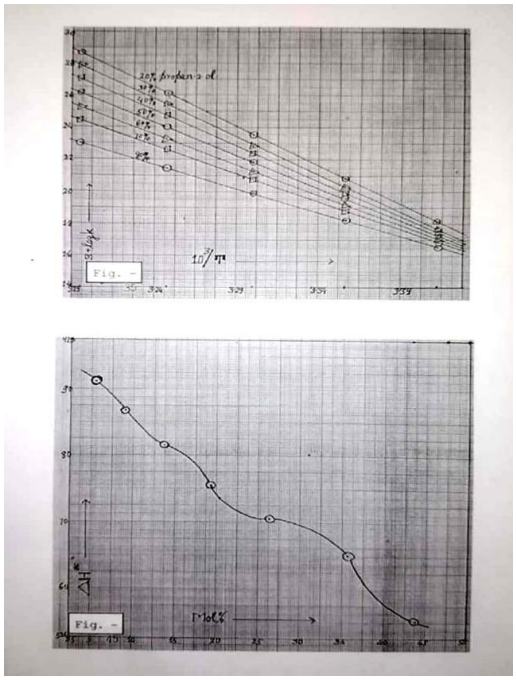

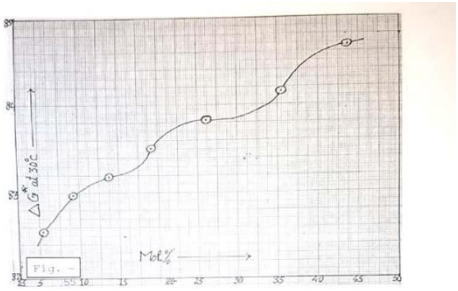

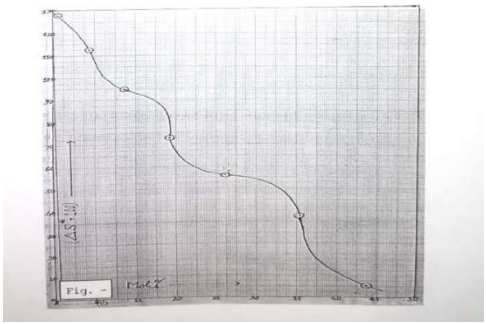

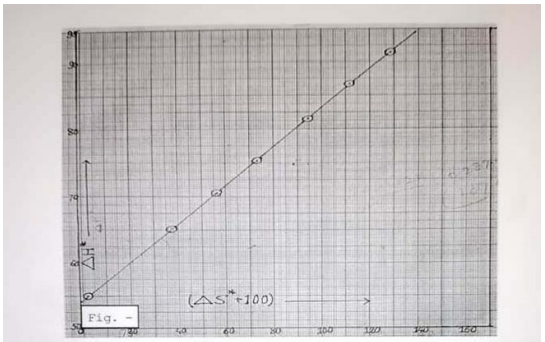

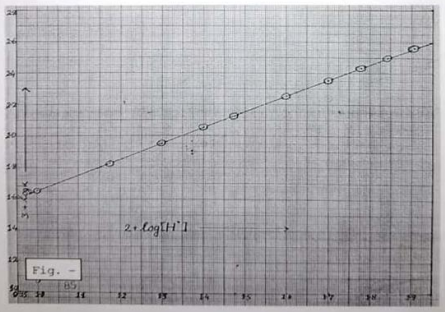

II. CONCLUSION

The present study demonstrates that secondary alcohols play a significant role in influencing both the kinetics and thermodynamic extensive properties of the catalysed solvolysis of substituted aliphatic formates. Variations in reaction rates observed in different secondary alcohol media highlight the strong dependence of solvolysis on solvent polarity, hydrogen-bonding ability, and steric effects. Secondary alcohols, due to their balanced nucleophilicity and moderate steric hindrance, effectively stabilize the developing carbocation or transition state through solvation, thereby facilitating the reaction.

Thermodynamic parameters such as activation energy, enthalpy, and entropy of activation further support the mechanistic interpretation. The relatively lower activation energies and favorable enthalpy changes indicate efficient solvation of the activated complex, while negative entropy values suggest an ordered transition state, consistent with a solvent-assisted ionization process. Substituent effects on the aliphatic formate also modulate the extent of these interactions, reinforcing the interplay between solvent structure and substrate reactivity.

Overall, the findings confirm that secondary alcohols are not merely passive reaction media but actively participate in

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determining the kinetic behavior and thermodynamic feasibility of catalysed solvolysis reactions. This understanding is valuable for optimizing reaction conditions and provides deeper insight into solvent effects in ester solvolysis mechanisms.

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