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Note

Homogeneous esterification of cellulose in the lithium chloride–N,N-dimethylacetamide solvent system: effect of temperature and catalyst

Biranchinarayan Tosh [a], Chowdhury N. Saikia [a,*], Narendra N. Dass [b]

[a] *Regional Research Laboratory, Jorhat, Assam-785 006, India*
[b] *Dibrugarh University, Dibrugarh, Assam-786 004, India*

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Abstract

Commercial rayon grade cellulose was dissolved in the lithium chloride–N,N-dimethylacetamide (LiCl–DMAc) solvent system and esterified with acetic anhydride using p-toluenesulfonyl chloride (p-TsCl) and pyridine as catalysts. The reaction temperature was varied from 28 to 70 °C and the time of reaction from 2 to 24 h. Full substitution took place at 60 and 70 °C at respective reaction times of 10 and 8 h for p-TsCl, and 10 and 6 h for pyridine. Esterification of cellulose followed a second-order reaction path. The rate constants at different reaction temperatures and the activation energy for the reaction are reported. Mechanisms for these reactions using the two catalysts are also suggested. The degrees of substitution (DS) of the esters prepared using both catalysts show that pyridine is a better catalyst than p-TsCl. Molecular weights of the esters, determined viscosimetrically, show that some degradation in the cellulose chain occurred at a reaction temperature of 70 °C. Hence, the optimum temperature for esterification appears to be 50–60 °C at 10 h reaction time to obtain full degree of acetyl substitution.

Keywords: Cellulose; Homogeneous acetylation; p-Toluenesulfonyl chloride; Pyridine; Mechanism of acetylation; Rate of reaction

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1. Introduction

Cellulose acetate is one of the commercially important cellulose derivatives with applications in the fields of coating, film and membrane preparation and textile and cigarette industries. Various methods exist for the acetylation of cellulose, in which acetic anhydride, acetyl chloride and ketene are used as acetylating agents. The anhydride is commercially applied. Acetylation by an acetic acid–trifluoroacetic anhydride mixture has also been reported [1,2]. There is much interest in developing new methods for the acetylation of cellulose to provide products with novel characteristics [3]. For a maximum conversion of cellulose to its derivatives, it is advisable to carry out the reaction in a homogeneous medium, requiring a suitable solvent system. Several cellulose solvents have been reported [4,5], but only some are true solvents that do not form derivatives during dissolution. Two new solvent systems are lithium chloride (LiCl) in N,N-dimethylacetamide (DMAc)

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* Corresponding author. Tel.: +91-376-370121 ext. 526; fax: +91-376-370011.
E-mail address: drrljt@csir.res.in (C.N. Saikia).

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and LiCl in *N*-methyl-2-pyrrolidinone, in which cellulose solutions of high concentration (up to 16%) can be prepared without degradation or formation of any derivative [6–8].

In the present paper, we describe the homogeneous acetylation of cellulose in the LiCl–DMAc solvent system, with acetic anhydride in the presence of *p*-toluenesulfonyl chloride (*p*-TsCl) or pyridine as catalysts. Esters of different degree of substitution (DS) were prepared at different temperatures and times of reaction. The products were characterized by IR and ^{1}H NMR spectroscopy. The kinetics of acetylation and the effect of temperature and catalysts are discussed in detail.

2. Experimental

Materials.—Rayon grade pulp containing 95.5% α-cellulose with an average degree of polymerization of 900 and 0.05% ash was obtained from Harihar Polyfibers, India. The cellulose was dried to less than 1% moisture before use. DMAc (CDH) was distilled under diminished pressure and stored under nitrogen over Riedel type 4 Å molecular sieves. LiCl (CDH) was dried at 200 °C under diminished pressure before use. Acetic anhydride (E. Merck), *p*-TsCl (E. Merck) and pyridine (CDH) were used as received.

Dissolution of cellulose.—A mixture of cellulose (8 g, 49.3 mmol based on glucose units) and DMAc (300 mL) was heated to 150 °C for 26 min in a round bottomed flask equipped with a short path condenser. Then, LiCl (6.5 g, 153 mmol) was added and the mixture was heated to 166 °C for 8 min. Then the reaction mixture was cooled to rt and stirred overnight for dissolution [9].

Acetylation of cellulose.—The cellulose solution prepared above was diluted to 1% by further addition of the solvent. To 50 mL of 1% (3.1 mmol) cellulose solution, 3.5 g (18 mmol) *p*-TsCl was added, followed by dropwise addition of 15 mL (0.16 mol) Ac_2O. For reactions using pyridine in place of *p*-TsCl, pyridine (10 mL, 0.124 mol) was added to the cellulose solution. Reaction times ranged from 2 to 24 h and temperatures from 28 to 70 °C. The reaction was terminated by pouring the mixture into cold distilled water. The products were filtered in a G-4 crucible, and washed thoroughly with cold distilled water. The filtrates were kept aside for determination of the DS. The products were further soxhlet extracted with water and then dried under diminished pressure in an oven at 40–45°C and then kept in a desiccator over P_2O_5.

Determination of the DS.—The filtrates which contained the unreacted anhydride along with liberated AcOH were titrated against 0.1 M NaOH (Procedure 1). The amount of anhydride consumed in the reaction is equivalent to the amount of AcOH liberated and, from this value, the DS was calculated as follows:

$$\text{Anhydride consumed (mmol)}$$
$$= (102/1000) \times (VSV_1/V_2)$$

where V is the volume (mL) of NaOH consumed, S is the concentration of NaOH, V_2 is the volume of filtrate taken for titration and V_1 is the total volume of the filtrate.

$$\text{DS} = \text{Anhydride consumed}/3.0864$$

The DS was also determined by saponification following the Ebrstadt procedure (Procedure 2) [10].

Molecular weight determination.—Molecular weight of the esters was determined viscosimetrically by using a standard Ostwald viscosimeter taking solutions in $CHCl_3$ and applying the Mark–Houwink–Sakurada equation [11]. Esters with low DS values were exempted from this study as these are insoluble in the solvent. Molecular weight of the esters was also calculated from the DS value.

Spectral analysis.—IR spectra of the esters were recorded on a Perkin–Elmer spectrometer (model 580B) using $CHCl_3$ as the solvent. ^{1}H NMR spectra were obtained using a Varian T-60 spectrometer at 60 MHz in $CDCl_3$ solution. Chemical shifts (δ) are given in ppm with Me_4Si as the internal standard.

3. Results and discussion

Cellulose was acetylated using both *p*-TsCl and pyridine as the catalyst at reaction tem-

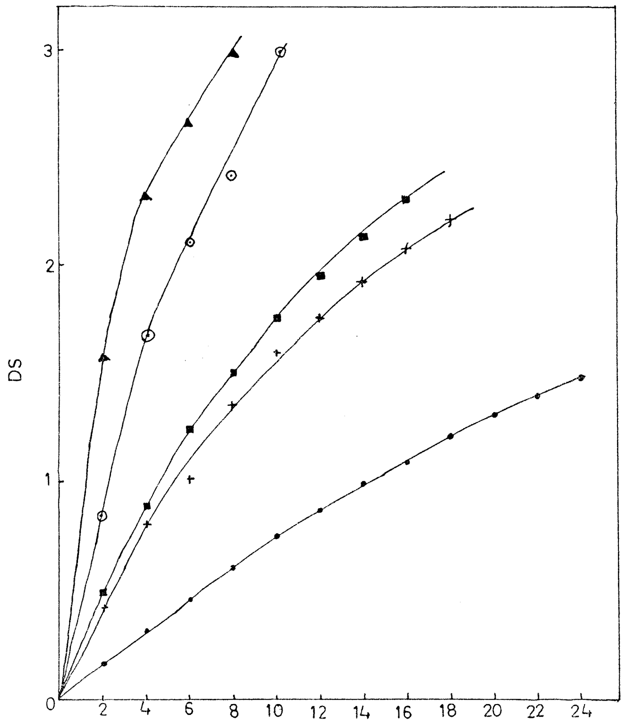


Fig. 1. DS vs. reaction time (h) at different reaction temperatures. (●) RT, (×) 40 °C, (◆) 50 °C, (⊙) 60 °C and (▲) 70 °C using *p*-TsCl as the catalyst.

peratures of 28, 40, 50, 60 and 70 °C. The DS values for a particular ester, determined by both procedures, were nearly equal and increased with reaction time at a particular reaction temperature as shown in Figs. 1 and 2. A comparison of calculated and experimentally determined molecular weights (Table 1) shows that at the temperatures 28, 40, 50 and 60 °C no degradation takes place. At 70 °C some chain degradation is observed in the case of *p*-TsCl catalysis. With pyridine catalysis, no degradation takes place at 70 °C.

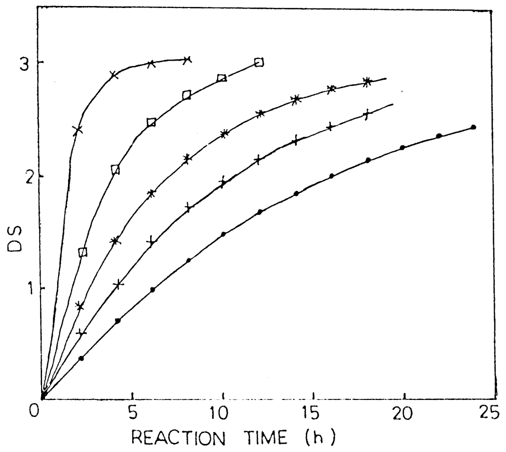


Fig. 2. DS vs. reaction time (h) at different reaction temperatures. (●) RT, (+) 40 °C, (*) 50 °C, (■) 60 °C and (×) 70 °C using pyridine as the catalyst.

The amounts of anhydride consumed (mmol) per mol of cellulose repeating unit were fitted to different rate equations. Best fit was obtained for a second-order equation in all temperature ranges, first-order in cellulose and first-order in anhydride. The rate constants for the second-order rate equation were obtained following an integration method (Figs. 3 and 4) using linear least-square method in FORTRAN 77.

Effect of the p-*TsCl catalyst.*—The second-order rate constants are given in Table 2 for

Table 1
DS and molecular weights of cellulose acetates at their highest conversions in different temperatures prepared using *p*-TsCl and pyridine as catalysts

Catalyst	Temperature (°C)	Time (h)	DS Procedure-1	DS Procedure 2	Amount of anhydride reacted (mmol)	Mw calculated	Mw experimental
p-TsCl	28	24	1.44	1.42	4.4382	196,000	199,000
	40	18	2.22	2.22	6.8672	225,000	225,000
	50	16	2.26	2.28	6.9845	227,000	227,000
	60	10	2.99	3.00	9.2590	255,000	254,000
	70	8	3.00	3.00	9.2592	255,000	204,000
Pyridine	28	24	2.39	2.36	7.3661	232,000	232,000
	40	18	2.54	2.50	7.8394	237,000	238,000
	50	18	2.81	2.90	8.6869	247,000	247,000
	60	10	3.00	2.81	9.2592	255,000	254,000
	70	8	3.00	3.00	9.2592	255,000	248,000

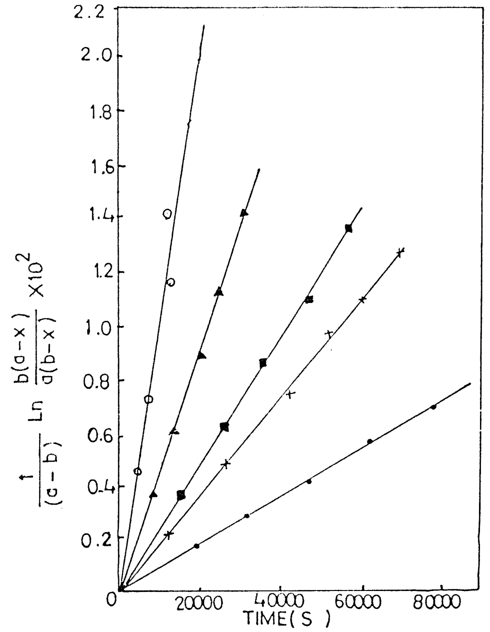


Fig. 3. Reaction time (s) vs. $1/(a-b)\ln[b(a-x)/a(b-x)] \times 10^2$ (L/mol) where a = initial concentration of cellulose; b = initial concentration of anhydride; x = amount of anhydride consumed at time t; at (●) RT, (×) 40 °C, (◆) 50 °C, (▲) 60 °C and (○) 70 °C with p-TsCl catalyst.

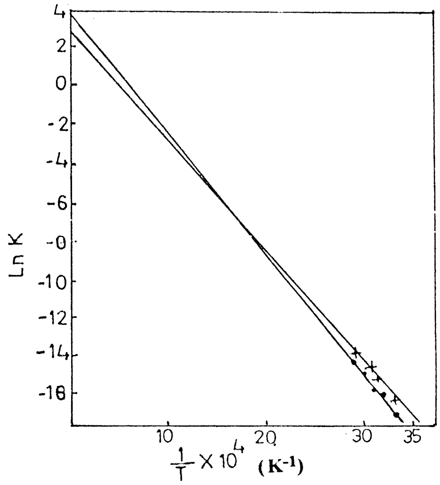


Fig. 5. $1/T \times 10^4$ (K^{-1}) vs. ln K for (●) p-TsCl and (×) pyridine.

the five temperatures studied and for both catalytic systems. Dissolution of cellulose in the LiCl–DMAc solvent system may be accompanied by interactions [6] as given in Scheme 1. The primary hydroxyl group is expected to be better solvated than the secondary hydroxyl groups. Hence, during acetylation, the anhydride might attack the secondary hydroxyl groups first. During acetylation the applied molar ratio between hydroxyl groups, p-TsCl and anhydride was 1:2:1. Upon decreasing the amount of p-TsCl to 50%, products with very low DS were formed at 70 °C, even for a reaction time of 24 h. The general mechanism for the esterification reaction with an alcohol using p-TsCl as a catalyst is still under debate. It may be similar to that for p-toluenesulfonic acid and

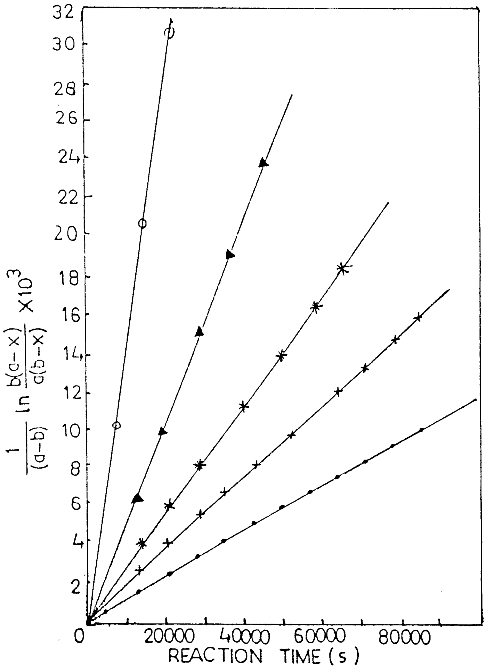
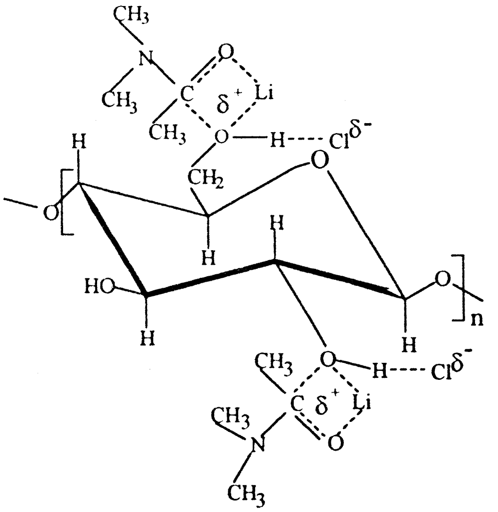


Fig. 4. Reaction time (s) vs. $1/(a-b)\ln[b(a-x)/a(b-x)] \times 10^3$ (L/mol) where a = initial concentration of cellulose; b = initial concentration of anhydride; x = amount of anhydride consumed at time t; at (●) RT, (×) 40 °C, (*) 50 °C, (▲) 60 °C and (○) 70 °C with pyridine catalyst.



Scheme 1. Possible interactions between cellulose and the LiCl–DMAc solvent system.

Table 2
Temperature and kinetic rate constants for second order reaction

Temperature (K)	$1/T \times 10^4$ (K^{-1})	p-TsCl		Pyridine	
		$k \times 10^7$	ln k	$k \times 10^7$	ln k
301	33.222	0.487	−16.837	1.188	−15.945
313	31.948	1.347	−15.820	1.875	−15.490
323	30.959	1.579	−15.661	2.808	−15.086
333	30.030	3.991	−14.734	5.174	−14.474
343	29.154	6.567	−14.236	14.024	−13.478

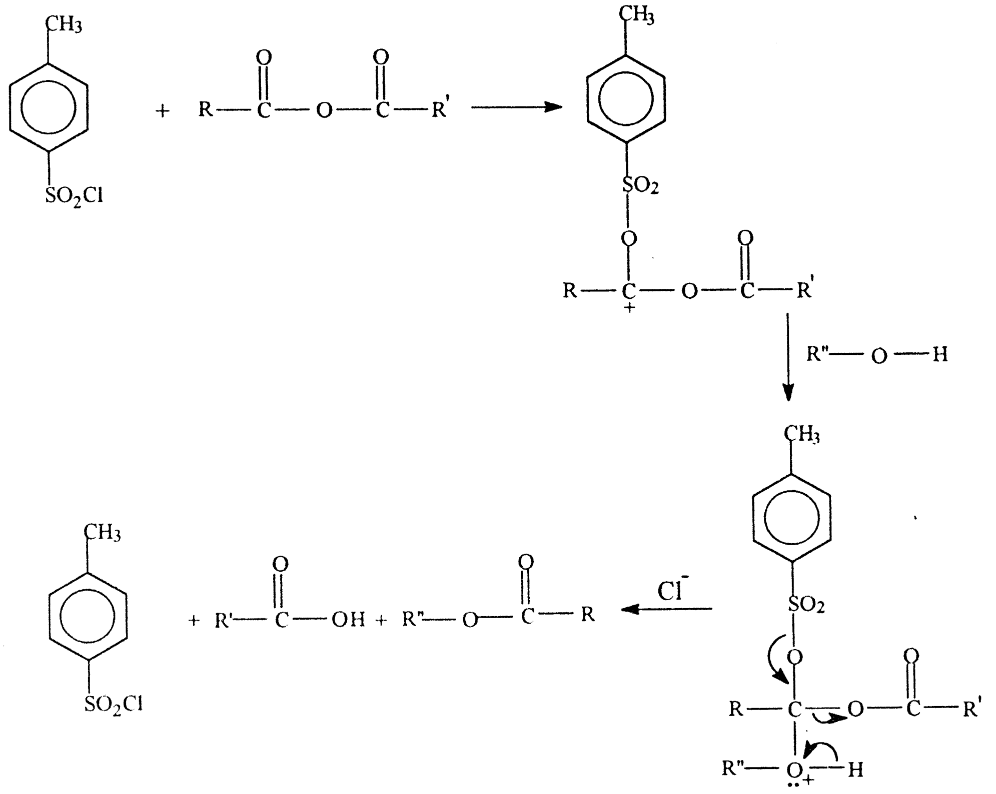
may be as given in Scheme 2 [12]. The second role of p-TsCl may be to attack a solvated hydroxyl group of the cellulose in the DMAc–LiCl solvent system. The overall tentative mechanism is given in Scheme 3.

Influence of the pyridine catalyst.—The reaction mechanism of esterification using pyridine as the catalyst is rather similar to the previous one. The overall suggested mechanism of reaction is given in Scheme 4. An N-acyl pyridinium ion is assumed to be the acetylating reagent.

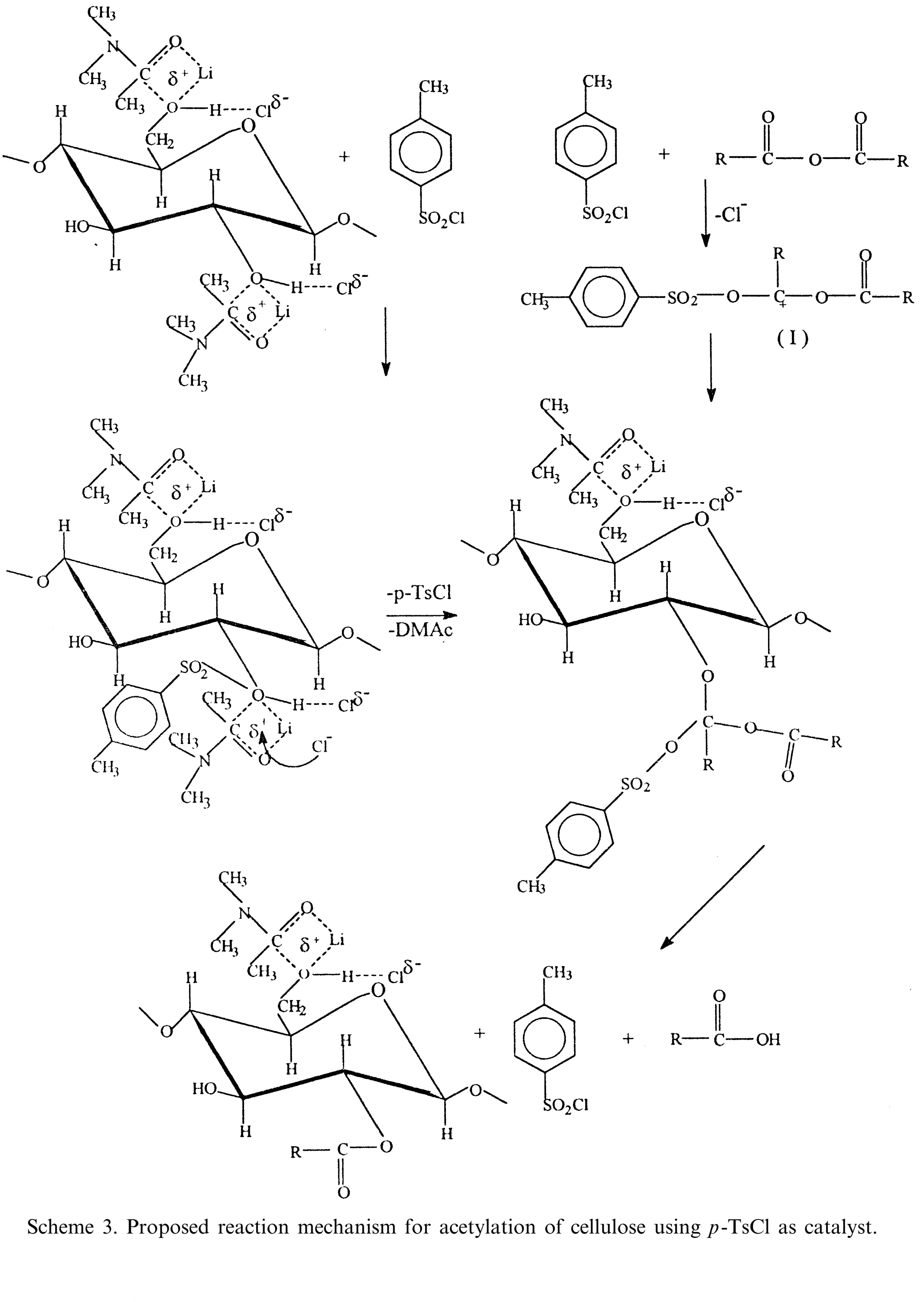
The activation energy for the acetylation reaction was found to be 51.7 kJ/mol with an Arrhenius factor of 44.7 for the p-TsCl catalyst and 48.4 kJ/mol with an Arrhenius factor of 24.05 for the pyridine catalyst (Fig. 5).

Thus, the activation energy for esterification using pyridine as catalyst was found to be less than that using p-TsCl as catalyst. This is reflected by a somewhat higher rate of acetylation (Fig. 2 versus Fig. 1).

The esters obtained were characterized by IR and ^{1}H NMR spectral analyses. The IR spectra of the cellulose acetates prepared represent the characteristics of esterified products by displaying essential bands of ester compounds at 1740 cm^{-1} ($>$C=O stretching vi-



Scheme 2. General reaction mechanism of alcohol with anhydride using p-TsCl as catalyst.

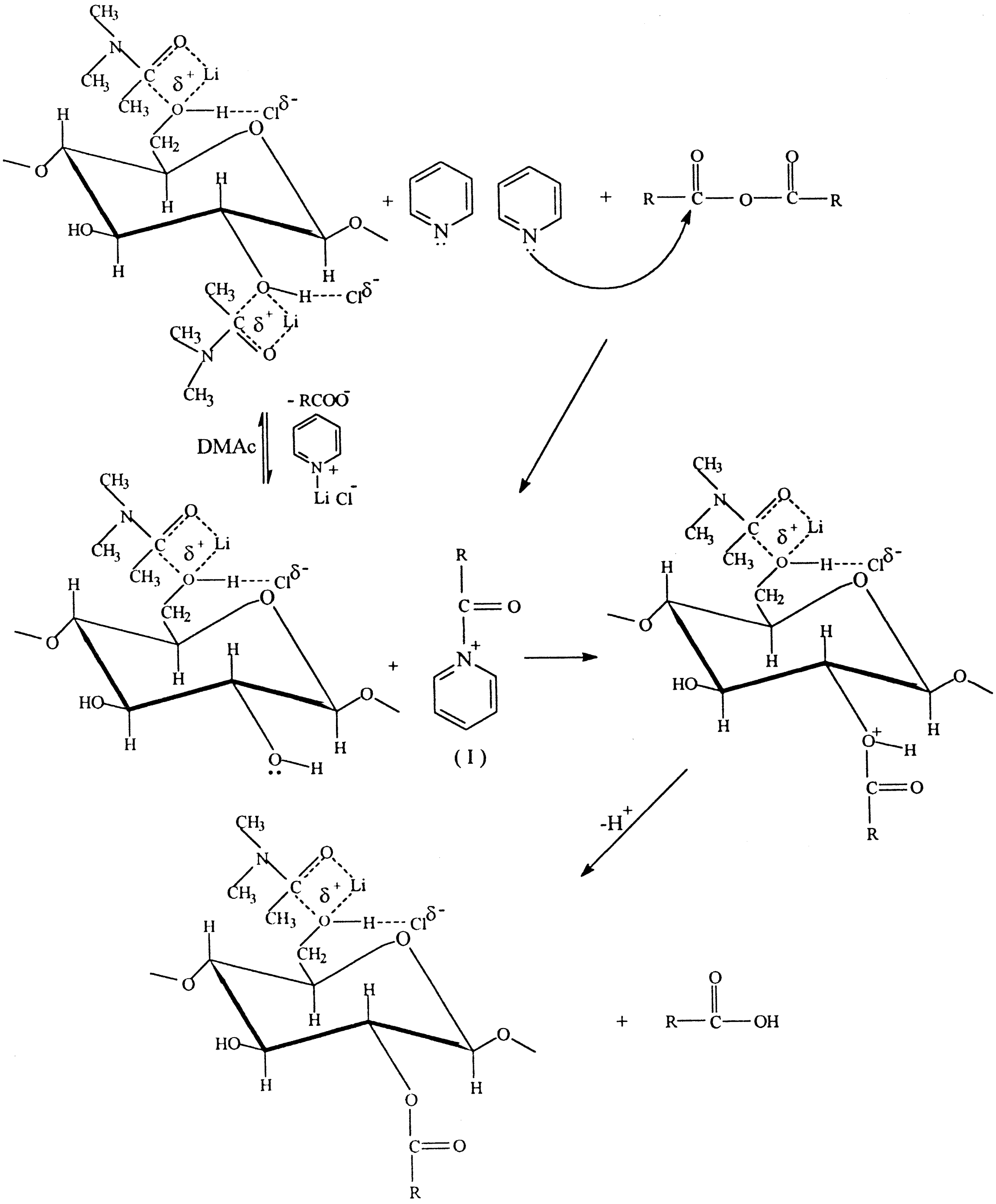


Scheme 3. Proposed reaction mechanism for acetylation of cellulose using *p*-TsCl as catalyst.

bration), 1375 cm^{-1} (–C–O–C– st.), 1225 cm^{-1} (–CH$_2$– wagging), 1075 and 800 cm^{-1} (rocking vibration of esters). The ^{1}H NMR spectra of all the esters showed characteristic peaks at δ 1.9 (–CO–CH$_3$). The signals at δ 5.31 and δ 4.85 may be attributed to the C-1 and the C-6 protons of acetylated –CH$_2$OH groups, respectively [13].

4. Conclusion

LiCl–DMAc was found to be an excellent solvent system for the acetylation of cellulose with acetic anhydride in the presence of *p*-TsCl or pyridine. The esterification was found to be a second-order reaction. Some degradation of the cellulose chain was ob-



Scheme 4. Proposed reaction mechanism for acetylation of cellulose using pyridine as catalyst.

served at a reaction temperature of 70 °C and the optimum temperature for esterification may be 50–60 °C. At 60 °C, 10–12 h suffices to obtain full acetyl substitution (DS 3). Pyridine is more active as a catalyst for esterification than *p*-TsCl. In case of esterification with higher anhydrides, *p*-TsCl might serve as a better catalyst.

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