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Best combination of promoter and micellar catalyst for the rapid conversion of sorbitol to glucose

Kakali Mukherjee, Aniruddha Ghosh, Rumpa Saha, Pintu Sar, Susanta Malik, Bidyut Saha *

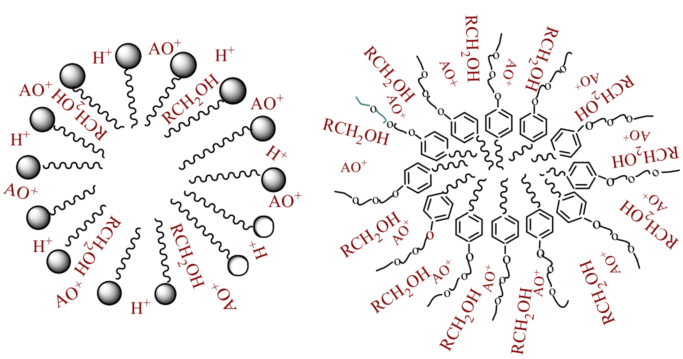
Homogeneous Catalysis Laboratory, Department of Chemistry, The University of Burdwan, Golapbag, Burdwan 713104, WB, India

HIGHLIGHTS

- The reaction is carried out in aqueous media.
- Toxic hexavalent chromium is completely reduced to trivalent chromium.
- The reaction can be carried out very rapidly.
- PA, bipy, phen are used as promoters to accelerate the rate in micellar media.
- Combination of phen and TX-100 catalyzes the oxidation of D-sorbitol most.

GRAPHICAL ABSTRACT

Picolinic acid, 2,2′-bipyndine and 1,10-phenanthroline promoted Cr(VI) oxidation of D-sorbitol to glucose in aqueous micellar media is shown here. The anionic surfactant (SDS) and neutral surfactant (TX-100) accelerate the rate of reaction. Combination of phen and TX-100 is the best choice for chromic acid oxidation of D-sorbitol to glucose in aqueous media although 2,2′-bipyridine is best promoter in absence of micellar catalyst.



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ABSTRACT

Kinetic data for oxidation of D-sorbitol to glucose by hexavalent chromium in aqueous medium and aqueous surfactant medium (SDS, TX-100) have been reported. Effect of promoter such as PA, bipy and phenanthroline on the reaction has been investigated. The reaction is performed under pseudo first order condition with an excess of substrate over the oxidant. The reaction is first order with respect to substrate and oxidant. The micelles have a catalytic effect on the reaction. Combination of phen and TX-100 produces almost twelve times increase in rate of oxidation.

Introduction

Carbohydrates are important biochemical compounds as they are the major sources of energy for living organism for vital metabolism processes [1]. Sugars and their derivatives play an important role in the chemistry of chromium in the environment [2,3] and in the mechanism of chromium-induced cancer [4]. As oxidation of carbohydrates is widely studied under the field of organic chemistry [5], the present research has been conducted to study the oxidation of sorbitol which is a sugar alcohol with Cr(VI) as an oxidizing agent in sulphuric acid medium. Sorbitol is a sugar alcohol which can be obtained by the reduction of glucose.

* Corresponding author. Fax: +91 0342 2530452.
E-mail address: b_saha31@rediffmail.com (B. Saha).

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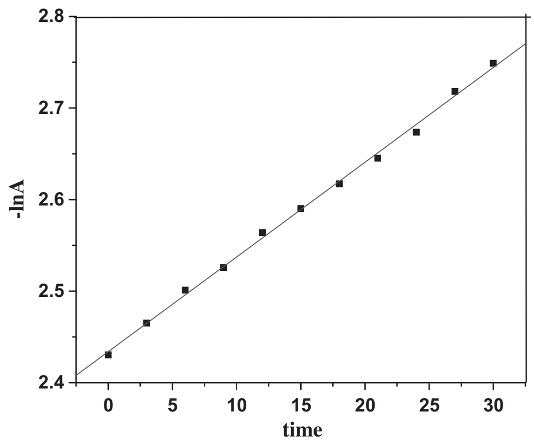

Fig. 1. plot of −lnA vs time at regular time interval (3 min).

Table 1
k_{obs} and half life of the reaction in presence and absence of promoter and non functional micellar catalyst.

Promoter (mol dm^{-3})		Micellar catalyst (mol dm^{-3})		$10^4 \times k_{obs}$ (s^{-1})	$t_{1/2}$ (h)
None		None		1.717 ± 0.001	1.121
Picolinic acid (PA)	0.0025	None		2.483 ± 0.0006	0.775
2,2′-Bipyridine (bipy)	0.0025	None		6.183 ± 0.001	0.311
1,10-Phenanthroline (phen)	0.0025			5.917 ± 0.0006	0.325
None		CPC		0.030 ± 0.005	64.16
None		SDS	0.01	3.433 ± 0.001	0.561
None		TX-100	0.01	3.483 ± 0.001	0.553
Picolinic acid (PA)	0.005	TX-100	0.01	3.583 ± 0.0001	0.537
	0.0075			4.633 ± 0.0005	0.415
	0.01			5.817 ± 0.0007	0.331
	0.0125			6.767 ± 0.0004	0.284
	0.0150			7.450 ± 0.0002	0.258
2,2′-Bipyridine (bipy)	0.005	TX-100	0.01	10.22 ± 0.002	0.188
	0.0075			13.95 ± 0.0005	0.138
	0.01			16.02 ± 0.0003	0.120
	0.0125			19.00 ± 0.0001	0.101
	0.0150			19.33 ± 0.0004	0.099
1,10-Phenanthroline (phen)	0.0025	TX-100	0.01	7.367 ± 0.002	0.261
	0.005			12.77 ± 0.0007	0.151
	0.0065			13.62 ± 0.0006	0.141
	0.0075			15.90 ± 0.001	0.121
	0.01			20.33 ± 0.0008	0.094
Picolinic acid (PA)	0.005	SDS	0.01	4.117 ± 0.003	0.467
	0.0065			4.951 ± 0.0009	0.388
	0.0075			5.283 ± 0.0002	0.364
	0.01			5.412 ± 0.0006	0.356
	0.0125			6.270 ± 0.001	0.307
2,2′-Bipyridine (bipy)	0.005	SDS	0.01	11.80 ± 0.005	0.163
	0.0065			13.40 ± 0.009	0.144
	0.0075			13.98 ± 0.006	0.138
	0.01			16.31 ± 0.002	0.118
	0.0125			18.20 ± 0.004	0.106
1,10-Phenanthroline (phen)	0.0025	SDS	0.01	4.612 ± 0.0006	0.417
	0.005			6.910 ± 0.0005	0.278

[Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4]$_T$ = 0.5 mol dm^{-3}, [D-sorbitol]$_T$ = 100 - × 10^{-4} mol dm^{-3}, Temp = 35 °C.

It is 60% as sweet as sucrose and is used as a sugar substitute for diabetics. It is a major intermediate for the production of fuels from biomass resources. Sorbitol can be oxidized to its corresponding aldohexose by employing different type of oxidants such as transition metal ions [6,7], inorganic acids, complex ions and hydrogen peroxide [8]. Present work describes how fast the terminal (primary) alcohol group of sorbitol can be oxidized by chromic acid to an aldehyde to yield glucose. Our aim is to perform the reaction in aqueous media and to accelerate the rate of the reaction as

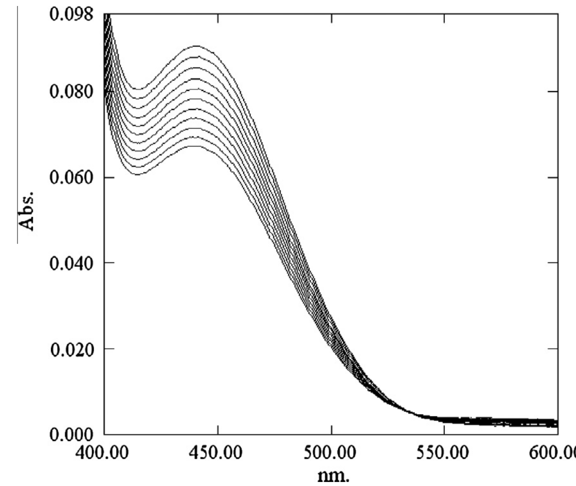

Fig. 2a. Scanned absorption spectra of the reaction in absence of promoter at regular time interval (3 min). [D-sorbitol]$_T$ = 100 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, Temp = 35 °C.

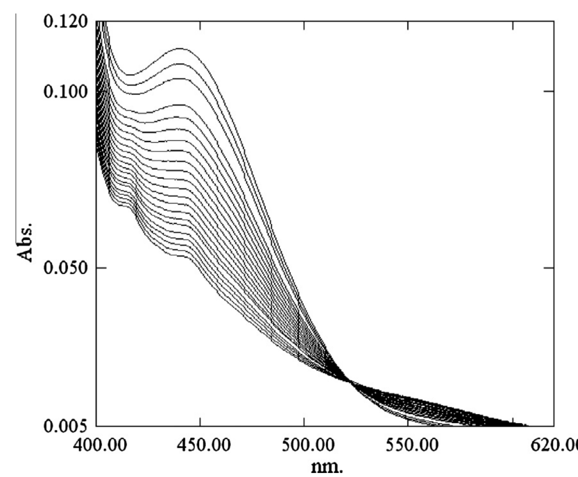

Fig. 2b. Scanned absorption spectra of the reaction mixture at regular time interval (1 min). [D-sorbitol]$_T$ = 100 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, [bipy]$_T$ = 25 × 10^{-4} mol dm^{-3}, Temp = 35 °C.

hexitols are more resistant to oxidation than are the familiar hexoses [9]. So we choose chromic acid as oxidizing agent as the other Cr(VI) containing agent like pyridinium chloro chromate (PCC), pyridinium dichromate (PDC), etc. are not soluble in water. Again by this reaction toxic and carcinogenic hexavalent chromium [10–12] is completely reduced to nontoxic trivalent chromium. But for large scale production of organic compound it is very much essential to know the velocity of the reaction. The catalytic effect of surfactants over a certain concentration called critical micellar concentration has been previously reported [13–18]. Surfactant entrapped water molecule provides unique microenvironments for interactions and reactions, as a result of which attention has been drawn to the effect of micelles on the nature and rates of reactions. Addition of surfactants above CMC creates two phases in the reaction medium. One is aqueous phase and the other is micellar phase. When the effective concentration of reactive species is greater in micellar phase then surfactants behave as positive catalyst. In this work the effects of anionic micelle sodiumdodecyl sulphate (SDS) and neutral micelle Triton-X-100 (TX-100) on the reaction rate are shown. Both of them accelerate the reaction rate. Rate of the reaction is further increased when we use some promoter in combination with the surfactants. Picolinic acid (PA), 2,