Reactivity of *t*-Butyl Chromate Resins with Substituted α-Phenylethanols: A Kinetic Study

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ABSTRACT: Polystyrene and polyacenaphthylene supports were functionalized to generate a *t*-butyl chromate function and the resulting polymer-supported reagents were used for the oxidation of alcohols. They were found to oxidize primary and secondary alcohols to the corresponding carbonyl compounds in quantitative yields. Oxidation of differently substituted α-phenylethanols was attempted for this purpose and the kinetics of oxidation reactions was studied. The reaction was found to be first order with respect to the substrate, the reaction being carried out with an excess of the *t*-butyl chromate reagent. The rate of oxidation was also found to be dependent on the nature of the substrate, concentration of the reagent function, and the nature and concentration of the acid catalyst used. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 799–804, 1998

Key words: polystyrene support; polyacenaphthylene support; *t*-butyl chromate; kinetics and mechanism of oxidation

INTRODUCTION

One of the major problems encountered with the use of polymeric reagents for general synthetic purposes is the difficulty in monitoring the course of the reactions. Only a few techniques are available for the measurement of the rate and determination of the mechanism of polymer-supported reactions.[1,2] By the adoption of the usual techniques available for kinetic and mechanistic investigation in the solution phase, with relevant modifications suitable for the solid phase, a familiarization about the kinetics and mechanism of polymer-supported reactions has been achieved. The difficulty often encountered in such studies is due to the heterogeneity of the reaction. It is assumed that the supporting of a particular molecular species on a polymer matrix would not be expected to influence the reaction rate as measured in the bulk, although the local rate may be considerably high.[2] Thus, if the total number of supported species is increased, keeping the loading on the support constant, the bulk measured rate would increase linearly as would be the case in the homogeneous reaction. Using the studies on the kinetics of polyesterification reactions, Flory demonstrated that the reactivity of functional groups was independent of the size of the polymer molecule to which they were attached.[3] But this concept cannot be applied in the case of crosslinked polymers because of diffusional limitations on the molecules entering and traversing through the crosslinked network. In highly solvated resins, the deviation from solution-phase reactions may not be very prominent. In the case of crosslinked resins, the nonequiva-

Table I Rate Constants and Energy of Activation Values of Oxidation of Substituted α-Phenylethanols

| Substrate | Rate Constant $\times 10^3$ (s^{-1}) | | | | | | | | Energy of Activation (kJ/mol) | | | |
| | 303 K | | | | 323 K | | | | | | | |
	1a	1b	2a	2b	1a	1b	2a	2b	1a	1b	2a	2b
α-Phenylethanol	5.68	6.16	6.81	7.53	11.75	13.52	14.22	16.02	37.63	35.13	30.6	28.75
p-Methoxy-α-phenylethanol	7.75	8.33	10.11	12.14	15.28	18.21	21.23	24.50	27.22	24.77	19.95	17.25
p-Methyl-α-phenylethanol	6.58	6.72	9.14	11.30	12.98	14.01	18.71	22.07	40.33	28.91	21.93	19.89
p-Chloro-α-phenylethanol	3.01	4.02	5.95	6.82	9.52	10.25	12.93	14.71	32.92	36.98	32.92	30.72
p-Nitro-α-phenylethanol	2.37	3.08	4.77	5.98	8.78	9.52	10.95	12.54	34.92	39.21	34.92	33.11

1a, DVB-crosslinked polystyrene supported t-butyl chromate; 1b, 1,4-BDDMA–crosslinked polystyrene-t-butyl chromate (PStBC); 2a, DVB-crosslinked polystyrene-t-butyl chromate (PStBC); 2b, 1,4-BDDMA-crosslinked PAtBC; Solvent, chloroform; [alcohol], 0.025M; resin-to-alcohol ratio, 8 : 1; catalyst, 2N H$_2$SO$_4$ (2 mL).

lence of the reactive sites may again pose problems. In the present article, an attempt was made to evolve some kinetic formulations to describe the nature of the oxidation reactions using t-butyl chromate resins.

EXPERIMENTAL

Preparation of t-Butyl Chromate Resin

Preparation of 2-Oxopropyl Resin

The polymer beads (styrene–divinylbenzene-[DVB], styrene–1,4-butanediol dimethacrylate [1,4-BDDMA] [2%], acenaphthylene–DVB, and acenaphthylene–1,4-BDDMA copolymers [10%]) were thoroughly washed with benzene, methylene chloride, and carbon tetrachloride and dried at 60°C. The polymer beads (10 g) were suspended in a mixture of carbon disulfide and methylene chloride (4 : 1 v/v 30 mL) for 12 h. Bromoacetone (20 g) and the solvent mixture (20 mL) was taken in a 500 mL round-bottomed flask, fitted with a reflux condenser, and cooled in an ice bath. Anhydrous AlCl$_3$ (20 g) was added in small portions over a period of 15 min to the bromoacetone with vigorous stirring. When the addition was over, the preswollen polymer was gradually added to the reaction mixture with occasional shaking and continuous stirring. The mixture was stirred at room temperature for 15 min and heated under reflux for 6 h. The reaction mixture was added to aqueous ethanol to break the Lewis acid complex. The resin particles were collected on a sintered glass filter and washed with water (20 mL, 3 times), ethanol (20 mL, 3 times), and acetone (20 mL, 3 times). The resin was dried in a vacuum to a constant weight.

Preparation of t-Butyl Alcohol Resins

Magnesium turnings (2.5 g) and a crystal of iodine was suspended in absolute dry ether (50 mL) and warmed gently. To the suspension, a solution of methyl iodide (6 mL) in dry ether (30 mL) was added in small quantities, so that gentle boiling was maintained. When all the magnesium was dissolved, the reaction mixture was cooled in ice and the suspension of the preswollen keto resin in tetrahydrofuran (50 mL) was added in small portions to the methylmagnesium iodide with constant stirring. The reaction mixture was heated under reflux in a water bath for 6 h. The resin

Table II Rate Constants for the Consumption of *t*-Butyl Chromate Function: 2% DVB-Crosslinked Polystyrene-Supported *t*-Butyl Chromate Reagent

Number of Methylene Groups in the Spacer Arm	Rate Constant $\times 10^3$ $(s^{-1})^a$	
	303 K	323 K
0	4.70	10.21
1	5.28	11.41
2	5.68	11.72
3	6.25	12.31
4	6.98	13.21
5	7.58	14.35

[a] Solvent, chloroform; [PS*t*BC], 25×10^{-4} *M;* [α-phenylethanol] 25, $\times 10^{-3}$ *M;* catalyst 2*N* H$_2$SO$_4$ (2 mL).

was filtered, washed with alcohol (20 mL, 3 times), THF–water (20 mL, 3 times), and acetone (20 mL, 3 times) and dried in a vacuum to a constant weight.

Preparation of the *t*-Butyl Chromate Resin

The *t*-butyl alcohol resin was suspended in an acetonitrile–water mixture (30 mL) for 12 h. A 2*M* solution of freshly prepared chromium trioxide (70 mL) in acetonitrile was added with cooling in an ice bath. The reaction mixture was stirred at room temperature for 24 h. The resin was filtered, washed with water (20 mL, 3 times), THF (20 mL, 3 times), methylene chloride (20 mL, 3 times), methanol (20 mL, 3 times), and acetone (20 mL, 3 times) and dried in a vacuum to a constant weight.

**Kinetics of Oxidation of Differently Substituted α-Phenylethanols**

α-Phenylethanol (0.025*M*) or substituted α-phenylethanols (0.025*M*) were dissolved in chloroform (20 mL). One milliliter of the solution was withdrawn, made up to 10 mL, and used as the blank solution. The *t*-butyl chromate resin (eightfold excess) was added to the α-phenylethanol solution and shaken well. An aliquot of the solution (1 mL) was withdrawn after regular intervals of time and diluted to 10 mL and the concentration of the acetophenone formed was measured spectrophotometrically. The experiment was repeated

at different intervals of time and at 50°C. The rate constant for the reaction was calculated.

RESULTS AND DISCUSSION

Oxidation of Substituted α-Phenylethanols Catalyzed by Sulfuric Acid

Oxidation of differently substituted α-phenylethanols was attempted using the *t*-butyl chromate reagents prepared from 2% divinylbenzene (DVB) and 1,4-butanediol dimethacrylate (1,4-BDDMA)-crosslinked polystyrenes (**1a, 1b**) and 10% DVB and 1,4-BDDMA-crosslinked polyacenaphthylene (**2a, 2b**)[4]


1a, 1b   2a, 2b
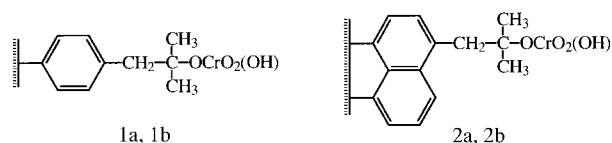
The substituted α-phenylethanols used for the present study, except the *p*-nitro-α-phenylethanol, were prepared by the reduction of the respective acetophenones using sodium borohydride. *p*-Nitro-α-phenylethanol was prepared by the low-temperature nitration of α-phenylethanol using a KNO$_3$/H$_2$SO$_4$ mixture. All the oxidation reactions were carried out in chloroform, at room temperature (30°C) and at 50°C. An alcohol-to-resin ratio of 1 : 8 was taken, and 2 mL of 2*N* sulfuric acid was used as the catalyst. The reactions were followed by measuring the concentration of the corresponding ketones formed at definite intervals of time by the spectrophotometric method. A simple first-order ki-

Table III Effect of Nature and Concentration of Catalyst on the Rate of Oxidation Reactions

Catalyst	Rate Constant $\times 10^3$ $(s^{-1})^a$	
	303 K	323 K
Sulfuric acid (0.5*N*)	4.05	8.33
Sulfuric acid (1.0*N*)	4.91	9.80
Sulfuric acid (2.0*N*)	5.68	11.75
Glacial acetic acid	3.97	7.02
Water	2.01	5.21
No catalyst	0.25	1.20

[a] Solvent, chloroform; [PS*t*BC], 75×10^{-3} *M;* [α-phenylethanol], 25×10^{-3} *M.*
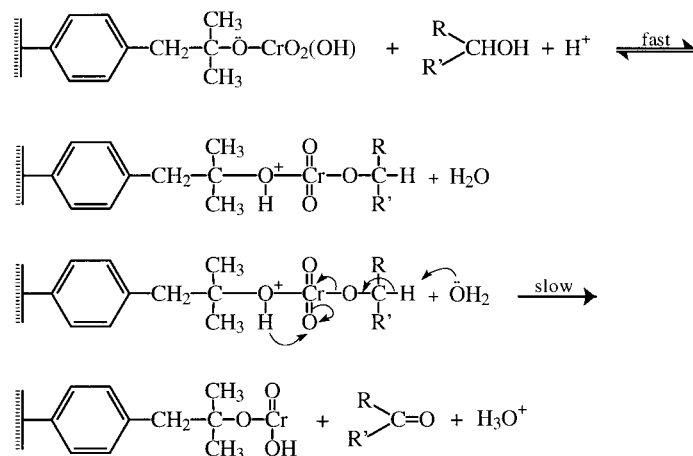
Scheme 1 Proposed mechanism of acid-catalyzed oxidation of alcohols using polymeric t-butyl chromate reagents.

netic equation was applied to calculate the rate constants of the reactions at the two different temperatures. The energy of activation (E_a) was thus computed. The experimentally observed values of the rate constants and energy of activation are presented in Table I. The values varied ± 0.07 from the mean values.

The oxidation of substituted α-phenylethanols using the different t-butyl chromate reagents has shown clearly that the reaction is first order with respect to the substrates, the reaction being carried out with a large excess of the t-butyl chromate reagent. Of the different t-butyl chromate reagents, the one prepared from 10% 1,4-BDDMA-crosslinked polyacenaphthylene resin is found to be the most reactive. The 1,4-BDDMA-crosslinked polyacenaphthylene-supported reagent is more hydrophilic and flexible. It provides a better hydrophilic–hydrophobic balance which facilitates an ionic reaction. The values of the rate constants (both at 30 and 50°C) for all the alcohols are found to be the highest while using this reagent; similarly, the activation energy values are correspondingly the lowest, indicating that the reactions are highly facilitated. The DVB-crosslinked polystyrene-supported reagent is the least reactive as exemplified by the low rate constant values and high energy of activation.

The rate of oxidation reaction was found to be dependent on the nature of the substrates. p-Methoxy-α-phenylethanol was found to be the most reactive, the nitro derivative being the least reactive. The relative rates of oxidation of *para*-substituted α-phenylethanols followed the order

MeO— > Me— > H— > Cl— > NO$_2$—, the electron-donating substituents favoring oxidation.

Dependence of the Rate of Oxidation on the Concentration of the Reagent Function

To study the dependence of the rate of oxidation reactions on the relative effective concentration of the reagent function, oxidation of α-phenylethanol was carried out using the t-butyl chromate reagent prepared from 2% DVB-crosslinked polystyrene resin. The concentration of the t-butyl chromate function was fixed at $25 \times 10^{-4} M$ and a 10-fold excess of the alcohol ($25 \times 10^{-3} M$) was used, assuming pseudo-first-order kinetics. $2N$ sulfuric acid (2 mL) was used as the catalyst. The consumption of the t-butyl chromate function was measured at definite time intervals by isolating the resin by filtration and estimating the residual capacity by the iodometric method. A first-order kinetic equation was used to calculate the rate constant. Reproducible values of the rate constants revealed a first-order dependence of the rate of oxidation on the effective concentration of the t-butyl chromate function. The results are presented in Table II.

Dependence of the Nature and Concentration of the Catalyst on the Rate of Oxidation Reaction

Oxidation of α-phenylethanol was carried out using the t-butyl chromate prepared from the 2% DVB-crosslinked polystyrene resin. The reagent
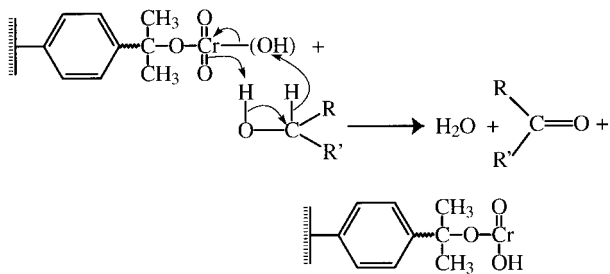
Scheme 2 Proposed mechanism of noncatalyzed oxidation of alcohols using the polymeric *t*-butyl chromate reagent.

having one methylene spacer arm was used. The reaction was carried out in the presence of various concentrations of sulfuric acid (0.5, 1, and 2N), glacial acetic acid, and water as catalysts. The reaction was also conducted in the absence of any catalyst, using the dry resin. The results are presented in Table III.
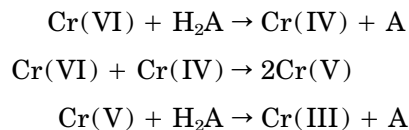
The results show that sulfuric acid is the most efficient catalyst. Also, there is a progressive increase in the rate of the reaction with an increase in the concentration of the acid. Acetic acid and even water was found to catalyze the reactions, water being less effective. Even in the absence of the catalyst, the reaction was found to take place, only at a reduced rate.

Mechanism of the Oxidation Using *t*-Butyl Chromate Reagents

The investigation of the kinetics of the oxidation of alcohols (substituted α-phenylethanols as model substrates) using the various polymeric *t*-butyl chromate reagents revealed first-order dependence of the rate on the substrate (alcohol), the reagent, and the catalyst. Thus, the rate law may be represented as $d[\text{alcohol}]/dt = \text{K}[\text{alcohol}][\text{P}t\text{BC}][\text{H}^+]$. Based on the available kinetic data, it may be assumed that the reaction is taking place in a two-step process: a rapid reversible acid catalyzed esterification of the alcohol followed by the slow oxidation step which may be a concerted base-catalyzed process giving quadrivalent chromium as an intermediate which finally decays to chromium(III) species. Thus, the reaction is supposed to follow the path as depicted in Scheme 1.

The oxidation of alcohols can thus be viewed as a two-electron transfer process, the alcohol acting as the electron donor. This results in the conver-

sion of Cr(VI) to Cr(IV). This can finally be converted to Cr(III) by a series of oxidation–reduction processes. The skeletal reaction may be represented thus:

$$\text{Cr(VI)} + \text{H}_2\text{A} \rightarrow \text{Cr(IV)} + \text{A}$$
$$\text{Cr(VI)} + \text{Cr(IV)} \rightarrow 2\text{Cr(V)}$$
$$\text{Cr(V)} + \text{H}_2\text{A} \rightarrow \text{Cr(III)} + \text{A}$$

H$_2$A and A are the reduced and oxidized forms of the reducing agent, alcohol. Here, the intermediates Cr(V) and Cr(IV) species are transient, although they may have some stability in a heterogeneous system.[5] In the second step of the reaction, water can act as the base to abstract a proton from the α-carbon atom. The cleavage of the C$_\alpha$—H bond is expected to take place in the second step, which is the rate-determining one. This has been proved by deuterium labeling in the case of the oxidation of alcohols using low molecular weight Cr(VI) reagents.[6] The proposed mechanism can very well explain the observed relative rates of oxidation of *para*-substituted α-phenylethanols, electron-releasing substituents favoring oxidation. The arguments put forward here could be supported by the previously obtained results in the case of oxidation of primary and secondary alcohols by low molecular weight Cr(VI) reagents.[7,8]

Mechanism of Uncatalyzed Reactions

Studies on the oxidation of various alcohols using the polymeric *t*-butyl chromate reagents have shown that the reaction could take place even in the absence of any catalyst. The reaction was found to be very sluggish. Here, an alternative mechanism may be proposed. The oxidation reaction may be proceeding by a bimolecular cyclic electron switch process (Scheme 2).

This cyclic mechanism is supposed to be more satisfactory in explaining the relative rates of oxidation of *para*-substituted α-phenylethanols.[9] This could explain the preferential oxidation of cyclic secondary alcohols with accessible (equatorial) hydrogen atoms compared to their hindered epimers (with axial H). This hypothesis assumes that the esterification equilibrium is not markedly influenced by steric conditions.[10]

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