Organic Process Research & Development **2003**, *7*, 936–938

A Kinetic Study of 2-Ethyl-1-hexanol Oxidation by Dichromate Using Clay-Supported 1-Butyl 4-aza-1-azonia Bicyclo[2.2.2]octane Chloride as the Phase-Transfer Catalyst

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Abstract:

Selective oxidation of primary alcohols to aldehydes is a long-standing problem of organic chemistry (Bueler, C. A.; Pearson, D. E. *Survey of Organic Synthesis*; Wiley-Interscience: New York, 1977; Vol. 2, p 480; House, H. O. *Modern Synthetic Reactions*, 2nd. ed.; W. A. Benjamin: Menlo Park, California, 1972; p 257; Epstein, W. W.; Sweet, F. W. *Chem. Rev.* 1967, *67*, 247; Landini, D.; Montanari, F.; Rolla, F. *Synthesis* 1979, 134). The use of potassium dichromate as a synthetically useful oxidizing agent is reported for the oxidation of an industrially important lipophilic alcohol, employing modified clay as the phase-transfer catalyst. The phase-transfer catalysis results in nearly complete oxidation of the 2-ethylhexanol in 40 min at room temperature, with high selectivity to the 2-ethylhexanal, compared to 48 h in its absence. Kinetic studies show the reaction occurs via transfer of $Cr_2O_7^{2-}$ into the organic phase. The emphasis will be on simplicity of the condition as a preparative organic method, selectivity with regard to over-oxidation, efficiency, and mildness of conditions.

Introduction

A significant and recurring problem facing the synthetic organic chemist[5,6] is how to effectively carry out reaction between a water-soluble reagent and a water-insoluble substrate. When reaction is attempted as an aqueous−organic biphase process, very low rates are usually observed due to the low concentration of at least one of the compounds in each phase. Rapid stirring has been shown, in certain cases, to have an accelerating effect by increasing the surface contact between the layers and thereby increasing the interfacial component of the reaction.[7,8] Soluble ammonium and phosphonium salts,[9] as well as crown ethers,[10,11] cryptands,[12] and surfactants[13] have proven extremely useful in catalyzing aqueous−organic biphase reactions. Interest in such phase-transfer and related two-phase catalytic techniques continues to grow in synthetic and mechanistic organic chemistry.[14,15] It seems that the development of a technique which uses insoluble catalysts to accelerate aqueous−organic phase reactions would not only be an interesting possibility but would also reinforce claims[16−18] that the future of synthetic organic chemistry rests with heterogeneous media rather than the currently predominant homogeneous systems. Modified-clay constitutes one such medium.

Our main purpose in this study was to examine the usefulness of surfactant-modified clay for oxidation of an industrially important lipophilic alcohol, i.e., 2-ethyl-1-hexanol. The other goal was to introduce easily made surfactant-modified clay to be compared with a series of cross-linked polystyrene resins bearing quaternary ammonium groups.[19−22]

Results and Discussion

1-Butyl-4-aza-1-azonia bicyclo[2.2.2]octane chloride was selected as the surfactant for modifying the clay. On the basis of preliminary phase distribution studies of dichromate between the aqueous phase and various organic solvents (petroleum ether, cyclohexane, toluene, carbon tetrachloride, chloroform, and methylene chloride) petroleum ether was selected because of the phase-transferred $Cr_2O_7^{2-}$ concentration in this solvent remains relatively constant during several hours of stirring with surfactant present.

According to the mechanism proposed by Wiberg[23] for oxidation of alcohols by $KMnO_4$ in the biphasic system, we proposed eqs 1, 2, and 3 as the overall stoichiometry of the oxidation reaction.

Results When No PTC was Used. To establish a blank for the phase-transfer catalyzed system, the reaction rate for the oxidation of 2-ethylhexanol by dichromate in the biphasic

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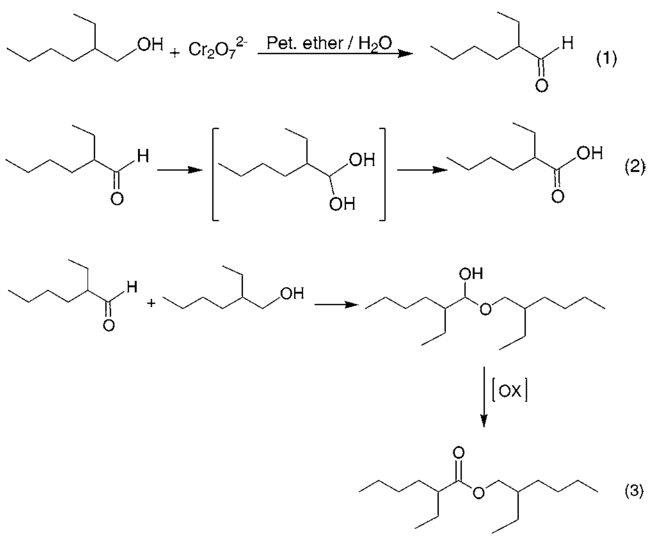
10.1021/op034120d CCC: $25.00



system was studied without phase-transfer catalyst present. Table 1 shows the amounts of reactants and initial rates that were determined from the graph of 2-ethylhexanal product formed versus time (Figure 1). Even though very little dichromate ion is extracted into the petroleum ether phase and very little 2-ethylhexanol is soluble in the aqueous phase, the 2-ethylhexanol is oxidized mainly to corresponding acid and ester after 48 h. Since the two phases are immiscible, a classical rate law analysis is not appropriate here; however, the comparison of initial rates does provide valuable data. Comparing experiments 1 and 3, when the amount of 2-ethylhexanol was kept constant, a 4-fold increase in the amount of $Cr_2O_7^{2-}$ resulted in a 3-fold increase in the initial rate. Comparing experiments 1 and 2, when the amount of $Cr_2O_7^{2-}$ was kept constant, a 2-fold increase in the amount of 2-ethylhexanol resulted in an initial rate only 1.4 times faster.

There are several possible paths for the reaction of dichromate ion with 2-ethylhexanol when no phase-transfer agent is used. These types of reactions tend to be limited not only by the concentration of the reactants at the interfaces but also by the interfacial area available and hence the stirring rate.[23,24] When the stirring rate was decreased, there was a decrease in the initial rate of formation of the 2-ethylhexanal.

Influence of Reactant and PTC Concentration on the Rate. The amount of 2-ethylhexanol, $Cr_2O_7^{2-}$, and PTC (1-butyl-4-aza-1-azonia-bicyclo[2.2.2]octane chloride**)** were systematically varied in order to determine the rate dependence on each species. Table 2 contains a summary of the results of these experiments. The initial rates were determined from the graphs of 2-ethylhexanal product formed versus time (Figures 2 and 3).

A comparison of the initial rates of 2-ethylhexanal formation for experiments 4 and 5 reveals that doubling the amount of 2-ethylhexanol increases the rate by a factor of 2. This is higher than the 1.4 factor observed when no PTC was used (see experiments 1 and 2). In experiments 4 and 6, doubling the amount of $Cr_2O_7^{2-}$ does, in fact, double the rate. This is higher than the 3-fold increase in the initial rate, when the amount of $Cr_2O_7^{2-}$ 4-fold increased in the absence of PTC (see experiment 3).

Table 1. **Initial rates[a] of 2-ethylhexanal formation with no PTC**

	amounts of reactants, mmol		
expt	2-ethylhexanol	$K_2Cr_2O_7$	initial rate × 10^3 M s^{-1}
1	50	25	0.051
2	100	25	0.073
3	50	100	0.148

[a] The initial rate r_0 can be found by plotting [alcohol] versus *t* and drawing the tangent line at $t = 0$.

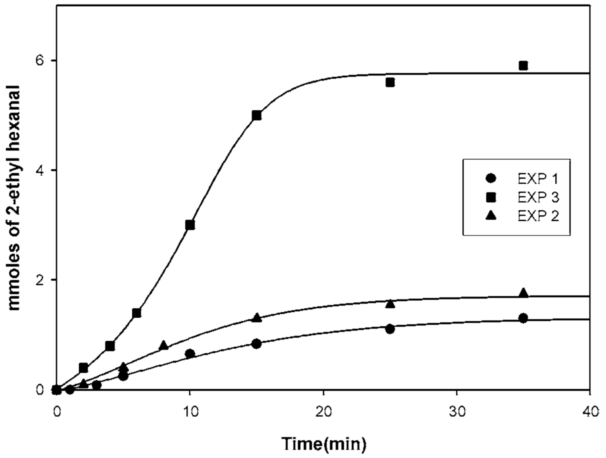


Figure 1. **Production of 2-ethylhexanal versus time for experiments 1−3.**

Table 2. **Initial rates of 2-ethylhexanal formation with PTC**

	amounts of reactants, mmol			
expt	2-ethylhexanol	$K_2Cr_2O_7$	PTC	initial rate × 10^3 M s^{-1}
4	50	25	1.75	0.54
5	100	25	1.75	1.088
6	50	50	1.75	1.08
7	50	25	8.75	5.9
8	100	25	8.75	11.54

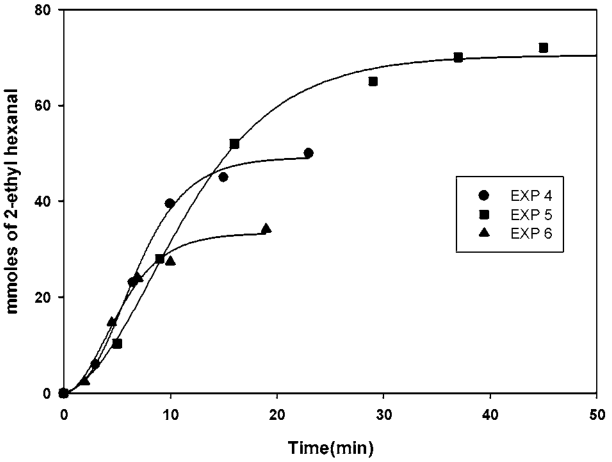


Figure 2. **Production of 2-ethylhexanal versus time for experiments 4−6.**

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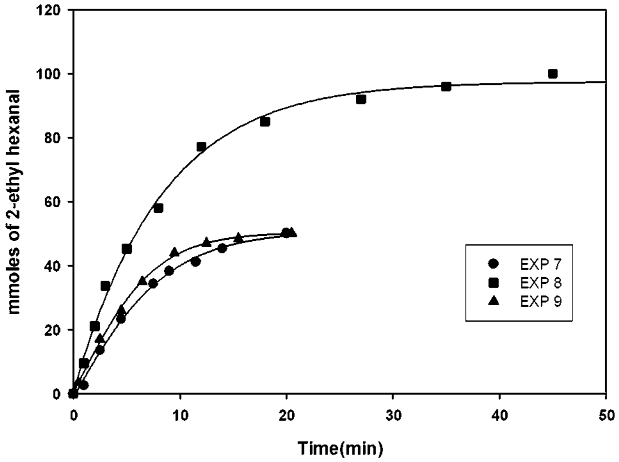

Figure 3. **Production of 2-ethylhexanal versus time for experiments 7−9.**

Table 3. **Initial rates of 2-ethylhexanal formation with PTC supported on clay**

	amounts of reactants, mmol			
expt	2-ethylhexanol	$K_2Cr_2O_7$	PTC supported on clay	initial rate × 10^3 M s^{-1}
9	50	25	0.358 g PTC on 1 g clay	6.43

Comparing experiments 4 and 7, we see that a 5-fold increase in the amount of PTC increases the rate more than 10-fold. A comparison of experiments 7 and 8 show that with substantially larger amount of PTC, doubling of the amount of 2-ethylhexanol does double the rate of oxidation.

Results When PTC Supported on Clay. A comparison of the initial rates of 2-ethylhexanal formation for experiments 4 and 9 reveals that by supporting 0.358 g of PTC (equivalent to 1.75 mmol used in experiment 4) on 1 g of clay increases the rate more than 11-fold (Table 3). Under this condition 2-ethylhexanol was oxidized to aldehyde in about 40 min in more than 90% yield. The amounts of 2-ethylhexanoic acid and corresponding ester were negligible. To determine the benefits of a PTC supported on clay, a separate run with unmodified clay (without phase-transfer catalyst) was performed. The result of this experiment was similar to that of experiment 4. In experiment 4, the 2-ethylhexanal was contaminated with 2-ethylhexanoic acid (9.5%) and corresponding ester (10.5%). Two other immediate advantages of this condition would be (1) simplified product workup and (2) easy and quantitative catalyst recovery. From the stand-point of industrial applications, this concept is a very attractive one due to low energy and capital requirements for processing. Furthermore, the data presented in this work amply demonstrate the efficiency of the surfactant-modified clay towards the selective oxidation of a lipophilic alcohol to the corresponding aldehyde.

Conclusions

The practical potential of this technique for laboratory as well as industrial applications is great. Preliminary studies in our laboratory reveal that a high degree of selectivity toward reactants is possible by using surfactant-modified clay as triphase catalysis. It appears highly probable that the use of surfactant-modified clay will expand significantly in future.

Experimental Section

Natural bentonite from Salafchegan, Iran, gray in color was used; it was sieved to a size range of 0.1−0.2 mm. It was homoionized by sodium exchange before use. The CEC measured was 70 meq/100 g of ignited materials. The BET surface area of the unmodified Na bentonite was 63 m^2/g. The petroleum ether (boiling range = 40−60 °C) was obtained from Isfahan refinery company, and the *n*-octane was from Merck Products.

The kinetic studies were carried out at ambient temperature (25 °C) in Morton flasks equipped with a mechanical stirrer (Heidolf type RZR50, stirring rate = 800 rpm) by first adding petroleum ether (250 mL), water (250 mL), 2-ethylhexanol (8.2 mL, 25 mmol), surfactant-modified clay, and an internal standard. Potassium dichromate (7.35 g, 50 mmol) dissolved in 5.5 mL of H_2SO_4 and 1.9 mL of HOAc was added last. Small samples of the organic phase were then analyzed on a Shimadzu GC-14A gas chromatograph (FID), using a 6 ft × 0.125 in. column packed with 10% SE-30 on Chromosorb PAW (80−100 mesh). An internal standard (*n*-octane) was used in all reactions, and calibration curves for the oxidation products of 2-ethylhexanal, 2-ethylhexanoic acid, and (2-ethylhexyl)-2-ethylhexanoate were prepared so that the number of moles of each product could be determined at various reaction times.

Acknowledgment

We thank the research council of Isfahan University of Technology and Center of Excellency in the Chemistry Department of Isfahan University of Technology for the support of this work.

Received for review August 25, 2003.

OP034120D