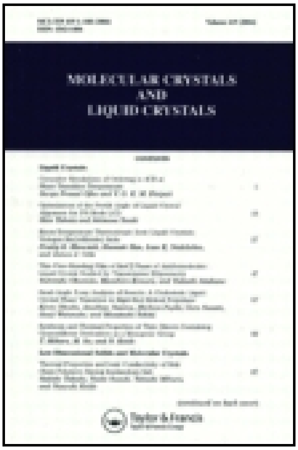

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OXIDATION OF SOME ALIPHATIC ALDEHYDES IN A LIQUID-LIQUID INTERFACIAL SYSTEM

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Abstract In the present study the oxidation by chromic acid of some long-chain aliphatic aldehydes is investigated in a liquid-liquid interfacial system. For comparison the same oxidation was performed with the aldehydes dispersed in water. Higher yields were obtained in interfacial experiments as compared to the ones obtained when the aldehydes were dispersed in water. These results are rationalized by the fact that in the interfacial experiments reactants and products are exposed for short periods of time to the oxidative action of chromic acid, being in a way protected in the organic phase. Concerning the crucial problem of the reaction site i.e. where actually the oxidation occurs in interfacial experiments, it seems, based on kinetics and activation parameter determination as well as by modification of the interface with surfactants, that the oxidation occurs at the liquid-liquid interface and to a lesser extent in the aqueous phase. However, futher work is under way for the complete elucidation of the interfacial process.

INTRODUCTION

In recent years there has been increased interest in elucidating the kinetics and mechanism[1-3] and, in general, the procedures[4-6] involved in liquid-liquid interfacial experiments. Also, fundamental investigations of interfacial chemistry and other specialized topics, with emphasis on polymerization,have been included in a two-volume work edited by Millich and Carraher[7]. Furthermore, several examples of two-phase or interfacial experiments have been reported, including hydrolysis[8,9], dehydration[10] or oxidation[10-12]. In oxidation, the two-phase system may prove extremely useful since the organic phase provides protection for the oxidation sensitive portion of the molecules[10,11].

In the present study,the interfacial or the two-phase chromic acid oxidation of some long-chain aliphatic aldehydes is investigated. It has to be noted that chromic acid oxidation of aldehydes has been extensively studied in homogeneous media[13-19] and therefore,in this work,only the parameters associated with the liquid-liquid system will be discussed. Interfacial reactions of this type could be considered as simplified model systems of analogous reactions occuring in biological systems.

EXPERIMENTAL

Two-phase Oxidation of n-Alkyl-Aldehydes

A typical two-phase chromic acid oxidation is performed as follows: In 20 ml of ethyl ether,10 mMoles of an aldehyde were dissolved. To this solution,10 ml of distilled water were added and the mixture was vigorously stirred in a thermostated specifically constructed reactor. A 20% excess of chromic acid solution (prepared[20] by dissolving 100g of sodium dichromate dihydrate in 300 ml of water followed by 136 g of sulfuric acid and diluting finally to 500 ml) was added in a period of 20 min. Subsequently the organic phase was separated and treated with 5% sodium carbonate solution. The separated aqueous solution was acidified and treated with ether. The ether solution was dried and then distilled off. The remaining material was identified by melting point and elemental analysis as the acid corresponding to the aldehyde subjected to oxidation.

It has to be noted that further increase of the reaction yield is not observed on increasing the reaction time because of the simultaneous oxidative destruction of the aldehyde. The destruction of the aldehydes in interfacial experiments is found to be about 10%, i.e. almost half of the loss occuring when oxidation is performed with the aldehydes dispersed in water (see below).

Oxidation of Aldehydes Dispersed in Water

The previous reactor was employed under the same experimental conditions except that an aqueous dispersion of the aldehyde was used for the oxidation by chromic acid.

Two-phase Oxidation Kinetics

Oxidation kinetics (dodecylaldehyde was used for the kinetic studies) were studied in the same reactor that was used for the synthetic experiments. An excess of the aldehyde was employed in order to secure pseudo-first-order kinetics with respect to the oxidizing agent. The oxidation was followed spectrophotometrically by the decrease in the absorption of chromic acid at~351 nm.

One-phase Oxidation Kinetics

The oxidation was performed in the same reactor as before but instead of the interfacial system a 75% w/w acetone/ /water solution was used.

RESULTS AND DISCUSSION

In Table I, below, the yields of the acids obtained by the oxidation of aldehydes (heptylaldehyde to tetradecylaldehyde) in dispersed and two-phase systems are shown. In two-phase experiments the volume ratio water to ether was varied while the same volume of oxidizing solution was always added.

TABLE I. Yields,%, of the acids obtained in the dispersed and two-phase experiments in various water to ether ratios for aliphatic aldehydes, $CH_3(CH_2)_x$ CHO, where x = 5-10 and 12

Vol.ratio H_2O:Ether in ml		Cr(VI) Sol[b]., in ml	Yield, %						
			Number, x, of aldehyde[a] methylene groups						
			5	6	7	8	9	10	12
30	0	10	20.6	14.8	8.6	16.9	10.8	8.5	5.0
20	10	10	21.0	17.8	14.7	25.8	14.9	21.0	7.8
10	20	10	25.4	22.8	26.3	27.2	25.4	22.0	13.2
0	30	10	36.4	33.1	33.5	49.2	37.7	48.7	22.9

a. 10 mMoles of each aldehyde was employed in these experiments.

b. 20% excess of chromic acid was used.

It is clear from this Table that higher yields are always obtained in two-phase experiments than in the ones in which aldehyde is dispersed in water. In the latter experiments (dispersed phase) the yields decrease on going from heptaldehyde to tetradecylaldehyde.This may be attributed, in the first place, to the increasing insolubility of the higher aldehydes in the aqueous chromic acid solution thus making their oxidation difficult. In the interfacial experiments, it is seen (within the limits of the accuracy of gravitational method) that there is an increase in the yields of the acids formed as the water:ether volume decreases. This may be attributed to the fact that higher amounts of aldehydes are distributed in the ether phase in which they are protected from the destructive action of chromic acid. From the same table it is also seen that the yields obtained for the lipophilic tetradecylaldehyde are significantly reduced as compared with the ones of the other aldehydes. This indicates that oxidation is taking place either in the aqueous phase or at the interface,i.e. in those areas in which tetradecylaldehyde is in low concentration due to its lipophilicity. In this connection, it has to noticed that an interface[22] is not just a geometrical plane in which two immiscible solvents come into contact but a region of certain thicknesss and medium polarity in which the two solvents and their solutes coexist. Thus the oxidation of the - CHO group to- COOH and the oxidative degradation of the hydrocarbon chains can occur not only in the aqueous phase but also at the interface.

The crucial problem in two-phase experiments is the determination of the site where the reaction actually occurs. Thus the yields of the acids obtained under the two modes of experiment are not only useful from the practical point of view but they also give some indication as far as the site of oxidation of aldehydes are concerned. For this purpose oxidation kinetics were investigated under conditions in which even the interface was modified by the addition of the surfactants e.g., cetyltrimethylammonium bromide (CTAB) or sodium dodecylsulfate (SDS). For comparison purposes only one aldehyde was used in these experiments.

In Table II the pseudo-first-order rate constants of the oxidation of dodecylaldehyde by chromic acid under interfacial conditions are shown. It is seen that, after a certain increase in the aldehyde concentration, a sluggishness is observed in the increase of the rate. This may be rationalized by the saturation of the interface by the aldehyde molecules and also by the inability of the interface to permit the transport of a higher amounts of the aldehyde to the aqueous phase. For simplicity, in all described kinetic measurments, stirring was so regulated that the oxidation process was only kinetically and not diffusion limited[1].

Table II. Pseudo-first-order rate constants of chromic acid[a] oxidation of dodecylaldehyde under interfacial conditions.

[Dodecylaldehyde] x 10^{-3} M	K_1 x 10^{-4} s^{-1}
1.42	0.62
2.30	1.27
2.85	1.90
3.85	3.31
4.32	3.39

[a] $[CrO_3] = 1.155 \cdot 10^{-4}$ M.

For a further examination of the effect of interfaces on oxidation they were modified by the addition of increasing concentrations of CTAB and SDS surfactants. The rate constants were measured and are tabulated in Table III. It is seen that by increasing the concentration of surfactants the rate is decreased, a result agreeing with the occupation of interfacial sites predominately by the surfactants. In this way the transport of the aldehydes to the chromic acid phase is hindered at the one hand and on the other their location at the interface is not facilitated. Therefore the rate decrease of oxidation is justified.

Table III. Effect of surfactants concentration on rate constants in interfacial oxidation of dodecylaldehyde.

[CTAB], M	$K_1 \times 10^{-4}, s^{-1}$	[SDS], M	$K_1 \times 10^{-4}, s^{-1}$
1×10^{-4}	0.89	1×10^{-4}	0.57
1×10^{-5}	1.28	1×10^{-5}	1.20
1×10^{-6}	1.72	1×10^{-6}	1.55

Comparison of oxidation rate in one-and two-phase experiments was not that easy since in the first case oxidation was extremely fast and one had to work at relatively low temperatures and concentrations. For instance, at 270°K, the second order rate constant for one-phase oxidation of dodecylaldehyde was $2.67 \times 10^2 dm^3 ml^{-1} s^{-1}$ as compared to $9.52 \times$ $\times 10^{-3} dm^3 mol^{-1} s^{-1}$ for the two-phase oxidation. In the latter experiments a portion only of concentration of the aldehyde is subjected to the oxidizing action of chromic acid either by transport in the aqueous phase of by suitable organization at the interface for the aldehyde groups to be attacked. Thus the lower oxidation rate is justified.

In Table IV, below, are shown the activation parameters, determined from the Arrhenius plots for the two types of experiments. It is interesting to notice that the high ΔH^* value for the two-phase oxidation is to some extent compensated by the less negative value of ΔS^*.The lower negative ΔS^* value for the two-phase oxidation as compared to

Table IV. Activation parameters for one - and two- phase oxidation of dodecylaldehyde.

Activation parameter	One-phase oxidation	Two-phase oxidation
ΔH^* Kjmol^{-1}	12.3	83.9
ΔS^* Jmol^{-1}deg^{-1}	-220.4	-19.3
ΔG^* Kjmol^{-1}	72.2	89.4

one-phase may be justified by the fact that the reactants are in some way "organized" at the interface and the formation of the activated complex does not involve much reorganization of the reacting species.Specifically, the aldehyde must be organized in such a way at the interface that its hydrophilic end points to the aqueous-phase while the lipophilic chain is solubilized into the ether phase.

Coming back to the problem of the actual reaction site of oxidation we may envisage two possibilities. According to the first model the aldehydes, as mentioned above,are properly organized at the interface where they are oxidized whereas according to the second reaction model the aldehydes are transported to the aqueous phase, where according to the accepted mechanism[15] (hydration followed by esterification) they are subjected to oxidation. A portion of the acid formed is then, according to the distribution law, transfered to the ether phase where it is protected from the oxidizing action of chromic acid. In this respect the higher yields obtained in the two-phase experiments are justified. The transport process of the aldehydes to the aqueous phase and of their corresponding acids backwards to the ether phase is repeated up to the exhaustion of aldehydes. An analogous mechanism had been proposed by Brown et al[20,21] for the oxidation of secondary alcohols to ketones. This second model of oxidation justifies to a certain degree the oxidative destruction observed in the two-phase experiment because aldehydes are exposed to chromic acid. However, due to the nature of interface, oxidative destruction cannot be completely excluded for molecules organized at the interface. Thus, the evidence of oxidative destruction of aldehydes cannot fully support the process of transport of aldehydes through the interface and their subsequent oxidation in the aqueous phase. It seems that both reaction models operate in the interfacial oxidation of aldehydes but the exact extent of the participation of each process cannot be estimated by the available data. However taking into consideration the significant difference in the values of the entropy of activation determined for the one-and two-phase experiments coupled with the effect of the surfactants on the oxidation rate in interfacial reactions,it may be assumed that oxidation takes place at the water-ether interface and only to a lesser extent in the aqueous phase.Further work is planned for completely elucidating the site where oxidation occurs in interfacial experiments.

REFERENCES

1. G.J. Hanna and R.D. Noble, Chem.Rev.,85,583 (1985).
2. M. Spiro, Faraday Discuss. Chem. Soc., 77 , 275 (1984).
3. F.M. Menger, Chem. Soc. Rev., 1, 229 (1972).
4. W. Nitsch, Faraday Discuss. Chem. Soc., 77, 85 (1984).
5. R. H. Guy, R.S. Hinz and M. Amantea, Faraday Discuss. Chem. Soc., 77, 127 (1984).
6. P. Meares, Faraday Discuss. Chem. Soc., 77, 7 (1984).
7. Interfacial Synthesis, Vol. I and II, F. Millich and C. E. Carraher, Jr, Eds, Marcel Dekker, New York and Basel, 1977.
8. A. Tomita, N. Ebina and Y. Tamai, J.Am.Chem. Soc.,99, 5725 (1977).
9. S. L. Regen and J. J. Besse, J.Am. Chem. Soc.,100, 7117 (1978).
10. D. J. Coldsmith, in Ref.7 p.57 and references cited therein.
11. C. M. Paleos and N. Mimicos, J. Colloid. Interface Sci., 65, 595 (1978).
12. J. Skrzewski and E. Cichacz, Bull.Chem.Soc. Jpn., 57, 271 (1984).
13. R. Stewart., in"Oxidation Mechanisms"(W. A. Benjamin, New York, 1964) p.33.
14. H. O. House in "Modern Synthetic Reactions" (W.A. Benjamin, Menlo Park, Calif., 1972) p 273.
15. J. March, in"Advanced Organic Chemistry",(J. Wiley and Sons, p.629, New York, 1985) p.629.
16. K. B. Wiberg and T. Mill, J. Am. Chem. Soc.,80,3022(1958)
17. G. T. Graham and F. E. Westheimer, J. Am. Chem. Soc.,80 3030 (1958).
18. K. B. Wiberg and P. A. Lepse, J. Am. Chem. Soc.,86, 2612 (1964).
19. J. Roček, Tetrahedron Lett., 5, 1 (1959).
20. H. C. Brown, C.P. Garg and K. T. Liu, J. Org. Chem.,36 , 387 (1971).
21. H. C. Brown and C. P. Carg, J. Am. Chem. Soc., 83,2952 (1961).
22. J. T. Davies and E. K. Rideal, in Interfacial Phenomena, (Academic Press, New York and London 1961) p.1.