

The Oxidation of Alcohols and Aromatic Hydrocarbons by Dichromate in Two Phase Systems

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A rapid and selective method for the oxidation of primary alcohols to aldehydes and polynuclear aromatic hydrocarbons to quinones is described. In the recommended procedure the substrate in an organic solvent is shaken with aqueous acidic dichromate and a phase-transfer agent and the effect of the reaction conditions on the selectivity and rate of the reactions is discussed.

THERE remains considerable interest in the development of improved procedures for the oxidation of primary alcohols to aldehydes and in recent years several papers¹⁻⁵ have described methods which employ a chromium(VI) species as the oxidising agent.

A recent communication⁶ reported a further method based on phase-transfer catalysis which was generally both selective (yields >75%) and rapid (<1 min). The reactions were, however, studied only over a limited range of conditions and although, in general, the yields of aldehydes were good, several exceptions were noted. Moreover, the procedure employs sulphuric acid of sufficient concentration to be difficult to handle in large volumes. Hence here we report an investigation of the effects of variations in the reaction conditions and show that lower acid concentrations may be employed with advantage. The data obtained are also used to consider the likely mechanisms of these reactions. Finally the extension of this phase-transfer procedure to the oxidation of anthracene and two naphthalenes is described.

RESULTS

In order to assist in the interpretation of the data below for the oxidation of alcohols in this two-phase system, the partition of dichromate and sulphuric acid between water and methylene chloride was studied using standard titration procedures. When the ratio of $\text{Bu}_4\text{N}^+:\text{Cr}_2\text{O}_7^{2-}$ was 2:1 and the concentration of sulphuric acid was in the range 0–3M the extraction of dichromate into the organic solvent was essentially total (>95%). At higher acid concentrations some oxidation of the phase-transfer catalyst occurred as shown by the appearance of green chromium(III) in the aqueous layer and the failure of the titrations to account for all the dichromate added. With less tetrabutylammonium ion, the extraction of dichromate depended strongly on the amount of tetrabutylammonium added and in its absence, no dichromate entered the methylene chloride. These results could be confirmed qualitatively by visual observations since in both solvents the dichromate has a characteristic, dark orange colour. Even with 10M-aqueous sulphuric acid the transfer of sulphuric acid to the organic phase was low and the concentration of acid in the methylene chloride was less than 10^{-2}M . When the aqueous solution was 1.0M- H_2SO_4 no acid could be detected in the methylene chloride.

It was also confirmed that the alcohols were essentially stable on the timescale of the oxidations (1 min) in the absence of the dichromate. For example when octanol (10 mmol) in methylene chloride (25 cm³) was shaken with 10M-aqueous sulphuric acid (25 cm³) for 10 min, 70% of the

alcohol was recovered unchanged. With 1M- H_2SO_4 the recovery was quantitative.

The two-phase oxidation of three alcohols, n-octanol, benzyl alcohol, and 3-phenylpropanol, was studied under a variety of conditions, *i.e.* in two solvents (CH_2Cl_2 and $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$) and at several concentrations of acid, sodium dichromate, and phase-transfer reagent. In all cases the alcohol (10 mmol) was dissolved in the organic solvent (25 cm³) and emulsified with the dichromate in aqueous sulphuric acid (25 cm³) and the phase-transfer reagent.

A series of oxidations of benzyl alcohol, using a stoichiometric quantity of sodium dichromate (3.3 mmol) and tetrabutylammonium bisulphate (1.0 mmol) but different concentrations of aqueous sulphuric acid, were carried out at room temperature. With 10M-sulphuric acid the reaction goes to completion (yield benzaldehyde 92%) within seconds of mixing of the two phases; the organic layer was then colourless and the aqueous layer green. The rate of oxidation decreases as the acidity is lowered and some gelatinous brown precipitate is observed during the reaction but even with 1M-sulphuric acid the reaction is over within minutes and the yield remains almost quantitative. With 0.1M-sulphuric acid, extensive precipitate is formed and never clears and the reaction goes only to 40% conversion after *ca.* 10 min (60% alcohol remains). Finally, without acid no reaction occurs and to obtain benzaldehyde (82%) it has been reported necessary to reflux the mixture for 15 h.⁵

The other two alcohols showed similar behaviour. With 0.1M- H_2SO_4 the progress of the reactions were followed and although each stopped at *ca.* 40% conversion, the rates of the initial oxidation process were different. The reaction rates decreased in the order $\text{PhCH}_2\text{OH} > \text{Ph}(\text{CH}_2)_3\text{OH} > \text{n-C}_8\text{H}_{17}\text{OH}$.

While it is not possible to determine the absolute rates of these alcohol oxidations with any confidence, the relative rates can be estimated by carrying out competitive oxidations of a pair of alcohols with a deficiency of oxidising agent and comparing the yields of the aldehydes. Table I reports the products from a series of such experiments using *p*-substituted benzyl alcohols and it can be seen that the rate of reaction is increased slightly by electron-donating substituents.

A whole series of alcohols were investigated using 10M-aqueous sulphuric acid and the other conditions described above. In all cases the dichromate is reduced within seconds and the yields of aldehydes are reported in Table 2, column 1. It can be seen that the yields of aldehydes are, in general, high although a few alcohols, namely the small aliphatic alcohols, allylic alcohols, and *p*-methoxybenzyl alcohols, give only very low yields. Several of the alcohol oxidations were repeated using 3M-sulphuric acid and

TABLE 1

Products from the oxidation of PhCH₂OH (10 mmol) and *p*-X-C₆H₄CH₂OH (10 mmol) in CH₂Cl-CH₂Cl (25 cm³) by sodium dichromate (3.3 mmol) in 3M-aqueous H₂SO₄ (25 cm³) in the presence of Bu₄NHSO₄ (1 mmol)

X	σ	% Recovery of alcohols		% Conversion to aldehydes		% <i>p</i> -X-C ₆ H ₄ CHO % PhCHO
		PhCH ₂ OH	<i>p</i> -X-C ₆ H ₄ CH ₂ OH	PhCHO	<i>p</i> -X-C ₆ H ₄ CHO	
H	0					1.0
OMe	-0.27	46	38	44	57	1.31
Me	-0.17	41	45	51	58	1.12
Cl	+0.23	39	50	58	47	0.81
NO ₂	+0.78	33	67	67	35	0.52

although the reactions were slower, they were all complete within a minute; the yields of aldehydes are reported in column 2 of Table 2. For all alcohols investigated the yields of aldehydes were better with this lower acid concentration and this was particularly the case for the alcohols

TABLE 2

Oxidation of alcohols (10 mmol) in CH₂Cl₂ or CH₂Cl-CH₂Cl (25 cm³) by dichromate in aqueous H₂SO₄ (25 cm³) in the presence of tetrabutylammonium bisulphate (1.0 mmol) ^a

Alcohol	Yield of corresponding aldehyde (%)		
	10M-H ₂ SO ₄ Stoicheio- metric Cr ₂ O ₇ ²⁻	3M-H ₂ SO ₄ Stoicheio- metric Cr ₂ O ₇ ²⁻	10M-H ₂ SO ₄ 25% Excess Cr ₂ O ₇ ²⁻
PhCH ₂ OH	92	100	64
<i>p</i> -MeC ₆ H ₄ CH ₂ OH	95		98
<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ OH	55		95
<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	1	93	
<i>p</i> -Cl-C ₆ H ₄ CH ₂ OH		92	
PhCH ₂ CH ₂ OH	62		90
<i>p</i> -Cl-C ₆ H ₄ CH ₂ CH ₂ OH	52		
Ph(CH ₂) ₃ OH	80		90
PhCH=CHCH ₂ OH	0	39 ^b	
EtOH	5	45	5
Bu ⁿ OH	34	97	45
1-C ₈ H ₁₇ OH	82	95	58
1-C ₁₆ H ₃₃ OH	90		
CH ₂ =CH(CH ₂) ₉ CH ₂ OH	95		
Nerol	1	71	
Adamantylmethanol	78		
MeCH(OH)-C ₆ H ₁₃	82 ^c		95 ^c
C-C ₆ H ₁₁ OH	65 ^c	88 ^c	34 ^c

^a Reactions carried out at room temperature by shaking for 1 min in a separating funnel. Analysis of organic phase by g.l.c. and n.m.r. ^b Also benzaldehyde (23%). ^c Corresponding ketone.

mentioned above which gave negligible yields with 10M-H₂SO₄.

The amount of dichromate in the system was important. With no alcohol could a large excess of the oxidising agent be tolerated without a considerable loss of yield. The stoichiometric quantity of dichromate was not necessarily the optimum. Column 3 of Table 2 reports the yield of aldehydes from the oxidation of ten alcohols when the reaction was carried out with a 25% excess of the oxidising agent. Comparison of columns 1 and 3 do not indicate a clear trend; the presence of an excess of dichromate can lead to a substantial increase or decrease in the yield of aldehyde. Reactions where 1,2-dichloroethane was used as a solvent for the alcohol gave identical results to those where the solvent was methylene chloride and in later experiments the two solvents were used interchangeably.

The oxidations of the alcohols were also found to occur in the absence of a phase-transfer catalyst, although the reactions were slower and considerably messier. The yields of products were, however, reasonable and after a reaction time of 15 min the % aldehydes from the oxidation of benzyl alcohol, 3-phenylpropanol, octanol, and 3,7-di-

methylocta-2,6-dien-1-ol (nerol) were 95, 73, 80, and 60 respectively. It was noted that in the early stages of these reactions the organic solvent became orange-brown and it was apparent that chromium(vi) was being transferred to the organic medium. Since under the same conditions but in the absence of an alcohol, no transfer of dichromate would be observed, it would seem that an organochromium intermediate is formed at the phase boundary as the first step in the reaction and that the oxidation again probably occurs in the organic solvent.

A series of experiments was carried out to investigate whether this phase-transfer procedure for the oxidation of alcohols could also be used for the conversion of polynuclear aromatic hydrocarbons into quinones. The data in Table 3 are typical for reactions of dichromate with three hydrocarbons in a water-dichloroethane emulsion containing a phase-transfer catalyst. The polynuclear aromatic hydrocarbons are more difficult to oxidise than the alcohols and, in consequence, it is necessary to use more forcing conditions (*i.e.* heat or excess of dichromate) or prolonged reaction times. The conversion of anthracene into anthraquinone could be carried out satisfactorily by warming for a short period the dichromate in 3M- or 10M-sulphuric acid with the hydrocarbon in dichloroethane. With the two naphthalenes, the yields of quinones were never high.

TABLE 3

Oxidation of polynuclear hydrocarbons (10 mmol) in CH₂Cl-CH₂Cl (25 cm³) by dichromate in aqueous H₂SO₄ (25 cm³) in the presence of Bu₄NHSO₄ (1.0 mmol) ^a

Hydrocarbon	Conditions	Products (% yield)
Anthracene	(a) 10M-H ₂ SO ₄ , 33% excess dichromate, 70 °C for 2 min	Anthraquinone (92)
	(b) 3M-H ₂ SO ₄ , 33% excess dichromate, 70 °C for 2 min	Anthraquinone (82)
Naphthalene	(a) 10M-H ₂ SO ₄ , stoichiometric dichromate, 25 °C for 2 min	Naphthalene (75) Naphthaquinone (13)
	(b) 10M-H ₂ SO ₄ , 100% excess dichromate, 25 °C for 5 min	Naphthalene (17) Naphthaquinone (39)
	(c) 3M-H ₂ SO ₄ , 100% excess dichromate, 25 °C for 10 min	Naphthalene (92)
2-Methyl-naphthalene	(a) 10M-H ₂ SO ₄ , stoichiometric dichromate, 25 °C for 10 min	2-Methylnaphthalene (48) 2-Methylnaphthaquinone (33)
	(b) 10M-H ₂ SO ₄ , 100% excess dichromate, 25 °C for 5 min	2-Methylnaphthalene (1) 2-Methylnaphthaquinone (56)

^a The reaction mixture was stirred vigorously under conditions stated and the organic phase analysed by g.l.c.

DISCUSSION

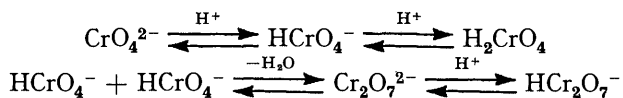
These two-phase oxidations of alcohols with aqueous acidic dichromate as the oxidising agent provide a

convenient method for the conversion of alcohols into aldehydes. The reactions are very rapid, require only common reagents and give high yields of product from a variety of alcohols. Certainly in all these respects the method would seem to compare favourably with others where a chromium(vi) species is the oxidising agent¹⁻⁵ and, indeed, with more complex procedures such as those using reagents based on ruthenium tetroxide⁷ and dimethyl sulphoxide.^{8,9} From the above study of the reactions under a variety of conditions, a procedure where the alcohol in methylene chloride is shaken at room temperature with a trace of phase-transfer catalyst and the stoichiometric amount of dichromate in 3M-aqueous sulphuric acid would be recommended. The use of a higher concentration of acid seems unnecessary and in some cases leads to a lower selectivity for the reaction. The small quantity of phase-transfer reagent, however, leads to a cleaner and faster reaction and phase separations occur more quickly.

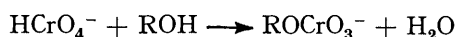
The oxidation of the polynuclear aromatic hydrocarbons requires more forcing conditions and this tends to lead to a loss of selectivity. Hence, although the conversion of anthracene into anthraquinone presents no problems and can be accomplished in good yield, the oxidations of naphthalene and 2-methylnaphthalene were not as successful.

While many details of the mechanisms for the oxidation of the alcohols are unclear, it is possible to deduce certain features of the reaction pathways. The oxidations involve a reaction between the alcohol and a chromium(vi) species in the organic solvent and when the aqueous phase contains at least 1M-H₂SO₄, one molecule of dichromate can be responsible for the oxidation of three molecules of the alcohol. Hence chromium(v) and/or chromium(iv) species must be intermediates; indeed the black-brown deposits observed in some conditions are probably chromium(v) and/or chromium(iv) oxy-species. The amount and persistence of these precipitates decreases with increased acidity of the aqueous phase and this suggests that the proton-catalysed disproportionation of Cr^v or Cr^{iv} to Cr^{vi} is important.

This, however, is not the only role of proton since with weakly acidic dichromate even the early stages of the reactions are slow and with a neutral aqueous medium, no significant reaction occurs at room temperature. Chromium(vi) in aqueous solution exists as a pH-dependent mixture of several species, *i.e.*

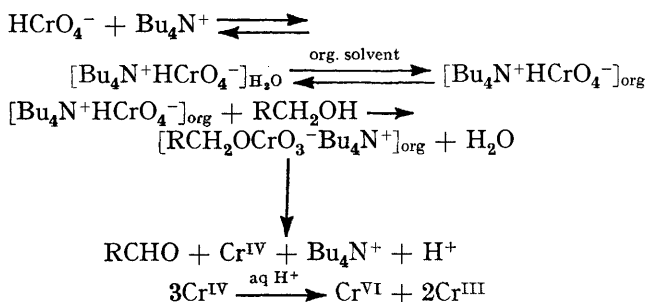


and while all the anionic species may form ion pairs and hence transfer to the organic solvent in the presence of phase-transfer catalyst (note the total Cr^{vi} transferred was found to be independent of [H⁺]), the different chromium(vi) species may not be equally active for alcohol oxidation. Indeed there is evidence that the first step in the oxidation of alcohols is



and that the chromate ester has greater stability in organic solvents than in water.^{1,10,11}

Hence we would propose a mechanism containing the following key steps:



In the absence of the phase-transfer agent we would propose a similar mechanism but the chromate ester now has to be formed at the interface between the two solvents and hence it is to be expected that the oxidation will be slower.

EXPERIMENTAL

Chemicals.—Benzyl alcohol, 2-phenylethanol, ethanol, butan-1-ol, octan-1-ol, octan-2-ol, 3,7-dimethyloctan-2,6-dien-1-ol (neral), *p*-methylbenzaldehyde, cinnamaldehyde, acetaldehyde, butanol, and cyclohexanone were supplied by B.D.H. Ltd., *p*-methyl-, *p*-nitro-, *p*-methoxy-, and *p*-chloro-benzyl alcohols, undecenyl alcohol, adamantyl-methanol, *p*-methylbenzaldehyde, and *p*-chlorobenzaldehyde by Aldrich Chemical Co. Ltd., 2-(*p*-chlorophenyl)ethanol by Chemical Procurement Laboratories, hexadecan-1-ol, cyclohexanol, 3-phenylpropanol, *p*-nitrobenzaldehyde, phenylacetaldehyde, 3-phenylpropionaldehyde, and octan-2-one by Koch-Light Ltd., cinnamyl alcohol by Hopkin and Williams Ltd., nerol by Bush, Boake, and Allen Ltd., benzaldehyde by May and Baker Ltd., and adamantylacetaldehyde by Ralph Emmanuel Ltd. A sample of hexadecanal was prepared by the procedure described in this paper.

Methylene chloride and 1,2-dichloroethane were supplied by B.D.H. Ltd. and were not purified. Tetrabutylammonium bisulphate (Labkemi AB) was also used as supplied.

Analysis.—G.l.c. analysis was carried out on a Pye-Unicam series 104 chromatograph with a FID; a 9 ft, 4% silica oil on Celite column was used with a carrier gas (N₂) flow rate of 20 cm³/min. The temperature varied between 50 and 225 °C. The quantitative analysis was, in general, carried out by comparison of the retention time and response with an authentic sample of the product. Where the authentic compound was not available the product was identified by g.l.c.-mass spectroscopy (A.E.I. MS12 spectrometer) and the product was estimated using an aldehyde of closely related structure.

The analyses were checked by comparison of the integrated aldehyde proton resonance, occurring in a range 9.5–10.5 p.p.m. (*vs.* SiMe₄), with that for an authentic sample of the product. N.m.r. spectra were obtained on a Perkin-Elmer R12 spectrometer.

Typical Reaction Procedure.—The alcohol (10 mmol) and tetrabutylammonium bisulphate (1.0 mmol) was dissolved in 25 cm³ dichloroethane and shaken in a separating funnel with sodium dichromate (3.3 mmol) in 25 cm³ aqueous

sulphuric acid (3M). After separation of the two solvents, the organic layer was dried (Na_2SO_4) and analysed by g.l.c. and n.m.r. spectroscopy.

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