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THE EFFECT OF PRESSURE ON THE OXIDATION OF BENZHYDROL BY ALKALINE PERMANGANATE[1]

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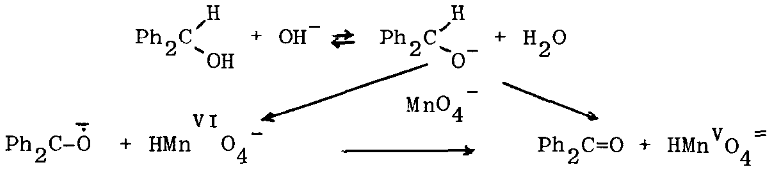
Summary. The rate of oxidation of benzhydrol and benzhydrol-d to benzophenone by alkaline permanganate has been measured over a pH range 10 to 12.5 and pressures from 1 to 1000 bar. The pressure effect on the rate is small, $\Delta\overline{V}^{\neq} = -6$ to $-8\ \mathrm{cm^3\,mol^{-1}}$. This is held to support a hydrogen atom transfer in the rate-determining step.

The oxidation of secondary alcohols by alkaline permanaganate is of first order in each of the substrate, permanganate and OH^- and invariably shows a large primary kinetic isotope effect.[2-4] The rate-determining step is inferred to consist in the transfer of hydrogen from the alkoxide ion to permanganate. Previous work has failed to clarify the nature of this step, whether a hydride ion or a hydrogen atom transfer is occurring since either could plausibly lead to the observed products, ketone and manganate.



Reaction constants, ρ, for the overall oxidations of substituted phenyltrimethylcarbinols are said to be small arguing against a hydride ion transfer.[8] However, the electronic requirements for ionisation and for hydride transfer are opposite and may well be cancelling. The difficulties of distinguishing such pathways have been discussed.[5] The volume of activation of this reaction should permit a distinction to be made since for hydride transfer alone there is a concentration of charge towards the manganate ion which would be accompanied by a large reduction in volume by electrostriction. One may compare the partial molar volumes of two similarly-sized ions, MnO_4^- and $CrO_4^{=}$, 42.5 and 19.7 $\mathrm{cm^3mol^{-1}}$ respectively (the value for $MnO_4^{=}$ in aqueous solution is not available). The difference, 23 $\mathrm{cm^3mol^{-1}}$ is attributable to the increased electrostriction which in turn depends upon the square of the charge. The following predictions of volume changes can be made;[6]

	$\Delta\bar{V}$· H· transfer	H:$^-$ transfer
$R_2CHOH + OH^- \rightarrow R_2CHO^- + H_2O$	0	0
$R_2CHO^- \rightarrow R_2C{=}O$		+5 to +10
$R_2CHO^- \rightarrow R_2C\text{-}O^{\dot{-}}$	+1	
$Mn^{VII}O_4^- \rightarrow Mn^{VI}O_4H^-$		0
$Mn^{VII}O_4^- \rightarrow Mn^{V}O_4H^=$	-23	
$R_2CHOH + MnO_4^- \rightarrow (R_2CHOH.MnO_4^-)$ (association)	-10	-10
	-30 ± 10	0 ± 5 cm^3mol^{-1}

Observed value of $\Delta\bar{V}^{\neq} = -6 \pm 2\ cm^3mol^{-1}$

We have measured rates of oxidation of benzhydrol and of benzhydrol-d (10^{-2}M) by permanganate (8.10^{-4}M) over the pH range 10 to 12.5 at pressures ranging from 1 to 1000 bar at 25°. A conventional high pressure kinetic cell was used for the slower reactions and a high pressure stopped-flow cell[7] for fast systems. In all cases, the reaction obeyed first-order kinetics (r at least 0.998) and the value of the activation volume was in the range -6 to -8 cm^3mol^{-1}. This small pressure effect clearly denies any extensive electrostrictive effect. If we assume that hydrogen transfer is advanced at the transition state, since the PKIE is a maximum, this result argues in favour of a hydrogen atom transfer process as the slow step.

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