Spectral Evidence for Chromium(IV) and Chromium(V) in the Chromyl Acetate Oxidation of Alkylaromatics in Acetic Anhydride

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Summary Spectrophotometric, kinetic, and e.s.r. data are presented for the first time for the formation of chromium(IV) and chromium(V) in the chromyl acetate oxidation of alkylaromatics in acetic anhydride.

ALTHOUGH the kinetics of the aqueous chromic acid[1–4] and non-aqueous chromyl chloride[5] oxidation of alkylaromatics have been extensively investigated, there are no experimental and spectral data to support the postulated intermediacy of chromium(IV) and chromium(V) in these reactions. Moreover, it appears that the kinetics and mechanisms of the non-aqueous chromyl acetate oxidation of alkylaromatics have not been studied.[2,3,6,7] Chromyl acetate in acetic anhydride, in the absence of acids, oxidizes alkylaromatics to alcohols, aldehydes, carboxylic acids, and ketones.[7,8]

We report that we have been able to observe, *via* spectrophotometric stopped flow techniques, a series of consecutive pseudo-first order reactions in the chromyl acetate oxidation of toluene, ethylbenzene, isopropylbenzene, diphenylmethane, and triphenylmethane, in acetic anhydride solvent.

At λ 520, 550, 589, 600, and 750 nm, there is an increase in absorbance (k_1) which is followed by a slower decrease in absorbance (k_2). The rates of both reactions are decreased by deuterium substitution at the benzylic position of toluene, ethylbenzene, isopropylbenzene, and diphenylmethane, respectively, indicating that both processes involve oxidation of the alkylaromatic and cleavage of the carbon–hydrogen bond in the rate-determining step.

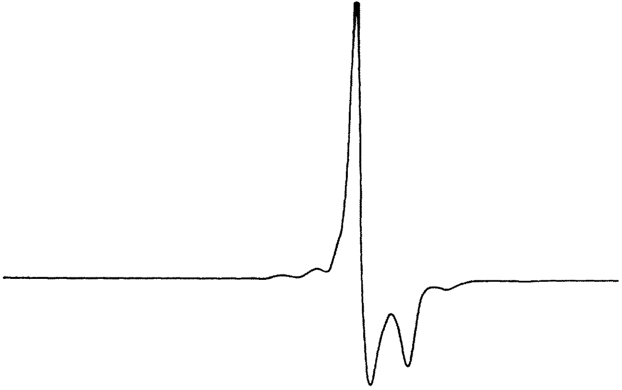
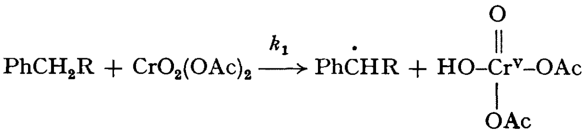
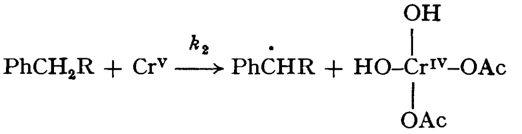


FIGURE 1. The liquid nitrogen temperature e.s.r. spectrum of chromium(V) formed during the chromyl acetate ($2\cdot5 \times 10^{-3}$ M) oxidation of ethylbenzene (0·20 M) in acetic anhydride. The centre of the band corresponds to $g = 1\cdot971$.

The relatively sharp e.s.r. spectrum observed in the oxidation of ethylbenzene (Figure 1) can only be due to chromium(V) since either chromium(IV) or chromium(III) would be expected to give a relatively broad signal.[8,9] Moreover, the intensity of the signal reaches a maximum at the same time the absorbance of the kinetic mixture reaches a maximum. Thus, the second step (k_2) appears to lead to a relatively stable chromium(IV) species (Figure 2). Although more data are necessary to establish fully the structures of chromium(IV) and chromium(V), Figure 2 is similar to the spectrum reported for chromium(IV) in the chromyl acetate oxidation of aromatic aldehydes.[7,8]



$$PhCH_2R + CrO_2(OAc)_2 \xrightarrow{k_1} Ph\dot{C}HR + HO\text{-}\underset{\underset{OAc}{|}}{\overset{\overset{O}{\|}}{Cr^{V}}}\text{-}OAc \quad (1)$$



$$PhCH_2R + Cr^{V} \xrightarrow{k_2} Ph\dot{C}HR + HO\text{-}\underset{\underset{OAc}{|}}{\overset{\overset{OH}{|}}{Cr^{IV}}}\text{-}OAc \quad (2)$$

The chromyl acetate oxidation of ethylbenzene is first order in oxidant and first order in reductant ($k_1 = 0{\cdot}52$ l mol^{-1} s^{-1}). A first order dependence on chromium(V) and a first order dependence on ethylbenzene are observed for the second step ($k_2 = 0{\cdot}0228$ l mol^{-1} s^{-1}). Thus, it appears that this chromium(IV) species is a more potent oxidant of alkylaromatics in acetic anhydride than chromium(V).

Although the above data, which include the first report of the chromium(V) oxidation of alkylaromatics, suggest the mechanism of the chromyl acetate oxidation of alkylaromatics in acetic anhydride is different from those postulated for aqueous chromic acid and for non-aqueous chromyl chloride, chromium(V) species have been observed in the chromyl acetate oxidation of aromatic aldehydes, and in the chromic acid oxidation of alcohols[10] and hydroxy-acids.[11]

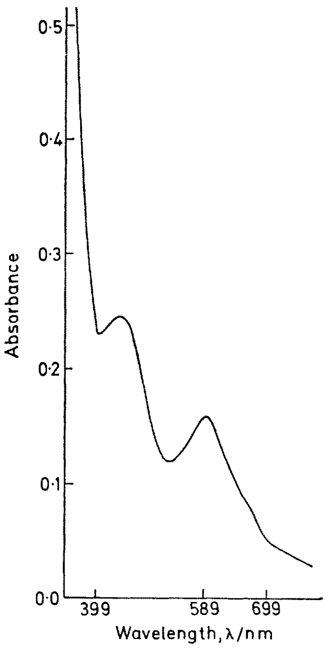


FIGURE 2. Spectrum of the kinetic solution [chromium(IV)] after the chromyl acetate ($2{\cdot}5 \times 10^{-3}$ M) oxidation of 10×10^{-2} M ethylbenzene (λ_{435} $\epsilon = 98$; λ_{589} $\epsilon = 62$).

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