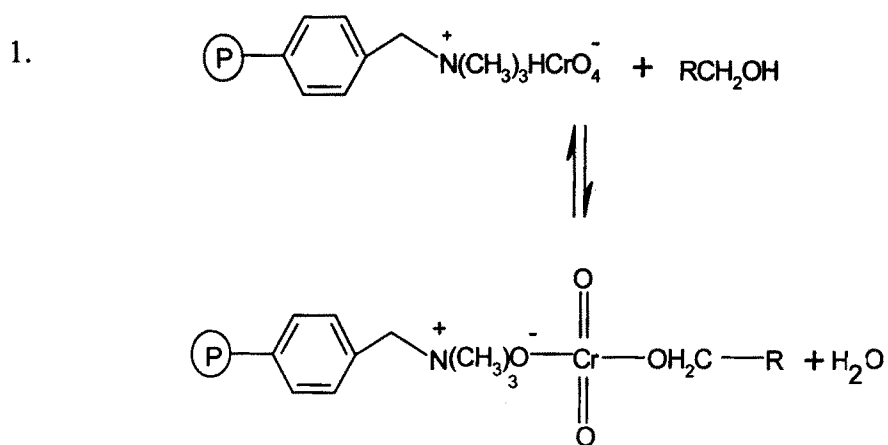


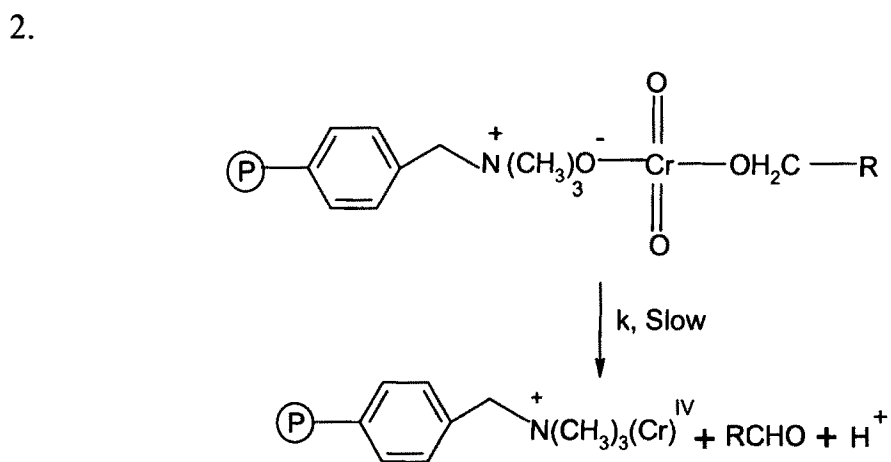
supported on a polymeric material the intermediate chromium (IV) will further oxidize another molecule of alcohol to a free radical. Thus based on the experimental results obtained for the oxidation of substituted benzyl alcohol which was found to be zero order, the mechanism may be suggested as follows.

Scheme (III):

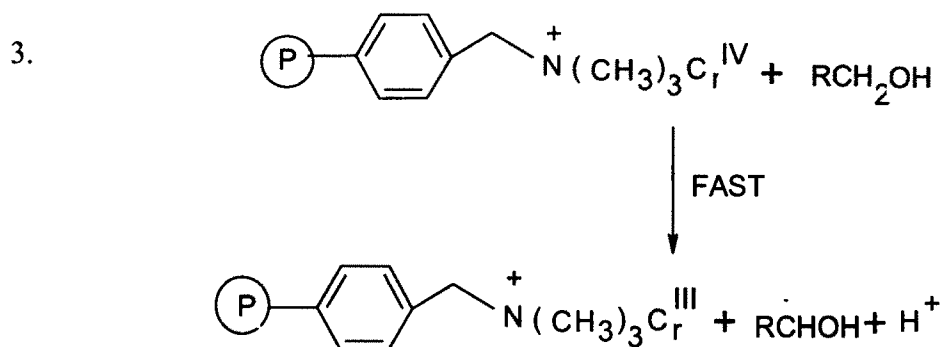
The mechanism involves an ester formation as preliminary step.



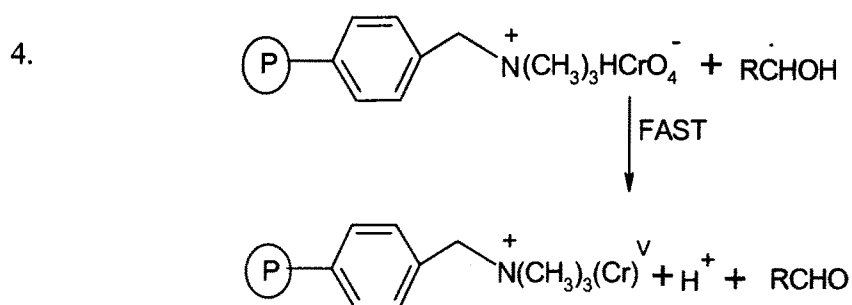
The ester formed will decompose into aldehyde and the intermediate chromium (IV) will be formed in the second and slow step.



The intermediate chromium (IV) thus formed will further react with another alcohol molecule to produce a free radical. The free radical formation in the reaction was confirmed by the polymerization of added acrylonitrile to the reaction mixture.

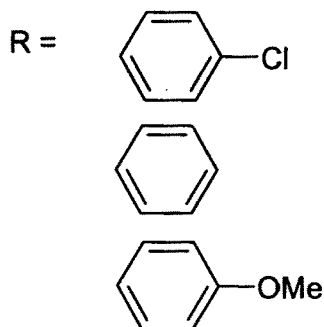
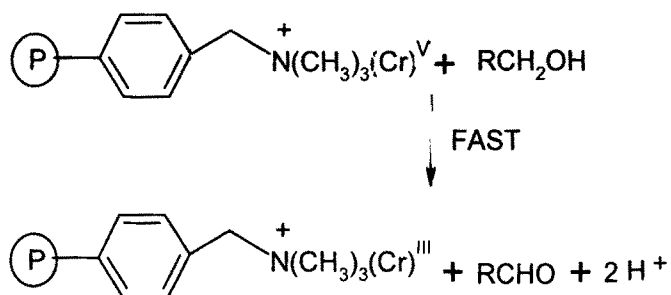


Subsequently the free radical will react with another oxidant site in the polymeric reagent in a fast steps leading to the formation of chromium (V).



The intermediate chromium V in the last step reacts with alcohol to produce aldehyde. The test for formation of chromium V and Chromium IV by their characteristic induced oxidation of iodide¹⁰ and Manganese (II)¹¹ were not successful, probably due to heterogeneity of the reaction mixture.

5.



According to Scheme III¹²⁻¹⁶, a second order rate law is expected. But since the 1st step of ester formation occurs in solid phase and assuming that this equilibrium does not contribute to the rate of reaction we obtain zero order dependence with rate constant k of the second slow step in which product aldehyde is formed.

References

1. B.Ozgun, N.Degirmenbasi, *Monatshefte Fur chemie.*, **135**(2004)483.
2. A.S.Kanade,G.S.Gokavi, M.M.Salunkhe, *Eur.Polym.J.*,**29**(4)(1993) 565.
3. E.S.Amis,*J.Chem.Educ.*,**30**(1953)351.,*Anal.Chem.*,**27**(1955)1672;
Solvent effects on reaction rates and mechanism.(Academic press,New York)(1966).
4. J.Y.Tong, E.L.King., *J.Am.Chem.Soc.*, **82**(1960), 3805.
5. F.H.Westheimer and A.Novick, *J.Chem.Phys.*, **11** (1943) 506.
6. M.Cohen and F.H.Westheimer, *J.Am.Chem.Soc.*, **74**(1952)4387.
7. F.H. Westheimer, *Chem, Rev.*, **45** (1949) 415.
8. W.Watanabe and F.H. Westheimer, *J. Chem. Phys.*, **61** (1949) 17.
9. G. Cainelii, G. Cardillo, M. Orena and S. Sardri, *J. Am. Chem. Soc.*, **98**(1976) 6737.
10. J.H.Espenson, *J.Am.Chem.Soc.*, **86** (1964) 5101.
11. F.H.Westheimer, *Chem.Rev.*, **45**(1949)419.
12. A. L. Jawanjal and N. P. Hilage, *Transition Metal Chemistry* **30**(2005) 290.
13. A. L. Jawanjal and N. P. Hilage, *Oxidation Communication*, **28** (2005) 894.
14. A. L. Jawanjal and N. P. Hilage,*Indian J. Chem.*,**44A** (2005) 1827.
15. V. Y. Sonawane, S.A. Wadkar and N. P. Hilage, *Asian J. Chem.*, **17**, 2, (2005) 1226.
16. V.Y.Sonawane and N.P.Hilage,*Asian J.Chem.*,**20** (2008) 132.