

Short Communications

The Catalytic Activity of Potassium Methoxy-Polyethylene Glycolates

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An investigation of the solvent effect on the catalytic activity of potassium *t*-butylate as measured by the rate of the conjugation isomerisation of poly-unsaturated fatty acid esters has been reported in a recent paper¹. The reaction was carried out in diethyl ether solution and the effect of the addition of small amounts of mono-, di- and tetraethylene glycol dimethyl ether on the rate of the isomerisation was investigated. The effect of the additives was compared at the same volume percentage and it was shown that there was a considerable increase in the co-catalytic effect with increasing chain length of the glycol. The co-catalytic effect of the glycol dimethyl ethers is thought to be due to their ability to solvate the K^+ ion, thereby activating the RO^- group. The increased effect with increasing chain length of glycol has been attributed to the cooperation of an increasing number of oxygen atoms in the same molecule in the solvation of the K^+ ion.

The association of the additives and the K^+OR^- ($S + K^+OR^- \rightarrow S \cdots K^+ \cdots OR^-$, where S stands for the additive) may be expected to be accompanied by a decrease in entropy. It was felt that this decrease in entropy would be less and the K^+ solvation more effective if the catalytically active $-O^-$ group and the K^+ solvating ether oxygen atoms were placed in the same molecule, as the K^+ solvation then might be accomplished within the same molecule.

The potassium alcoholates of some mono-methyl ethers of polyethylene glycols of general formula $CH_3(OCH_2CH_2)_nO^-K^+$ therefore were prepared. Their catalytic effect on the conjugation isomerisation of linolenic acid methyl ester in diethyl ether solution (50 mg ester/10 ml) was compared with the catalytic effect of potassium *t*-butylate in the same solvent.

Also in the case of the glycolates a striking increase in the catalytic activity was observed when their chain length increased.

At a concentration of catalyst = 0.1 mole/l the relative rate of the reaction at 25°C had the following approximative values: Potassium *t*-butylate = 1,

$CH_3(OCH_2CH_2)_2O^-K^+ = 20$,
 $CH_3(OCH_2CH_2)_3O^-K^+ = 70$,
 $CH_3(OCH_2CH_2)_{7-8}O^-K^+ = 600$. (The latter compound was prepared from Methoxy Polyethylene Glycol 350 from Union Carbide Co., molecular weight 335-365.) With the latter "self-solvating" catalyst the reaction is very fast, being completed within ~ 1.5 min at 25°C. The results are the more surprising as the *t*-butylate ion due to the branching at the α C-atom is more basic than the glycolate ions. Other advantages of the "self-solvating" catalysts are that they are much more soluble than ordinary alcoholates in nonpolar solvents, and that their catalytic activity seems to be more independent of the solvent. Thus they are readily soluble in benzene and their catalytic activity in benzene solution was found to be approximately the same as in ether solution.

1. Ugelstad, J., Rokstad, O. A. and Skarstein, J. *Acta Chem. Scand.* 17 (1963) 208.

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