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The Effect of the Solvent on the Base Catalyzed Conjugation-Isomerisation of Poly-unsaturated Fatty Acid Compounds

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The rate of the conjugation-isomerisation of linseed oil in a solution of K-butoxide in butanol is increased enormously by the presence of an excess of dimethylsulfoxide, dimethylformamide or tetramethylurea. The reaction may thereby be caused to proceed rapidly at room temperature.

In the literature concerning the effect of the solvent on the rate of organic reactions most authors have tried to correlate the effect to the polar properties of the solvent. This theory has led to equations which, for each type of reaction, postulate a certain relationship between the rate and the dielectric constant of the solvent. In two recent publications we discussed these problems [1,2], and gave several examples of reactions where there seems to be no such correlation. In many cases special types of interaction between the reactants and the nearest neighbour solvent molecules seem to outweigh the integral electrostatic effect of the polar forces. As an example of this type of effect we have described briefly some types of base-catalyzed reactions. One of the reactions mentioned was the conjugation-isomerisation of poly-unsaturated fatty acid compounds. In the present paper some of the preliminary results of these investigations are described.

When analyzing a fatty acid compound for the content of different poly-unsaturated fatty acids, conjugation of the double bonds is usually brought about by treatment of the compound at 180°C with a solution of KOH or K-alcoholate in alcohol. From the amount of conjugated diene, triene *etc.*, as determined from UV absorption spectra, the content of the original poly-unsaturated fatty acids may be estimated.

As will be shown below, we have found that the conjugation-isomerisation proceeds rapidly even at 25°C when using a mixture of K-alcoholate in alcohol and an excess of dimethylsulfoxide, dimethylformamide or tetramethylurea as the reaction medium for the conjugation process.

PROCEDURE

Due to its high content of linolenic acid, linseed oil was chosen as a suitable compound for the preliminary investigation of the effect of the solvent on the rate of the conjugation reaction. 30 mg linseed oil was dissolved in dimethylsulfoxide, dimethylformamide or tetramethylurea. After deaeration of the solution with N_2 the sample was placed in a thermostat bath at 25°C. Then the catalyst solution was added. (The catalyst solution was prepared by dissolving potassium in butanol. In each case the catalyst solution contained 2.3×10^{-3} mole K-butoxide per g solution.) After certain time intervals, the reaction was stopped by dilution with methanol. UV-spectra of the samples were taken with a Beckman Recording Spectrophotometer, Model DK 9500. In the preliminary investigation of the solvent effect on the rate of isomerisation, only the content of conjugated triene, as determined from the absorption peak at $\sim$267 mμ, was considered. This determination gave good reproducible values.

In Table 1 the values for the extinction coefficient k, in a reaction medium consisting of 4 g catalyst-solution and 10 g of dimethylsulfoxide, dimethylformamide or tetramethylurea, are given for various reaction times, ($k = \varepsilon / c \cdot L$ where ε = absorption, c = g/l and L = the length of the cell (= 1 cm)). The results of some experiments with the catalyst-solution only as reaction medium have also been included in the table for comparison.

In Fig. 1 the values for the extinction coefficient are plotted as a function of the reaction time for the mixture of catalyst-solution and dimethylformamide or dimethylsulfoxide. In Fig. 2 the results of some experiments are given where the relative amount of butanol and dimethylsulfoxide in the reaction medium were varied. In these experiments the concentration of catalyst and the reaction time were kept constant.

The linseed oil used in these investigations was also isomerized by the usual method for analysis: treatment at 180°C with 10 g of a solution consisting of 18 % KOH in ethyleneglycol. The extinction coefficient at $\sim$267 mμ after this treatment was 37.5.

Table 1. Extinction coefficient, k, at $\sim$ 267 mμ after different time intervals. Linseed oil, 30 mg. Temp. 25°C.

	Reaction medium	1 min	2 min	5 min	10 min	15 min	20 min	30 min	60 min	120 min	180 min	24 h
A	10 g dimethylsulfoxide, 4 g catalyst-solution	8.2	13.2	24.0	29.0		30.0	31.0	33.0	33.0		
B	10 g N,N-dimethylformamide, 4 g catalyst-solution		3.8	7.4	11.6	19.0		26.0	31.5	34.5	35.0	
C	10 g tetramethylurea 4 g catalyst- solution								32.0	35.0		
D	4 g catalyst- solution									0	0	$\sim$0

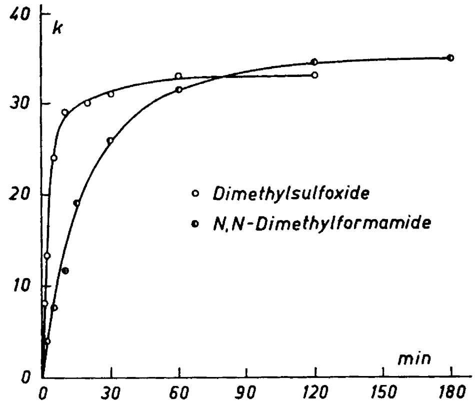


Fig. 1. The extinction coefficient, k, as a function of reaction time. Linseed oil, 30 mg. Catalyst solution, 4 g. DMSO or N,N-dimethylformamide, 10 g. Temp. 25°C.

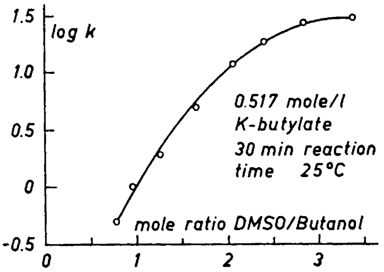


Fig. 2. Log (extinction coefficient) as a function of mole ratio DMSO/butanol.

It may be seen from the table that even after 24 h at 25°C there are only traces of conjugation when the linseed oil is treated with the pure catalyst solution (K-butoxide in butanol). In the mixtures of catalyst solution and dimethylformamide, tetramethylurea or dimethylsulfoxide however, the conjugation-isomerisation takes place with remarkable speed. In each case the extinction coefficient approaches a practically constant value of 33—35, which is reached already after 30 to 60 min.

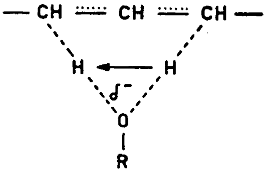
DISCUSSION

The conjugation reaction is initiated by an attack of the RO^- ion on the CH_2 group in α position to two double bonds. A twostep reaction mechanism may be formulated as follows:

$$-CH{=}CH-CH_2-CH{=}CH- + OR^- \rightleftharpoons -\bar{C}H-CH{=}CH-CH{=}CH- + ROH \quad (1)$$

$$-\bar{C}H-CH{=}CH-CH{=}CH- + ROH \rightarrow -CH_2CH{=}CH-CH{=}CH- + OR^- \quad (2)$$

In this case, (1) is most probably the rate determing step. Possibly the proton transfer may also take place without a complete ionization:



The observed effect of N,N-dimethylformamide, tetramethylurea and dimethylsulfoxide on the rate of the conjugation reaction may possibly be due to: 1. The ability of these substances to act as strong H-acceptors by the formation of H-bonds. 2. Their ability to solvate specifically the K^+-ion.

The effect of H-bond formation may be explained as follows: In alcoholic solution the RO^- ion will be highly solvated by H-bond formation with the alcohol, $RO^- - - - H-OR$, which in turn leads to a deactivation of the catalyst. (It should be noted that alcohol is present in all the experiments.) However, dimethylformamide, tetramethylurea or dimethylsulfoxide present in excess, may effectively bind the alcohol by H-bond formation and thus reduce the deactivation of RO^- by the alcohol. N-Alkylamides are known to act as very strong H-binding "acceptors". The relative strength of dimethylsulfoxide, in this respect is less known. From nuclear resonance studies, Drinkard and Kivelson [3] conclude that dimethylsulfoxide forms stronger H-bonds than acetone with methanol. Lindquist *et al.*[4,5] conclude from measurements of the addition reaction to $SnCl_4$ and $SbCl_5$ that dimethylsulfoxide, like N-alkylamides has a much higher donor-strength than acetone and ethylacetate. A comparison of substances with the same donor atom seems to show a correlation between the electrondonating capacity of the substance and the strength of the H-bond formed.

While the alcohol solvates the catalyst by interaction with the RO^- ion, N-alkylamides and dimethylsulfoxide, with a high electron density at the O atom, might be expected to solvate specificially the K^+ ions. An activation of the catalyst would then occur through a decrease in the $K^+ - - - \bar{O}R$ interaction. Zaugg [6] found that addition of N-alkylamides and dimethylsulfoxide to a solution of sodio malonic esters in benzene markedly increased the rate of the alkylation with alkyl halides, and ascribed this effect to a solvation of the Na^+ ion by these substances. Zaugg concluded that this ability is primarily due to the presence of a region of high electron density in the π-orbital at the O atom of these substances.

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