

ALKALINE HYDROLYSIS OF PIVALIC ESTERS OF ETHYLENE GLYCOL IN WATER-ACETONE SOLUTIONS*

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The paper reports alkaline hydrolysis of ethylene dipivalate and 2-hydroxyethyl pivalate as compounds modelling the structural unit and crosslinking site of hydrophilic gels, *i.e.*, copolymers of 2-hydroxyethyl methacrylate and ethylene dimethacrylate. The kinetics of hydrolysis was investigated in water-acetone solutions containing respectively 50, 75, 80, 85 and 90% by vol. (related to 20°C) of acetone at 20, 30, 40, and 50°C. It was demonstrated that, owing to steric hindrance, the preferential hydrolysis of monoester was more pronounced in the case of pivalic esters of ethylene glycol compared with acetic esters of ethylene glycol. The results are discussed in connection with the selectivity of the alkaline hydrolysis of ester bonds in "pendant" parts of structural units in hydrophilic methacrylate gels.

We have found in earlier papers^{1,2} that transformations of ester groups in glycol methacrylate gels (copolymers of 2-hydroxyethyl methacrylate with ethylene dimethacrylate, or of 2-(2-hydroxyethoxy)ethyl methacrylate with 2,2'-oxydiethyl dimethacrylate) proceed selectively to high degrees of conversion, so that the ester groups in inter-chain linkages are transformed only at the end of the process. When studying the causes of the selective course of the alkaline hydrolysis of glycol methacrylate gels², we investigated the alkaline hydrolysis, in water-acetone solutions of 2-hydroxyethyl acetate and ethylene diacetate, which served as the simplest model compounds of the structural unit having a "pendant" functional group and of the structure of inter-chain linkage. We demonstrated³ that up to a content of 85% of acetone in the reaction mixture the preferential hydrolysis of hydroxyethyl acetate increases compared with ethylene diacetate in the sense of Sakurada's^{4,5} conception of the hydrophilic effect. The similar character of hydrolysis of these model compounds in a water-organic solution and of glycol methacrylate gels in aqueous solutions of sodium hydroxide was interpreted so that in swollen gels the macromolecules themselves act as the organic component, enhancing the selectivity of water-organic hydrolyzing mixtures⁶.

2-Hydroxyethyl acetate and ethylenediacetate adequately model conditions existing in glycol-methacrylate gels, as regards the number of ester groups present in the structural unit, the presence or absence of the hydroxylic group, its formation during the hydrolysis of the diester (*i.e.* of the structural crosslinking unit), and also with respect to the distance between functional groups in the structural units. On the other hand, however, they do not adequately reflect steric conditions in glycol methacrylate gels.

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In this work we have investigated ethylene dipivalate and 2-hydroxyethyl pivalate as models of the structural units of glycol methacrylate gels. These model compounds keep all the advantages of acetate esters, being however more adequate with respect to steric conditions in that their ester group is adjacent to a quaternary carbon atom.

EXPERIMENTAL

Chemicals

Ethylene dipivalate and 2-hydroxyethyl pivalate were prepared as described elsewhere⁷. The other chemicals used (Lachema, Brno) were reagent grade. Acetone was dried with anhydrous potassium carbonate and rectified⁸; distilled water was freed from carbon dioxide by boiling *in vacuo* until constant conductivity was reached, and aqueous sodium hydroxide solution was prepared by diluting Sörensen alkali (carbonate free 50% NaOH). Hydrolysis was investigated titrimetrically by using an apparatus already described⁹. The initial concentrations of reaction mixtures were each time about 0.005 mol dm⁻³ NaOH and 0.005 mol dm⁻³ of ester groups, both with 2-hydroxyethyl pivalate and ethylene dipivalate.

The rate constants of hydrolysis of ethylenedipivalate to the first and second degree were calculated by employing a procedure with transformed variables in differential equations describing competitive consecutive reactions; the procedure consists in the minimization of a suitably chosen object function, thus avoiding the numerical solution of a set of differential equations¹⁰. The values of the Arrhenius activation energies and frequency factors (A_i) were calculated for reaction mixtures having a constant content of acetone, using the dependences of the rate constants (dm³ mol⁻¹ s⁻¹) of ethylene dipivalate (k_1)_{imp} and of 2-hydroxyethyl pivalate (k_2)_{exp} on absolute temperature (T_j). The values of the activation enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) were calculated similarly from the temperature dependences of the rate constants: $\ln (k_i/T_j) = \ln (k/h) + \Delta S_i^\ddagger/R - \Delta H_i^\ddagger/(R \cdot T_j)$, where $i = \langle 1, 2 \rangle$ and $T_j = 273.16 + \{20, 30, 40, 50\}$.

RESULTS AND DISCUSSION

The alkaline hydrolysis of 2-hydroxyethyl pivalate and ethylene dipivalate was investigated under conditions similar to those used with 2-hydroxyethyl acetate and ethylene diacetate³. In contrast with ethylene diacetate, where the formation of turbidity in the reaction mixture was observed as a result of phase separation only at 51°C in a mixture containing 90% by vol. of acetone, hydrolytic mixtures with pivalate were turbid at a 90% content of acetone at all temperatures; for this reason, the values given below for this concentration of acetone are only illustrative. The rate constants of the alkaline hydrolysis of 2-hydroxyethyl pivalate (aqueous acetone, 1 : 1 by vol., 20°C) were on the one hand calculated from the alkaline hydrolysis of ethylene dipivalate by a simultaneous minimization of the object function for hydrolytic constants to the 1st and 2nd degree (these we designated (k_2)_{opt}), and on the other, determined from the alkaline hydrolysis of authentic samples of 2-hydroxyethyl pivalate, ((k_2)_{exp}). In the latter case the calculation was made with the same

optimization programme wherein zero concentration of ethylene dipivalate was substituted.

| Temperature, °C: | 20·00 | 30·00 | 40·00 | 50·00 |
|---|-------|-------|-------|-------|
| $(k_2)_{\text{opt}}$, $10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$: | 5·14 | 10·34 | 24·76 | 53·05 |
| $(k_2)_{\text{exp}}$, $10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$: | 6·75 | 11·96 | 24·69 | 45·78 |

The agreement between the two independent ways of determining the rate constant k_2 is satisfactory, but the values $(k_2)_{\text{exp}}$ obtained from the hydrolysis of authentic samples of 2-hydroxyethyl pivalate are regarded as more plausible, firstly, because according to the preceding model calculations¹⁰ a reliable determination of the rate constant of hydrolysis of diester to the second degree requires a comparatively high degree of conversion and, secondly, because the $(k_2)_{\text{opt}}$ values calculated by simultaneous optimization showed higher scatter in the correlation according to Arrhenius.

In the calculation of the rate constants for alkaline hydrolysis of ethylene dipivalate (aqueous acetone, 1:1 by vol., 20°C) we employed the original procedure, *i.e.* the simultaneous minimization of the object function for hydrolytic constants to the first and second degree (constant $(k_1)_{\text{opt}}$), and also a modified procedure (constant $(k_1)_{\text{imp}}$), for which the object function could be minimized only for the hydrolytic constant to the first degree, while the hydrolytic constant to the second degree had a prescribed constant value $(k_2)_{\text{exp}}$, determined from a direct investigation of the hydrolysis of pure 2-hydroxyethyl pivalate. A very good agreement of data was obtained for the temperature range 20–50°C:

| Temperature, °C: | 20·00 | 30·00 | 40·00 | 50·00 |
|---|-------|-------|-------|-------|
| $(k_1)_{\text{opt}}$, $10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$: | 5·01 | 9·12 | 15·07 | 24·79 |
| $(k_1)_{\text{imp}}$, $10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$: | 4·92 | 8·84 | 15·07 | 25·52 |

Fig. 1 shows connecting line diagrams of the dependence of the rate constants of alkaline hydrolysis on the acetone content at various temperatures for 2-hydroxyethyl pivalate and ethylenedipivalate, and for the sake of comparison also for 2-hydroxyethyl acetate and ethylenediacetate³. Because of steric hindrance the rate constants for pivalates are lower by 1 to 2 orders of magnitude than those for acetates. The values for ethylenediacetate increase monotonically at constant temperature with increasing acetone content, but for 2-hydroxyethyl acetate they pass through a distinct maximum near 85% by vol. of acetone in the mixture. The maximum becomes more pronounced with increasing reaction temperature. The constants for pivalic esters increase only slightly at constant temperature with increasing acetone content up to 80%. At this concentration the isotherms of the rate constants of both pivalic

esters swing upwards and this bending becomes more pronounced with increasing temperature. The steep rise in the rate constants (Table I) is attributed to the increased solvation stabilization of activated complexes for both mono- and diester, as confirmed also by the entropy values ΔS^\ddagger given in Table II.

Through the ratio of the rate constants of diester to monoester, $(k_1)_{\text{imp}}/(k_2)_{\text{exp}} \equiv k_1/k_2$, we express the extent of the hydrophilic effect³ first observed by Sakurada^{4,5} in the alkaline hydrolysis of ethylenediacetate and of other acetates of poly-functional alcohols in water-acetone solutions. The ratio k_1/k_2 becomes 2 in solutions where all the ester groups are reaction-equivalent, as is the case in the alkaline hydrolysis of acetic esters of ethylene glycol in aqueous solutions¹¹. The preferential alkaline hydrolysis of hydrophilic monoester compared with the initial diester in water-organic solutions (*i.e.* the hydrophilic effect) causes a decrease in this value.

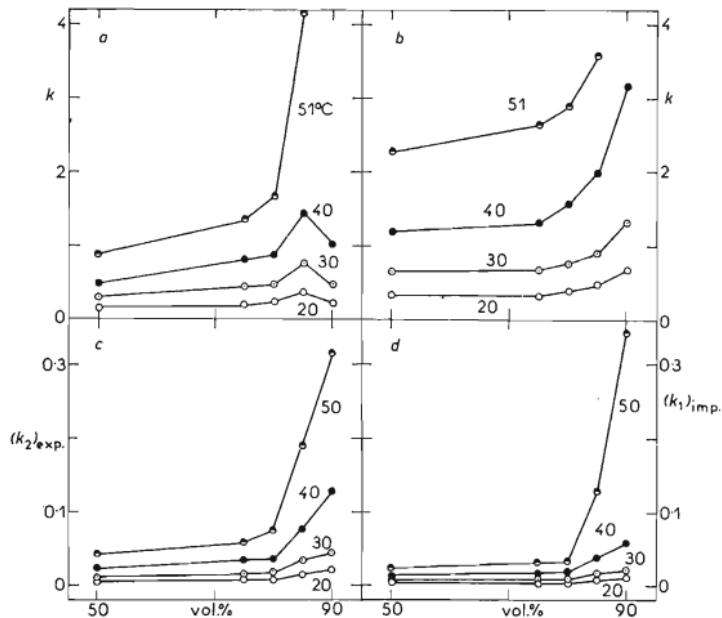


FIG. 1

Dependence of the Rate Constant ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) on the Acetone Content (vol.%, related to 20°C)

a 2-Hydroxyethyl acetate, *b* ethylene diacetate, *c* 2-hydroxyethyl pivalate and *d* ethylene di-pivalate.

TABLE I

Rate Constants of the Alkaline Hydrolysis of Ethylene Dipivalate (k_1)_{imp} and 2-Hydroxyethyl Pivalate (k_2)_{exp} ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) in Water-Acetone Solution as a Function of Temperature and Acetone Content in the Reaction Mixture (vol.%, related to 20°C)

Initial concentration of sodium hydroxide and ester groups about 0.005M.

| Acetone content | 20°C | | 30°C | | 40°C | | 50°C | |
|-----------------|------------------|------------------|------------------|------------------|------------------|---------------------|---------------------|---------------------|
| | $k_1 \cdot 10^3$ | $k_2 \cdot 10^3$ | $k_1 \cdot 10^3$ | $k_2 \cdot 10^3$ | $k_1 \cdot 10^3$ | $k_2 \cdot 10^3$ | $k_1 \cdot 10^3$ | $k_2 \cdot 10^3$ |
| 50 | 4.92 | 6.75 | 8.84 | 11.96 | 15.07 | 24.69 | 25.52 | 45.78 |
| 75 | 5.46 | 8.72 | 9.57 | 16.23 | 18.19 | 36.40 | 35.07 | 60.68 |
| 80 | 4.40 | 8.29 | 9.55 | 17.66 | 20.22 | 36.45 | 34.24 | 75.14 |
| 85 | 8.36 | 16.48 | 19.09 | 36.17 | 38.83 | 79.05 | 129.46 ^a | 189.03 ^b |
| 90 | 12.14 | 21.91 | 22.93 | 45.28 | 58.18 | 129.12 ^d | 344.47 ^c | 317.11 ^e |

Actual temperature: ^a 50.30°C; ^b 50.72°C; ^c 50.17°C; ^d 40.13°C; ^e 49.73°C.

TABLE II

Dependence of the Frequency Factor (A , $\text{dm}^3 \text{ s}^{-1} \text{ mol}^{-1}$), of the Arrhenius Activation Energy (E_{exp}), of the Activation Enthalpy (ΔH^\ddagger) and Entropy (ΔS^\ddagger) on the Acetone Content (volume per cent, related to 20°C) in the Reaction Mixture in the Alkaline Hydrolysis of 2-Hydroxyethyl Pivalate and Ethylene Dipivalate in Water-Acetone Solutions

r correlation coefficient.

| Acetone content | $\log A$ | $E_{\text{exp}} \cdot 10^{-4}$ J mol^{-1} | r | $\Delta H^\ddagger \cdot 10^{-4}$ J mol^{-1} | ΔS^\ddagger $\text{J mol}^{-1} \text{ K}^{-1}$ | r |
|---|----------|---|----------------------|--|---|----------------------|
| Hydrolysis of 2-hydroxyethyl pivalate, (k_2) _{exp} | | | | | | |
| 50 | 6.84 | 5.07 | —0.9983 | 4.81 | —122.5 | —0.9982 |
| 75 | 7.12 | 5.15 | —0.9965 | 4.90 | —117.2 | —0.9961 |
| 80 | 8.10 | 5.71 | —0.9999 ₈ | 5.46 | —98.4 | —0.9999 ₈ |
| 85 | 9.36 | 6.26 | —0.9994 | 6.00 | —74.3 | —0.9994 |
| 90 | 11.06 | 7.16 | —0.9959 | 6.91 | —41.7 | —0.9957 |
| Hydrolysis of ethylene dipivalate, (k_1) _{imp} | | | | | | |
| 50 | 5.38 | 4.32 | —0.9999 | 4.06 | —150.4 | —0.9999 |
| 75 | 6.44 | 4.90 | —0.9980 | 4.64 | —130.1 | —0.9979 |
| 80 | 7.35 | 5.44 | —0.9981 | 5.18 | —112.8 | —0.9979 |
| 85 | 10.30 | 6.96 | —0.9914 | 6.71 | —56.4 | —0.9908 |
| 90 | 13.16 | 8.53 | —0.9662 | 8.27 | —1.53 | —0.9642 |

Though k_1/k_2 is sensitive to experimental errors, the overall dependences of k_1/k_2 on the acetone content in the mixture (Fig. 2) are so conclusive that they corroborate the role played by the hydrophilic effect for acetates up to 85% of acetone in the mixture and for pivalates within the whole concentration range under investigation. (In the case of acetates, an inversion in the solvation of activated complexes takes place in the range above 85% of acetone in the mixture³, so that at 90% of acetone it is the initial diester that is preferentially hydrolyzed).

With pivalates, the hydrophilic effect is much more pronounced within the whole concentration range, and this is connected with the steric hindrance in the vicinity of ester bonds; this hindrance leads to the already mentioned overall decrease in the rate constants of alkaline hydrolysis, but especially to a considerable increase in the preferential hydrolysis of the hydrophilic (and moreover sterically less hindered) 2-hydroxyethyl pivalate.

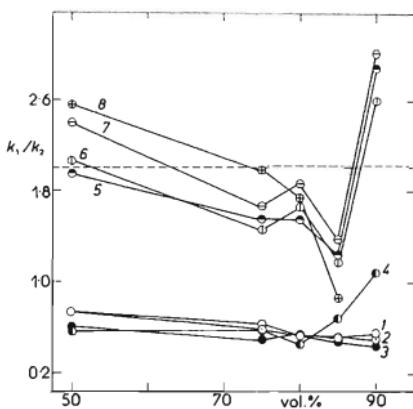
This paper, along with a preceding study³ on the alkaline hydrolysis of ethylene diacetate and 2-hydroxyethyl acetate, confirms that macromolecular chains participate in the observed selectivity of alkaline hydrolysis of glycol methacrylate gels². In aqueous solutions these chains replace the organic component in water-organic hydrolyzing mixtures with enhanced selectivity and, at the same time, by their steric influence, they reduce the reactivity of methacrylic esters because of the impaired accessibility of hydrolytic agents to ester groups. In the case of inter-chain linkages, in which both ester bonds are hindered by powerful barriers of the polymeric backbone, the attack by the hydrolyzing agent is made very difficult, which again greatly contributes to the selectivity of the hydrolysis of the ester bonds of pendant functional sections in the monomeric units.

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FIG. 2

Ratio of Rate Constants k_1/k_2 in Hydrolysis of Diester and Monoester as a Function of Acetone Content in the Reaction Mixture (vol.%, related to 20°C)

Pivalates (reaction temperatures (°C)): 1 20, 2 30, 3 40, 4 50. Acetates (reaction temperatures (°C)): 5 20, 6 30, 7 40, 8 51.



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