Kinetics of esterification of 1-pentanol by isobutyric acid and benzyl alcohol by acetic acid

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

The authors of this paper investigated the temperature dependence of equilibrium constant for the formation of 1-pentyl isobutyrate from 1-pentanol and butyric acid as well as benzyl acetate from benzyl alcohol and acetic acid by using sulfuric acid as a catalyst. Moreover, they examined the temperature dependence of the rate constants of esterification for these esters and expressed it by the Arrhenius equation in the form $\ln \{k_{v+}\} = f(1/T)$.

Авторами исследована температурная зависимость равновесной константы образования 1-пентилизобутирата из 1-пентанола и маслянной кислоты и бензилацетата из бензилового спирта и уксусной кислоты при использовании серной кислоты в качестве катализатора. В работе была также исследована зависимость констант скорости этерификации указанных сложных эфиров и выражена через уравнение Аррениуса: $\ln \{k_{v+}\} = f(1/T)$.

Among the great number of compounds used in the industry of flavour and fragrance substances, the esters of organic acids and alcohols have an important position [1—3]. Though these compounds may be prepared by several ways, it seems that the most convenient method of their preparation is the esterification of the pertinent acid with apt alcohol in view of raw material base, method of preparation or production and demands on the purity of these substances needed in alimentary industry.

1-Pentyl isobutyrate and benzyl acetate are two of the rather great number of esters used as flavour and fragrance substances. There are mentions in literature about occurrence, synthesis, and application of these substances [4—9], but no data concerning equilibrium constants and kinetic parameters of their preparation are, in principle, to be found in available literature.

The aim of our investigations was to find out basic kinetic and equilibrium data concerning preparation of 1-pentyl isobutyrate and benzyl acetate from the corresponding alcohols and acids by using sulfuric acid as a catalyst.

Experimental

Chemicals

1-Pentanol, acetic acid, isobutyric acid, 1,4-dioxan, phenolphthalein, 96 % sulfuric acid, NaOH were anal. grade chemicals whereas benzyl alcohol was designated as pure chemical (the substances were dried with excess anhydrous Na_2SO_4). All chemicals were products of Lachema, Brno.

Method and working procedure

The kinetic and thermodynamic measurements were carried out in sealed glass ampoules which were fixed in a special rotating equipment and dipped in a thermostatted bath the temperature of which was held at a certain value accurate to ± 0.1 °C.

The quantity of 5 ml of 4 M-solution of organic acid was dosed into the glass ampoule where the necessary quantity of sulfuric acid was put beforehand. The ampoules were cooled to the temperature of -30 °C. Afterwards, 5 ml of 4 M-solution of the starting alcohol were dosed and the ampoules were sealed. 1,4-Dioxan was used as solvent. The temperature of substances in the ampoules continued to be held at -30 °C. Then the ampoules were dipped into the thermostatted bath and subjected to rotation. The ampoules were taken in certain time intervals, the reaction was stopped by cooling to -10 °C, and the concentration of the nonconsumed acid was determined by titration with 1 M-NaOH by using phenolphthalein as an indicator.

Results and discussion

A. 1-Pentyl isobutyrate

Dependence of equilibrium constant on temperature

The equilibrium constant of the esterification of 1-pentanol by isobutyric acid was determined at the temperatures: $\theta/°\text{C} = 40$, 50, 60, 70, and 80 in sealed glass ampoules after establishment of equilibrium, the initial concentrations of 1-pentanol and isobutyric acid being 2 mol dm^{-3}. The concentration of sulfuric acid was equal to 0.01 mol dm^{-3}. It was assumed that the equilibrium was established if three samples taken one after another in 6 h intervals gave equal values within the range of experimental error. The resulting value was calculated as the average of three measurements. The results obtained are presented in Table 1.

Table 1

Variation of equilibrium constant and rate constant with temperature for 1-pentyl isobutyrate

$\frac{T}{\mathrm{K}}$	K_c	$\frac{k_{v+}\cdot 10^5}{\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$	$\frac{k_{\mathrm{correl}}\cdot 10^5}{\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$
313.15	4.012	2.11	2.9
323.15	3.871	3.46	3.67
333.15	3.853	6.14	5.97
343.15	3.802	9.39	9.44
353.15	3.735	14.87	14.54

These values as well as regression analysis were used for determining the mathematical relationship between equilibrium constant and temperature in the form

$$\log K_c = \frac{78.14\ \mathrm{K}}{T} + 0.3509 \qquad (1)$$

$$s_{yx}^2 = 1.2 \times 10^{-5}$$

Dependence of rate constant on temperature for the formation of 1-pentyl isobutyrate

The rate constant for the formation of 1-pentyl isobutyrate was determined under these conditions: initial concentration of isobutyric acid $c_{\mathrm{A},0} =$ 1.95 mol dm^{-3}, initial concentration of 1-pentanol $c_{\mathrm{B},0} = 2$ mol dm^{-3}, initial concentration of 1-pentyl isobutyrate $c_{\mathrm{R},0} = 0$, initial concentration of water $c_{\mathrm{S},0} = 0$ and concentration of catalyst $c_{\mathrm{H_2SO_4}} = 0.05$ mol dm^{-3}. The rate constant was calculated from the rate equation valid for inverse reactions of the second order [10] the general kinetic solution of which has the following form

$$k_{v+} = \frac{1}{t_r c_{\mathrm{B},0}\sqrt{\Delta}} \ln \frac{2c - (b - \sqrt{\Delta})X_\mathrm{A}}{2c - (b + \sqrt{\Delta})X_\mathrm{A}} \qquad (2)$$

where k_{v+} is the rate constant of esterification (dm^3 mol^{-1} s^{-1}), t_r reaction time (s), and X_A degree of transformation of component A (*i.e.* isobutyric acid). The constants Δ, a—c are defined by eqns (3—6)

$$\Delta = b^2 - 4ac \tag{3}$$

$$a = \frac{c_{A,0}}{c_{B,0}}\left(1 - \frac{1}{K_c}\right) \tag{4}$$

$$b = \frac{c_{A,0} + c_{B,0}}{c_{B,0}} + \frac{c_{R,0} + c_{S,0}}{K_c c_{B,0}} \tag{5}$$

$$c = 1 - \frac{c_{R,0} c_{S,0}}{K_c c_{A,0} c_{B,0}} \tag{6}$$

The resulting rate constants obtained as the average of eight measurements performed at each temperature are given in Table 1 while the relationship $\ln\{k_{v+}\} = f(1/T)$ is represented in Fig. 1.

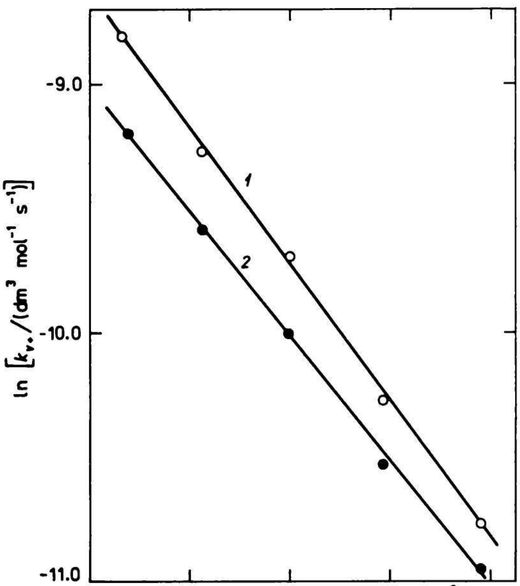

Fig. 1. Equilibrium constant for the formation of 1-pentyl isobutyrate and benzyl acetate as a function of $1/T$.
1. 1-Pentyl isobutyrate; *2.* benzyl acetate.

The values given in Table 1 as well as regression analysis were used for determining the Arrhenius equation which expresses the rate constant as a function of temperature. In our case, it assumes the form

$$\{k_{v+}\} = 3.982 \times 10^2 \exp\left(-\frac{43\,500 \text{ J mol}^{-1}}{RT}\right); \; [k_{v+}] = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (7)$$

The correlated values of the rate constants for the preparation of 1-pentyl isobutyrate were calculated from eqn (7). They are also given in Table 1.

B. Benzyl acetate

Dependence of equilibrium constant on temperature

The equilibrium constant for the formation of benzyl acetate was determined at the temperatures: $\theta/°\text{C} = 40$, 50, 60, 70, and 79 in sealed glass ampoules containing the solution of benzyl alcohol and acetic acid. The initial concentrations of these substances were 2 mol dm^{-3} while the concentration of sulfuric acid was 0.01 mol dm^{-3}. The results obtained are given in Table 2.

Table 2

Variation of equilibrium constant and rate constant with temperature for benzyl acetate

$\frac{T}{\text{K}}$	K_c	$\frac{k_{v+} \cdot 10^5}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$	$\frac{k_{\text{correl}} \cdot 10^5}{\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}$
313.15	1.313	1.76	1.74
323.15	1.240	2.67	2.82
333.15	1.190	4.51	4.45
343.15	1.136	6.83	6.81
353.15	1.079	10.28	9.82

These values as well as regression analysis were used for determining the analytical form of the relationship between equilibrium constant and temperature, *i.e.*

$$\log K_c = \frac{230 \text{ K}}{T} - 0.6167 \qquad (8)$$

$$s_{yx}^2 = 8.1 \times 10^{-7}$$

Dependence of rate constant on temperature for the formation of benzyl acetate

The rate constant for the formation of benzyl acetate was determined at temperatures: $\theta/°\text{C} = 40$, 50, 60, 70, and 79 under these conditions: initial concentration of acetic acid $c_{\text{A},0} = 1.95$ mol dm^{-3}, initial concentration of benzyl alcohol $c_{B,0} = 2$ mol dm^{-3}, initial concentration of benzyl acetate $c_{R,0} = 0$, initial concentration of water $c_{S,0} = 0$, and concentration of catalyst $c_{H_2SO_4} = 0.05$ mol dm^{-3}. The rate constants were calculated by means of eqns (*2—6*).

The measured values and calculated rate constants (average of 6—8 measurements) for a few temperatures are given in Table 2 and the relationship $\ln\{k_{v+}\} = f(1/T)$ is represented in Fig. 1.

These results as well as regression analysis were used for calculating the Arrhenius equation for the rate constant. It assumes the form

$$\{k_{v+}\} = 1.01 \times 10^2 \exp\left(\frac{-40\,300 \text{ J mol}^{-1}}{RT}\right); [k_{v+}] = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (9)$$

The correlated results calculated according to eqn (*9*) are also given in Table 2.

Conclusion

As obvious from Table 1 and Table 2, the equilibrium constant has the tendency to decrease slightly with temperature. In accordance with expectation, the value of equilibrium constant for the ester containing alcohol with higher molecular mass is lower. The activation energies calculated from measured data by the use of the Arrhenius equation (E(1-pentyl isobutyrate) = 43.5 kJ mol^{-1}; E(benzyl acetate) = 40.7 kJ mol^{-1}) are relatively low, owing to which the variation of reaction rate with temperature is relatively small (Fig. 1).

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