KINETICS OF CONDENSATION OF BENZALDEHYDE AND ITS DERIVATIVES WITH ACETONE AND METHYL ETHYL KETONE CATALYSED BY ALUMINIUM OXIDE

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Kinetics of condensation of benzaldehyde with excess acetone and methyl ethyl ketone in the liquid phase and in the presence of aluminium oxide as the catalyst was investigated in the range of temperatures from 60 to 160°C. The pseudo-first order kinetics for the condensation of benzaldehyde with acetone and the positive value of the Hammett reaction constant ($\varrho = 1.43 \pm 0.08$ at 90°C) found for the condensation of substituted benzaldehydes with acetone, both lead to the conclusion that the formation of 4-hydroxy-4-phenylbutan-2-one is the rate-determining step. The ϱ constant decreases with increasing temperature and the estimated isokinetic temperature corresponds to 449 ± 8 K. At temperatures ranging from 60 to 90°C, the retroaldolisation of the above β-hydroxy ketone is the minor and the dehydration of the β-hydroxy ketone the major reaction; the proportion of the dehydration reaction increases with increasing polarity of the reaction medium and decreases with increasing temperature. In the benzaldehyde condensation with methyl ethyl ketone at 90—160°C, the formation of 1-phenyl-1-penten-3-one, which is catalysed by basic sites of aluminium oxide, is the favoured reaction. The apparent activation energy for the reaction producing the latter ketone is c. 11.5 kJ mol^{-1} larger than that for the formation of 4-phenyl-3-methyl-3-buten-2-one resulting from the condensation catalysed by acidic sites of the catalyst.

The aldol condensation of aldehydes and ketones has been a subject of a great number of studies and is well documented[1]. Nevertheless, the data on the kinetics and reaction mechanism are still incomplete and frequently contradictory. In the heterogeneous condensation reactions catalysed by metal oxides[2,3] the situation is further complicated by the presence of acidic as well as basic sites on the catalyst surface and by the relatively low basicity of the active sites contrasting with a generally high basicity of homogeneous catalysts. A relatively well explored reaction is the Claisen–Schmidt homogeneous condensation of benzaldehyde with various ketones[4–9]. The kinetics of the benzaldehyde condensation with acetone catalysed by hydroxide ion were reported by Nikitin[4] to be second order in benzaldehyde in the presence of an excess of acetone and first order in acetone in an excess of benzaldehyde. Gettler and Hammett[5] have found that the condensation of benzaldehyde with an excess of methyl ethyl ketone in aqueous dioxane is first order both in aldehyde and ketone and half order in the hydroxide ion. Noyce and Reed[9] have found the condensation of benzaldehyde with acetone in aqueous sodium hydroxide solutions to be first order each in aldehyde, ketone and hydroxide ion; the base catalysed condensation of substituted benzaldehydes with acetophenone, 2-hydroxy-4-methoxypropiophenone[6] or cyclohexanone[7] in aqueous ethanol obeyed the same rate law. The base catalysed reaction of benzalde-

hyde with methyl ethyl ketone is known to produce nearly exclusively 1-phenyl-1-penten-3-one (*III*); on the other hand, the product of the acid catalysed reaction is only 4-phenyl-3-methyl-3--buten-2-one (*IV*) (refs[5,8,9]). The kinetic results led to the conclusion that in alkaline solutions the methyl as well as the methylene group in methyl ethyl ketone participates in the reverse reaction forming β-hydroxy ketones *I* and *II*; their dehydration is the slow step and thus the relative rates of formation of the unsaturated ketones *III* and *IV* determine the product composition. In a solution of a strong acid both β-hydroxy ketones *I* and *II* undergo a rapid dehydration and the selectivity of the reaction of benzaldehyde with methyl ethyl ketone is given by the relative rates of formation of β-hydroxy ketones[9,10]. The base catalysed dehydration reaction exhibits low sensitivity toward changes in the structure of β-hydroxy ketones[9]. The acid catalysed dehydrations of substituted 1,2-diphenylethanols[11] and the acid catalysed isomerisation of substituted chalcones[12] are characterised by negative values of the Hammett reaction constants.

In continuation of our research of aldolisation reactions catalysed in solution by metal oxides[2,3], we investigated the kinetics of condensation of benzaldehyde and substituted benzaldehydes with acetone and of benzaldehyde with methyl ethyl ketone, all in the presence of aluminium oxide as the catalyst. The substituent effect determined in the former reaction was expected to provide informations on the rate-determining step. Since the homogeneous catalytic condensation of benzaldehyde with methyl ethyl ketone is known to produce the unsaturated ketones *III* and *IV* in dependence upon basicity or acidity of the reaction medium, the product composition should be in relation to the participation of basic and acidic sites of the catalyst in the aluminium oxide catalysed condensation reaction.
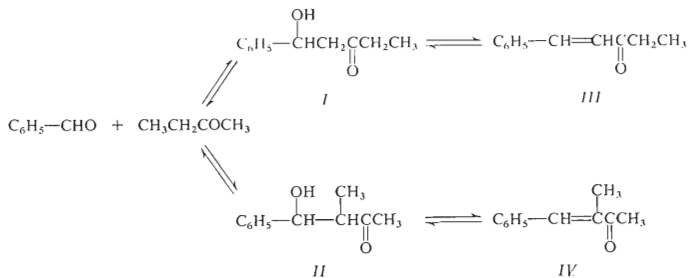
SCHEME 1

EXPERIMENTAL

Chemicals. Acetone (Lachema, Brno), methyl ethyl ketone (Reanal, Budapest, Hungary) and benzaldehyde (Lachema) were purified by rectification before use, the latter in an atmosphere of nitrogen. Substituted benzaldehydes (Koch-Light Ltd., Colnbrook, Great Britain), all pure chemicals, were used without further purification. 1-Phenyl-1-penten-3-one (*III*), 4-phenyl-3-

-methyl-3-buten-2-one (*IV*), 4-hydroxy-4-phenylbutan-2-one (*V*) and 4-phenyl-3-buten-2-one were obtained according to known procedures[9,13]. The purity of all compounds was checked by gas chromatographic analysis.

Catalysts. Three samples of aluminium oxide were prepared. Ammonium hydroxide was added to an aluminium nitrate solution and the precipitated aluminium hydroxide was calcined at 450°C (catalyst X_1). Aluminium oxide for chromatography, Brockmann's II-Neutral (Reanal), was calcined at 450°C (catalyst X_2) and 650°C (catalyst X_3). Catalyst samples with a particle size 40 μm were used for the measurements. The specific surface of the catalysts was measured by the BET method (error ∼5%). The specific surface basicity was determined by using a method reported earlier[14]. The properties of catalysts are summarised in Table I.

Kinetic measurements. Kinetics of the benzaldehyde condensation with acetone and the molar ratio of the ketone *III* to the ketone *IV* in the product of the benzaldehyde condensation (conversion ≦10%) with methyl ethyl ketone were determined in a stirred stainless-steel reactor[15], in an atmosphere of nitrogen and under pressure of 0·2 MPa. The ratio of the initial rate of dehydration to that of retroaldolisation of the β-hydroxy ketone *V* (ketone conversion ≦10%) in heptane and dioxane was measured in a stirred 20 ml glass reactor. The ratio of the rate constants k_i/k_0 for the condensation of benzaldehyde and of substituted benzaldehydes with acetone in the presence of catalyst X_2 was determined in sealed, vibrationally stirred glass tubes. For the gas chromatographic analysis, the pairs of aldehydes were combined so as to attain a complete separation of all the components present in the reaction mixture and of the internal standard (tetradecane, hexadecane and octadecane). The tube contents were analysed at time intervals corresponding to a 40—60% aldehyde conversion. All measurements were carried out in the kinetic region (>500 rev./min). The reaction temperature was maintained within ±0·5°C.

Analytical methods. The reaction mixtures were analysed by using a Chrom 4 instrument (Laboratory Instruments, Prague) which was equipped with a flame-ionisation detector and a stainless-steel column (1·5 m × 4 mm) packed with OV 17 (3%) on Gas-Chrom Q. The course of the dehydration and retroaldolisation of the β-hydroxy ketone *V* was followed by means of liquid chromatography. The liquid chromatograph[16] consisted of a column (20 cm × 4 mm) packed with Lichrosorb Si 60 silica gel (particle size 10 μm) (Merck AG., Darmstadt, FRG), a two-beam UV analyzer (254 nm) and a TZ 21S linear recorder (Laboratory Instruments). The chromatographic column was operated at a flow rate of 1·0 ml min^{-1}, inlet pressure 10 MPa and at room temperature. Heptane–diethyl ether mixture (5 : 1, v/v) was used as the mobile phase. Samples of the reaction mixtures (5 μl) were injected as 2% solutions in the mobile phase.

RESULTS AND DISCUSSION

Kinetics of the benzaldehyde condensation with excess acetone catalysed by aluminium oxide has been shown to be first order in benzaldehyde (Fig. 1). Examination of the data in Table I reveals that the specific pseudo-first order rate constants k_s appear to rise with increasing specific basicity of the catalyst. The pseudo-first order kinetics in benzaldehyde is in harmony with the presumption that the rate-determining step in the condensation reaction is the formation of 4-hydroxy-4-phenylbutan-2-one (*V*); acetone in excess is adsorbed on basic sites of the catalyst surface and reacts with benzaldehyde present in the liquid phase. This conception is consistent with the reaction mechanism suggested earlier for the homogeneous, base catalysed reaction[9,10].

Starting from the general equations (A) and (B):

$$R + L_B \rightleftharpoons RL_B \qquad (A)$$

$$RL_B + Q \rightleftharpoons \text{Products}, \qquad (B)$$

where R denotes acetone, Q benzaldehyde and L_B basic sites of the catalyst surface, one can derive the kinetic equation (1) of the Langmuir–Hinshelwood type[17].

$$-d[Q]/dt = \{k_0 K_R[R] [L_B]/(1 + K_R[R])\} [Q] = k_{exp}[Q] , \qquad (1)$$

where K_R is the equilibrium adsorption coefficient for acetone, k_0 the rate constant for the formation of β-hydroxyketone V and k_{exp} the experimentally determined pseudo-first order rate constant for the reaction of benzaldehyde with acetone. The time dependence of concentration of a substituted benzaldehyde in the pseudo-first order reaction with acetone can be described by Eq. (2):

$$c/c_0 = e^{-k_{exp}t} , \qquad (2)$$

where c is the aldehyde concentration at time t, c_0 the initial concentration and k_{exp} the pseudo-first order rate constant. A simple modification of Eqs (1) and (2) for a pair of benzaldehyde and a substituted benzaldehyde leads to Eq. (3):

$$k_i/k_0 = \ln (c/c_0)_i/\ln (c/c_0)_0 , \qquad (3)$$

TABLE 1

Specific Surface S ($m^2 g^{-1}$) and Specific Basicity B_s (mol m^{-2}) of Samples of Aluminium Oxide, Pseudo-First Order Rate Constants k_{exp} (l h^{-1} kg_{cat}^{-1}) and Specific Pseudo-First Order Rate Constants k_s (l h^{-1} m_{cat}^{-2}) for the Condensation of Benzaldehyde (Q) with Acetone Catalysed by Aluminium Oxide

$[Q]_0 = 0·2$ mol l^{-1}; $[Al_2O_3] = 50$ g l^{-1}; temperature 100°C.

Aluminium oxide	S	$B_s{}^a$	k_{exp}	$k_s . 10^2$ ^{a}
X_1	220 ± 11	$1·37 \pm 0·07$	$14·10 \pm 0·14$	$6·4 \pm 0·3$
X_2	82 ± 4	$1·46 \pm 0·07$	$7·90 \pm 0·10$	$9·6 \pm 0·5$
X_3	76 ± 4	$1·58 \pm 0·08$	$7·10 \pm 0·08$	$9·4 \pm 0·5$

^{a} Refers to an unity of the specific surface of catalysts.

where k_i is the rate constant for the reaction of a substituted aldehyde with excess acetone. The Eq. (3) makes it possible to determine the rate constant ratio k_i/k_0 which is independent of K_R, $[R]$ and $[L_B]$. Values of k_i/k_0 for the condensation of substituted benzaldehydes with excess acetone catalysed by aluminium oxide (catalyst X_2) were determined by the method of competition reactions in the range of temperatures of $90-140°C$ and were summarised in Table II. The linear relationship (Fig. 2) between the logarithms of k_i/k_0 (Table II) and the σ constants (ref.[18]), which was determined at $90°C$, gave the reaction constant ϱ equalling to 1.43 ± 0.08 (correlation coefficient $r = 0.9942$); the value of the ϱ constant is indicative of a reaction facilitated by a low electron density at the reaction center. In accordance with the expectation[6,7,19], the ϱ constant decreases with increasing temperature (Fig. 2) and at 120 and $140°C$ its value corresponds to 0.80 ± 0.03 ($r = 0.9910$) and 0.56 ± 0.00 ($r = 0.9933$), respectively. The positive values of the reaction constant support the assumption that in the aluminium oxide catalysed reaction of benzaldehyde with acetone and in this range of temperatures the base catalysed formation of the β-hydroxy ketone V is the rate-determining step. As has been found earlier, both the homo-
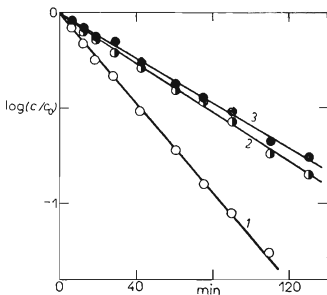

Fig. 1

Condensation of Benzaldehyde (Q) with Excess Acetone Catalysed by Aluminium Oxide (X_i)

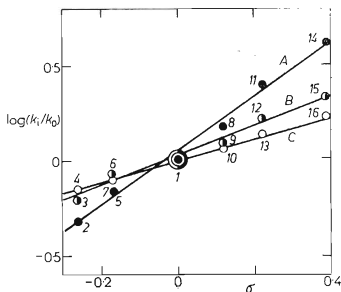$[Q]_0 = 0.2$ mol l^{-1}; $[X_i] = 50$ g l^{-1}; temperature $100°C$; 1 X_1, 2 X_2, 3 X_3.

Fig. 2

Hammett Plot for the Condensation of Benzaldehyde (1) and p-Methoxy- (2, 3, 4), p-Methyl- (5, 6, 7), m-Methoxy- (8, 9, 10), p-Chloro- (11, 12, 13) and m-Chloro- (14, 15, 16) Substituted Benzaldehydes with Acetone Catalysed by Aluminium Oxide (X_2) at $90°C$ (A), $120°C$ (B) and $140°C$ (C)

TABLE II

Temperature Dependence of the Rate Constant Ratios k_i/k_0 for the Condensation of Benzaldehyde and Substituted Benzaldehydes with Acetone Catalysed by Aluminium Oxide (X_2)

Substituent	k_i/k_0		
	90°C	120°C	140°C
p-Methoxy	0·49	0·63	0·72
p-Methyl	0·70	0·85	0·82
H	1·00	1·00	1·00
m-Methoxy	1·53	1·24	1·19
p-Chloro	2·54	1·69	1·27
m-Chloro	4·14	2·13	1·71

TABLE III

Ratios of the Initial Rates of Dehydration (r_o^d) and Retroaldolisation (r_o^r) of 4-Hydroxy-4-phenylbutan-2-one (V) Catalysed by Aluminium Oxide in Heptane and Dioxane at Various Temperatures
$[V]_0 = 0·2\ \text{mol}\,l^{-1}$; $[Al_2O_3] = 50\ \text{g}\,l^{-1}$.

Aluminium oxide	r_o^d/r_o^r at					
	60°C		75°C		90°C	
	heptane	dioxane	heptane	dioxane	heptane	dioxane
X_1	5·5	12·6	2·8	6·4	1·8	4·5
X_2	4·4	10·7	2·7	5·5	1·7	3·4
X_3	4·0	10·2	2·1	3·1	1·4	2·9

TABLE IV

Molar Ratio (MR) of 1-Phenyl-1-penten-3-one (III) to 4-Phenyl-3-methyl-3-buten-2-one (IV) in the Product of Condensation of Benzaldehyde (Q) with Methyl Ethyl Ketone Catalysed by Aluminium Oxide at Various Temperatures
$[Q]_0 = 0·2\ \text{mol}\,l^{-1}$; $[Al_2O_3] = 50\ \text{g}\,l^{-1}$.

Aluminium oxide	MR at			
	90°C	120°C	140°C	160°C
X_1	1·9	2·5	3·0	3·6
X_2	2·0	2·7	3·1	3·9
X_3	2·9	3·5	4·0	5·1

geneous acid catalysed aldolisation reaction and aldol dehydration are characterised by a negative value of the ϱ constant; moreover, the homogeneous base catalysed aldol dehydration is insensitive to the change in the aldol structure[8,9].

From the linear dependence of the ϱ constant on the reciprocal of the absolute temperature[19,20], the isokinetic temperature for the condensation of substituted benzaldehydes with acetone in the presence of aluminium oxide as the catalyst was estimated as 449 ± 8 K ($r = 0.9948$); this value is very near to that found by Kandlikar and coworkers[6,7] for the homogeneous base catalysed condensation of substituted benzaldehydes with acetophenone ($\beta = 455$ K) and cyclohexanone ($\beta = 430$ K).

The condensation of benzaldehyde with acetone has been described as a system of two consecutive reversible reactions in which the β-hydroxy ketone V is the intermediate[9,21,22]. A critical look at the initial rate ratios of dehydration (r_0^d) and retroaldolisation (r_0^r) of the ketone V (conversion $\leqq 10\%$) in heptane and dioxane and in the presence of aluminium oxide as the catalyst (Table III) shows that at temperatures ranging from 60 to 90°C the dehydration is the favoured reaction; its proportion increases at the expense of the retroaldolisation reaction as the polarity of the reaction medium is increased and decreases with increasing temperature. These relations are affected to some extent also by conditions chosen for the catalyst preparation (Table III). At temperatures higher than 140°C, the dehydration of ketone V, which proceeds at basic as well as acidic sites of the catalyst, can become the rate-determining step.

The benzaldehyde condensation with excess methyl ethyl ketone catalysed by aluminium oxide was investigated in the range of temperatures of 90—160°C. The molar ratios (MR) of 1-phenyl-1-penten-3-one (III) to 4-phenyl-3-methyl-3-buten-2-one (IV) (Scheme 1) in the product obtained after 10% conversion of benzaldehyde at various temperatures and using various kinds of aluminium oxide are given in Table IV. The results show that the predominating reaction is always the condensation reaction catalysed by basic sites on the aluminium oxide surface and leading to the ketone III; the minor reaction is the formation of ketone IV catalysed by acidic sites on the catalyst surface. The proportion of the former reaction (65—74% mol. of ketone III at 90°C) rises with increasing temperature and at 160°C it corresponds to 78—84% mol. of ketone III in the reaction product. At higher temperatures, the course of the condensation reaction catalysed by aluminium oxide therefore resembles still more the homogeneous base catalysed reaction. From the dependence of the logarithm of MR on the reciprocal of the absolute temperature it follows that the apparent activation energy for the formation of ketone III ($\Delta\Delta E$) is c. 11·5 kJ mol⁻¹ larger than that for the reaction producing the ketone IV. The differences in $\Delta\Delta E$ for different samples of the catalyst are statistically unimportant.

To summarise, it can be concluded that in the presence of aluminium oxide the condensation of benzaldehyde with acetone and methyl ethyl ketone is catalysed

first of all by the basic sites of the catalyst. The reaction course, which exhibits a strong analogy with the homogeneous base catalysed condensation reaction, is significantly affected by temperature and by polarity of the reaction medium.

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