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KINETICS OF THE TISCHENKO REACTION OF ACETALDEHYDE WITH ALUMINIUM ISOPROPOXIDE[1]

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Abstract—The products of the Tischenko reaction of acetaldehyde with aluminium isopropoxide in benzene at 20° are ethyl acetate and a small amount of isopropyl acetate. The formation of the latter may be ascribed to the transfer of alkoxide ion from catalyst to aldehyde in the transition state. The rate law is first-order in aldehyde and first-order in catalyst. The mechanism involving the transfer of alkoxide and then of hydride ions is discussed.

THE action of metal alkoxide on aldehyde to form ester was first studied by Tischenko, who applied this reaction to a number of aliphatic and aromatic aldehydes.[2] The structural effect of aldehydes or catalysts on the conversion as well as the effect of solvents has been reported.[3] The addition of a small amount of water or alcohol results in a marked decrease in rate, while some metal chlorides act as promotors. Mixed esters are obtained by using a mixture of different aldehydes, where the aldehyde coordinating more easily to catalyst tends to constitute, after completion of the reaction, the acidic side of the esters produced.[4]

The kinetics of the Tischenko reaction have been studied to a limited extent only and there seem to be two possible mechanisms. One involves the preliminary addition of the free aldehyde oxygen atom to the carbonyl carbon atom of the coordinated aldehyde (mechanism A), and the other involves the preliminary shift of alkoxide ion to the coordinated carbonyl carbon atom (mechanism B). Both preliminary steps are followed by the transfer of hydride ion.

The present study on the kinetics of the condensation of acetaldehyde catalysed by aluminium isopropoxide, provides further information on the mechanism.

RESULTS AND DISCUSSION

Isopropyl acetate as well as ethyl acetate are products in the aluminium isopropoxide-catalysed condensation of acetaldehyde. It is apparent from the Table 1 that the initial rate of the formation of isopropyl acetate is faster than that of ethyl acetate with high catalyst concentration, e.g., above 5 mole % of acetaldehyde. A similar result was obtained on the kinetic runs in benzene.

Tischenko[2] found that both ethyl and methyl formates were formed on the treatment of paraformaldehyde with aluminium ethoxide. In addition, mixed esters having

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[1] Contribution No. 88.

[2] V. E. Tischenko, *J. Russ. Phys. Chem. Soc.* **38**, 355, 482 (1906).

[3] W. C. Child and H. Adkins, *J. Amer. Chem. Soc.* **45**, 3013 (1923); **47**, 798 (1925).

[4] [a] I. Lin and A. R. Day, *J. Amer. Chem. Soc.* **74**, 5133 (1943); [b] K. Kasano and T. Takahashi, *J. Soc. Org. Synth. Chem. Japan* **23**, 144 (1965).

TABLE 1. THE CONVERSION OF ACETALDEHYDE (ca. 1·4M) TO ISOPROPYL AND ETHYL ACETATES WITH ALUMINIUM ISOPROPOXIDE (ca. 0·07M) IN n-HEXANE AT 20°

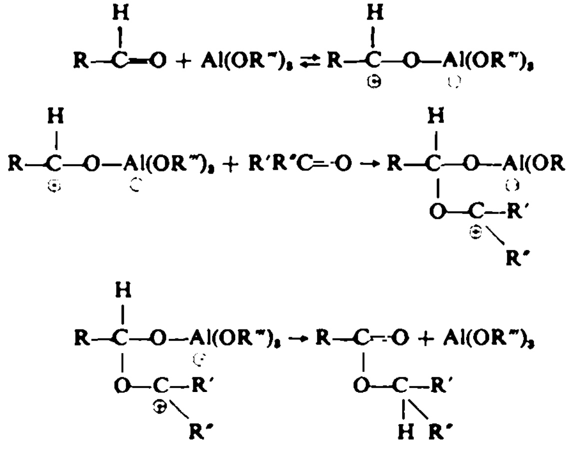
Time (min)	AcO·i-Pr (M)	AcOEt (M)
2	ca. 0·01	none
5	0·025	0·015
10	0·045	0·07
30	0·07	0·13
40	0·09	0·155
60	0·10	0·18
90	0·115	0·225

alkoxide or acyl groups derived from the alkoxide group of catalyst were observed besides simple esters in the following system:[4b] butyraldehyde with aluminium ethoxide forms ethyl acetate, ethyl butyrate, butyl acetate and butyl butyrate. These facts may be explained in terms of the alkoxide ion transfer during the condensation, i.e., mechanism B.

Another explanation for the formation of mixed ersters is the transesterification between simple ester and catalyst, or the crossed Tischenko reaction (mechanism A) between aldehyde and carbonyl compound derived from catalyst, i.e., by the Meerwein-Ponndorf-Verley-Oppenauer (MPVO) reaction, which, in the present study, occurs as a side reaction.

The reaction between n-butyraldehyde and 1,3-dichloroacetone giving dichloroisopropyl acetate made Lin[4a] suggest mechanism A:

Mechanism A



(1)

(2)

(3)

(R:n-Pr; R',R'':CH_2Cl)

This mechanism involves the preliminary complex formation (step 1), followed by the addition of aldehyde (or ketone) oxygen atom to the carbonium ion of the complex (step 2) and then the hydride transfer.

In order to obtain more definite evidence for the mechanism, a series of experiments were carried out and the results may be summarized as follows: (i) No transesterification was observed with a mixture of ethyl acetate and aluminium isopropoxide.

(ii) No increase in the amount of isopropyl acetate was observed on addition of acetone to a mixture of acetaldehyde and isopropoxide. (iii) No isopropyl acetate was formed by addition of acetone to a mixture of acetaldehyde and aluminium t-butoxide. These results indicate that the isopropoxide group directly moves from catalyst to coordinated aldehyde (mechanism B), and exclude mechanism A.

The reported observation[4a] can be explained by the equilibrium between ketone and alkoxide:

$$Al(OCHMe_2)_3 + O{=}C(CH_2Cl)_2 \leftrightarrows Al[OCH(CH_2Cl)_2](OCHMe_2) + O{=}CMe_2$$

From a report[5] on the MPVO reaction of methyl ketones, it may be predicted that the above equilibrium is favourably shifted to the right.

However, with a mixture of acetaldehyde and aluminium t-butoxide, no t-butyl acetate was observed. This is probably due to a change of mechanism since aluminium t-butoxide, behaves differently from isopropoxide in the reaction with diamine.[6]

As the reaction proceeds, the total concentration of unchanged acetaldehyde and of esters produced decreases gradually owing to side reactions. The decrease, however, was within 10% of the conversion of acetaldehyde, and it was negligible during early stages of the reaction. The plot of the conversion *vs* time shows an initial retardation followed by the first-order kinetics with respect to aldehyde. The calculated kinetic data are shown in Table 2. The pseudo-first-order rate coefficient (k_1), however, increased slightly by increasing the initial concentration of acetaldehyde. These observations may be due to the small contribution of another factor in a more complicated rate law.

TABLE 2. THE EFFECT OF INITIAL ACETALDEHYDE CONCENTRATION ON THE RATE OF CONDENSATION WITH ALUMINIUM ISOPROPOXIDE (0·039M) IN BENZENE AT 20°

$[CH_3CHO]$ (M)	$10^4\,k_1$ (sec^{-1})
1·55	2·76
1·44	2·15
1·14	2·41
1·04	2·03
1·00	1·92
0·92	2·15
0·78	2·15
0·70	1·69
0·63	1·57
0·43	1·38

The effect of catalyst at acetaldehyde concentration of ca. 1·0M is shown in Fig. 1. Here, the first-order dependence on aluminium isopropoxide is indicated. The rate may be written:

$$v = k[\text{acetaldehyde}][\text{aluminium isopropoxide}]$$

The second-order rate coefficient k was found to be $8{\cdot}7 \times 10^{-3}$ l. mole^{-1} sec^{-1}.

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[5] B. J. Yager and C. K. Hancock, *J. Org. Chem.* **30**, 1174 (1965).

[6] V. J. Shiner, Jr. and D. Whittaker, *J. Amer. Chem. Soc.* **87**, 843 (1965).

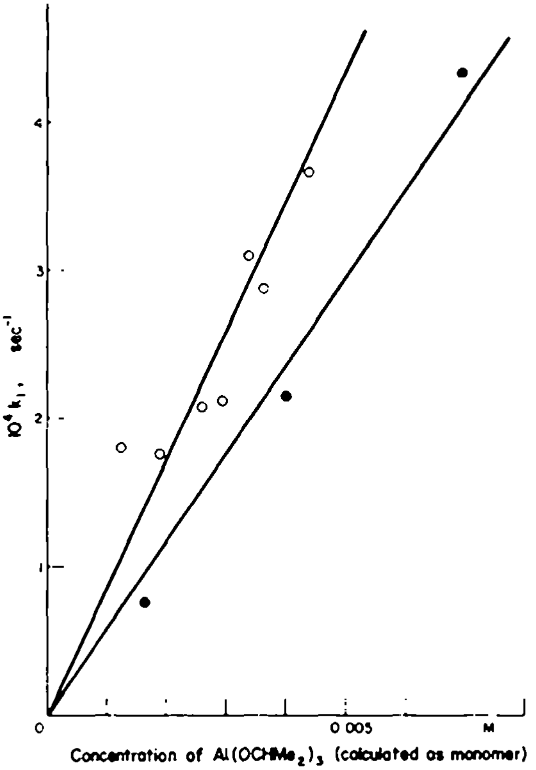

Fig. 1 The effect of the concentration of aluminium isopropoxide on the first-order rate constant for the condensation of acetaldehyde (ca. 1·0M) in benzene at 20°. ○, tetramer; ●, trimer.

It was recently reported[7] that aluminium isopropoxide exists as a tetramer in a number of organic solvents. It is converted on melting into a cyclic trimer which only slowly reverts to the tetramer in these solutions. Hence, the rate of the condensation of aldehyde was measured using a benzene solution of aluminium isopropoxide which had been melted at 140° before dissolution. Figure 1 indicates that the rate law for trimeric aluminium isopropoxide is almost identical with that for the tetramer, but the rate coefficient is somewhat smaller, i.e., $k = 5{\cdot}9 \times 10^{-2}$ l. $mole^{-1}$ sec^{-1}. The same first-order dependence both on tetramer and trimer suggests that the true active species may be these associated catalysts.

The kinetic result of the isopropoxide-catalysed condensation of acetaldehyde together with the product study support the mechanism B.

Steps 4 and 6 involve the coordination of aldehyde to aluminium alkoxide. Step 5 is the transfer of alkoxide ion from catalyst to the carbonyl carbon atom of aldehyde. The hydride transfer occurs in step 7, where catalyst is regenerated.

The second-order rate law requires that the rate-controlling step must be step 4 or 5 in the mechanism B or step 1 in the mechanism A. The coordination of aldehyde to catalyst, however, has been considered to be fast equilibrium;[6] hence the mechanism B with rate-determining step of 5 is preferable.

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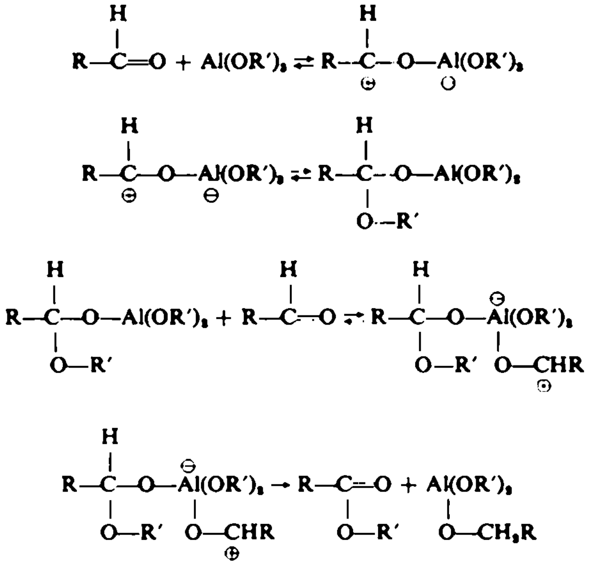
[7] V. J. Shiner, Jr., D. Whittaker and V. P. Fernandez, *J. Amer. Chem. Soc.* **85**, 2318 (1963).

Mechanism B



$$R-\overset{\overset{H}{|}}{C}=O + Al(OR')_3 \rightleftarrows R-\underset{\oplus}{\overset{\overset{H}{|}}{C}}-O-\underset{\ominus}{Al}(OR')_3 \quad (4)$$

$$R-\underset{\oplus}{\overset{\overset{H}{|}}{C}}-O-\underset{\ominus}{Al}(OR')_3 \rightleftarrows R-\underset{\underset{O-R'}{|}}{\overset{\overset{H}{|}}{C}}-O-Al(OR')_2 \quad (5)$$

$$R-\underset{\underset{O-R'}{|}}{\overset{\overset{H}{|}}{C}}-O-Al(OR')_2 + R-\overset{\overset{H}{|}}{C}=O \rightleftarrows R-\underset{\underset{O-R'}{|}}{\overset{\overset{H}{|}}{C}}-O-\underset{\underset{O-\underset{\oplus}{CHR}}{|}}{\overset{\ominus}{Al}}(OR')_2 \quad (6)$$

$$R-\underset{\underset{O-R'}{|}}{\overset{\overset{H}{|}}{C}}-O-\underset{\underset{O-\underset{\oplus}{CHR}}{|}}{\overset{\ominus}{Al}}(OR')_2 \rightarrow R-\underset{\underset{O-R'}{|}}{C}=O + \underset{\underset{O-CH_2R}{|}}{Al}(OR')_2 \quad (7)$$

($R:CH_3$; $R':CHMe_2$)

EXPERIMENTAL

Materials. Acetaldehyde was prepared from paraldehyde. Paraldehyde was decomposed by H_2SO_4, acetaldehyde being distilled through a Widmer column. Distilling acetaldehyde was passed through a tube of 15 cm long filled with $CaCl_2$ and then condensed. It was redistilled; b.p. 20·5–21·5°.

The aluminium isopropoxide prepared,[8] had b.p. 123–129° (3·5 mm). The aluminium t-butoxide[9] was purified by recrystallization from benzene after extraction with ether, instead of centrifuging.

The solvent and the standard samples of the gas chromatography analysis were purchased from commercial sources or prepared by standard methods. These were purified by distillation through a Widmer column, after being dried over $CaCl_2$ or Na_2SO_4, except benzene which was distilled over Na.

Analytical procedure

Procedure I. Six experiments (0·8–1·7M acetaldehyde, 0·05–0·15M aluminium isopropoxide) in either n-hexane or CCl_4 (ca. 100 ml) were carried out in 300 ml flasks thermostated in a water bath at 20·0 ± 0·05°.

At regular intervals of time, an aliquot (10 ml) was pippeted out, and 6N HCl (5 ml) added to decompose the catalyst. The mixture was then filtered through a glass-filter, and the organic layer dried over Na_2SO_4. It was analysed by gas chromatography, and the concentration of AcOEt and isopropyl acetate were determined from the area ratio of each peak to solvent peak.

Procedure 2. The kinetic runs in a benzene soln were carried out in 20 ml flasks at 20·0 ± 0·05°. The reaction mixture was taken into the syringe through a packing of silicone rubber and injected directly into the gas chromatograph. The direct injection did not spoil the analysis. The peaks of the following substances were observed: acetaldehyde, EtOH, acetone, isopropanol, AcOEt, isopropyl acetate and benzene. It was apparent that the MPVO reaction occured, but the amount of isopropanol, probably derived from the hydrolysis of catalyst, was so small that it was negligible.

The experiments involving acetone or AcOEt were studied under similar conditions.

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[8] H. Adkins, *J. Amer. Chem. Soc.* **44**, 2175 (1922).

[9] W. Wayne and H. Adkins, *Organic Syntheses* Coll. Vol. **III**, 48 (1955).

The concentration of acetaldehyde and esters were calculated from the ratio of the height of the peaks, using the solvent as an internal standard for convenience. The error of the analysis was ±3%. The following column conditions were selected:

Procedure	Column	Carrier gas	Temp
I	silicone 703 (5 mm × 2 m)	He 25 ml/min	75°
II	DOP (5 mm × 2 m)	H_2 20 ml/min	76°

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