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THE PROMOTING EFFECT OF CARBOXYLIC ACIDS AND ANHYDRIDES ON THE TISHCHENKO REACTION OF BENZALDEHYDE*

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Abstract—The effect of carboxylic acids and anhydrides on the Tishchenko reaction of benzaldehyde with aluminum benzyloxide have been studied kinetically by means of GLC. Acetic and benzoic acids and their anhydrides promote the reaction, but sulfonic acids, benzyl alcohol, water, sodium carboxylates do not. The rates vary with molar ratio of promoters *vs* aluminum benzyloxide and the corrected molar ratio of these promoters *vs* aluminum benzyloxide at maximum rate is *ca.* unity. Aluminum alkoxide undergoes dealkoxycarboxylation to give benzyl alcohol or benzyl carboxylates by carboxylic acids or anhydrides, respectively. Dialkoxyaluminum carboxylate is probably an active catalyst for the hydride transfer step.

IT HAS been reported that Lewis acids such as ferric, aluminum, zinc, cupric and mercuric chlorides promote the Tishchenko reaction by the complex formation with aluminum alkoxide in a molar ratio of 1:3 or 1:2, while water and alcohol retard the reaction.[1] Careful purification of aldehyde has been recommended, but the effect of carboxylic acid or anhydride on the reaction has not been described.[2]

During the course of our study on the Tishchenko reaction[3, 4] with aluminum benzyloxide or t-butoxide, impure benzaldehyde was found to react much faster than purified benzaldehyde. This anomaly is due to the promoting effect of contaminative benzoic acid on the Tishchenko reaction.

The present study was undertaken to clarify the promotion by carboxylic acids and anhydrides, which implies formation of dialkoxy-aluminum carboxylate from aluminum alkoxide by carboxylic acid or anhydride, which is a more active catalyst.

$$2\,PhCHO \xrightarrow{Al(OCH_2Ph)_3} PhCO_2CH_2Ph \qquad (1)$$

RESULTS AND DISCUSSION

The aluminum benzyloxide-catalyzed reaction of benzaldehyde gives benzyl benzoate quantitatively and a small amount of benzyl alcohol. The reaction is second-order in benzaldehyde as reported previously.[4]

The reaction with impure benzaldehyde. Since aluminum t-butoxide-catalyzed Tishchenko reaction of benzaldehyde has a long induction period (15–20 hr),[4] aluminum benzyloxide alone or a mixture of aluminum t-butoxide and benzyloxide was used as a catalyst. The reaction was relatively slow with benzaldehyde, but it was

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faster with impure benzaldehyde, and a small amount of precipitate was observed. When pure benzaldehyde was used in the presence of a small amount of benzoic acid, the reaction was much faster with formation of a small amount of precipitate. Therefore, benzoic acid contained in impure benzaldehyde promotes the reaction. In support of this, the reaction in air is fast even with pure benzaldehyde.

The effect of various acids. To clarify the effect of benzoic acid, the effect of various acids and their derivatives was studied, the results being shown in Table 1.

TABLE 1. THE EFFECT OF ADDITIVES ON THE TISHCHENKO REACTION OF BENZALDEHYDE IN BENZENE AT 20°[a]

Additive	Concentration[b], M	Conversion[c], %
Benzoic acid	0·023	73·7
Acetic acid	0·024	75·0
p-Nitrophenol	0·036	31·0
Phenol	0·071	<5·0
p-Toluenesulfonic acid	(0·038)	8·0
2,4-Dimethylbenzenesulfonic acid	(0·038)	4·5
Sulfamic acid	(0·034)	6·5
Benzyl alcohol	0·034	<5·0
Water	0·037	<5·0
Sodium benzoate	(0·030)	4·0
Sodium acetate	(0·033)	5·5
None	—	5·7
Acetic anhydride[d]	0·031	80·5[e]
Benzoic anhydride[d]	0·025	56·8

[a] Initial concns.: [benzaldehyde] = 1·40 M; [aluminum benzyloxide] = 0·029 M; [aluminum t-butoxide] = 0·029 M.

[b] Brackets mean that additives do not dissolve completely.

[c] Formation of benzyl benzoate at 100 min.

[d] Aluminum benzyloxide alone (0·057 M) was used.

[e] Formation of benzyl benzoate at 50 min.

As apparent from the Table, benzoic and acetic acids as well as their anhydrides show a strong promoting effect, while their sodium salts, strong acids (e.g., sulfonic acids) and very weak acids (e.g., phenol, water and benzyl alcohol) have substantially no effect. *p*-Nitrophenol shows also a weak promoting effect. These facts suggest that the promoting effect of benzoic acid is other than that of an acid.

The relationship between the promoting effect and the molar ratio of promoter vs. *aluminum alkoxide.* At constant concentration of aluminum alkoxide, the rate constant increases at first with increasing concentration of promoter, but excess promoter gradually decreases the rate constant with increasing concentration of promoter. Therefore, the optimum ratio of promoter *vs.* catalyst exists as shown in Fig. 1 and Table 2.

The observed ratio of the maximum rate with acetic anhydride is ca. 0·46. Analogous values were also obtained with the other promoters (Table 2). Aluminum tribenzyloxide, however, may in part undergo hydrolysis by a trace of water contained in

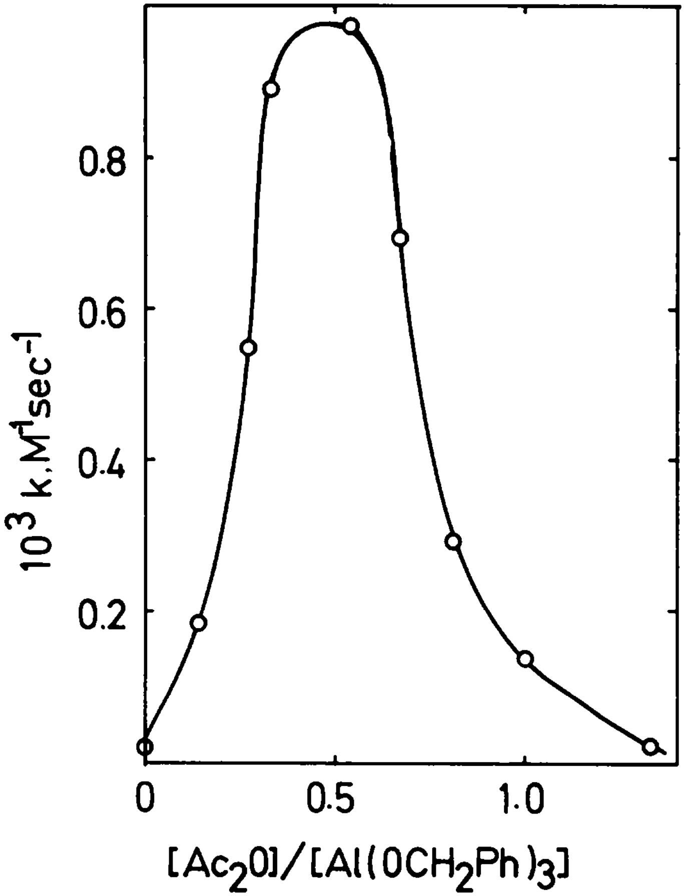


FIG. 1 The effect of acetic anhydride on the Tishchenko reaction of benzaldehyde in benzene at 20°.
Initial concn.: [PhCHO] = 1·40 M; $[Al(OCH_2Ph)_3]$ = 0·057 M

TABLE 2. THE OBSERVED MOLAR RATIO OF PROMOTERS VS. ALUMINIUM BENZYLOXIDE AT MAXIMUM RATE OF REACTION

Promoter	$Al(OCH_2Ph)_3$ M	Apparent Molar Ratio[a] at Maximum Rate	Corrected Molar Ratio[b]
Acetic anhydride	0·031	0·42	0·93
	0·057	0·46	1·02
	0·057	0·40	0·89
Acetic acid	0·031	0·55	1·22
Benzoic anhydride	0·057	0·44	0·98
Benzoic acid	0·031	0·43	0·96

[a] $[Promoter]/[Al(OCH_2Ph)_3]_{added}$.

[b] "Normal" aluminum benzyloxide is 45% of the added benzyloxide.

solvent benzene. In fact, GLC analysis of a benzene solution of aluminum benzyloxide shows the presence of benzyl alcohol (55% on the basis of aluminum alkoxide) under the reaction conditions, i.e., only 45% of the added alkoxide may exist as "normal" benzyloxide, $Al(OCH_2Ph)_3$, because of low concentration of the added alkoxide. If the correction is made for the alkoxide, the molar ratio of the acetic anhydride *vs.* the alkoxide at maximum rate becomes 0·46/0·45 = 1·02. Therefore, addition of equimolar acetic anhydride to the "normal" alkoxide is recommended. The molar ratios for the other promoters are nearly unity (Table 2) independent of promoters. These facts indicate the reaction is catalyzed by the combination of each one mole of promoters and aluminum alkoxides.

Reaction of aluminum alkoxide with carboxylic acids or anhydrides. The reaction products of aluminum benzyloxide with carboxylic acids and their anhydrides at room temperature in benzene have been studied. As apparent from Table 3, the reaction of aluminum benzyloxide and carboxylic acid gives benzyl alcohol (67–92%) and a little benzyl carboxylate (15–24%) (Eq. 2), while the reaction of aluminum benzyl oxide and carboxylic anhydride gives benzyl carboxylate (above 89%) and a little benzyl alcohol (3–6%) (Eq. 3). A small amount of free benzyl alcohol involved in the solution also reacts with carboxylic acids or anhydrides, but the reaction of benzyl alcohol is only to a small extent even in the presence of aluminum t-butoxide catalyst, compared with the reactions of aluminum benzyloxide (Eqs 2 and 3).

TABLE 3. REACTION OF ALUMINIUM BENZYLOXIDE WITH PROMOTERS IN BENZENE AT 20°[a]

Promoter	Concentration M	Products[b], M		
		$PhCH_2OH$	$PhCO_2CH_2Ph$	$CH_3CO_2CH_2Ph$
$PhCO_2H$	0·072	0·066	0·011	—
CH_3CO_2H	0·100	0·067	—	0·024
$(PhCO)_2O$	0·072	0·004	0·064	—
$(CH_3CO)_2O$	0·076	0·002	—	0·086

[a] Initial concentration: $[Al(OCH_2Ph)_3] = 0·114$ M.

[b] Determined by GLC.

$$Al(OCH_2Ph)_3 + CH_3CO_2H \rightarrow CH_3CO_2Al(OCHPh)_2 + PhCH_2OH \tag{2}$$

$$Al(OCH_2Ph)_3 + (CH_3CO)_2O \rightarrow CH_3CO_2Al(OCH_2Ph)_2 + CH_3CO_2CH_2Ph \tag{3}$$

Analogous stepwise reactions of aluminum alkoxides have been reported.[5, 6]

$$Al(OR')_3 + (RCO)_2O \rightarrow RCO_2Al(OR')_2 + RCO_2R' \tag{4}$$

$$RCO_2Al(OR')_2 + (RCO)_2O \rightarrow (RCO_2)_2AlOR' + RCO_2R' \tag{5}$$

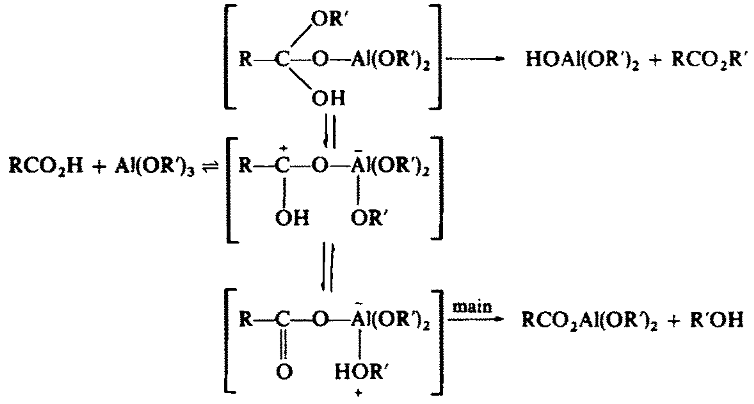
$$(RCO_2)_2AlOR' + (RCO)_2O \rightarrow (RCO_2)_3Al + RCO_2R' \tag{6}$$

Reactions 4 and 3 are easy, but Eq. 6 occurs only with difficulty.[5] If excess carboxylic acid or anhydride is used, $(RCO_2)_2AlOR'$ and $(RCO_2)_3Al$ may be formed. $(RCO_2)_3Al$

is inactive as a catalyst, since it has no alkoxide group. $(RCO_2)_2AlOR'$, which is formed by the reaction of one mole of aluminum alkoxide with two moles of promoter, is a less active catalyst in view of the molar ratio of unity at maximum rate, though it has one alkoxide group. The substitution of aluminum alkoxide by carboxylate ion does not occur because of the stronger basicity of alkoxide ion than of carboxylate ion.

Although there is no evidence, the promoting effect of $RCO_2Al(OR')_2$ is probably due to the stronger acidity of aluminum catalyst than that of $Al(OR')_3$ and/or depolymerization of the parent polymeric aluminum alkoxide to monomeric active aluminum catalyst by the reaction with promoters.

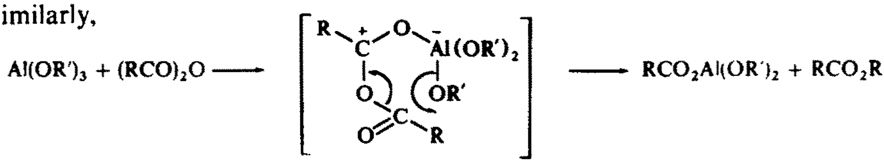
The reaction product of aluminum t-butoxide and benzoic acid. On addition of benzoic acid to aluminum t-butoxide in benzene precipitation was observed at room temperature. The IR spectrum of the precipitate is different from that of parent benzoic acid or aluminum t-butoxide, i.e., the bands at 3500–2500 cm^{-1} (ν_{OH}, broad) and 930 cm^{-1} (δ_{OH}) of benzoic acid vanish and new bands at 3600 cm^{-1} (ν_{OH}, sharp) and 1680 cm^{-1} ($\nu_{C=O}$) appear. Although the band at 1720 cm^{-1} ($\nu_{C=O}$) remains, its strength decreases. From these data together with Table 3 the precipitate is probably a mixture of $RCO_2Al(OR')_2$ and $HOAl(OR')_2$. The reaction scheme seems to be as follows:



(7)

(8)

Similarly,



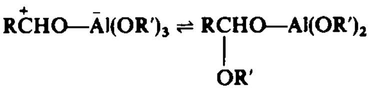
(9)

The precipitate of aluminum t-butoxide-benzoic acid mixture also promotes the aluminum benzyloxide-catalyzed reaction of benzaldehyde, which suggests dibenzyloxyaluminum benzoate formation via a following reaction.

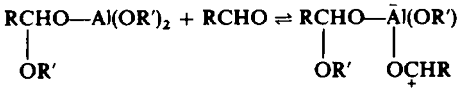
$$Al(OCH_2Ph)_3 + PhCO_2Al(O\text{-}t\text{-}Bu)_2 \rightarrow PhCO_2Al(OCH_2Ph)_2 + PhCH_2OAl(O\text{-}t\text{-}Bu)_2 \quad (10)$$

The mechanism. As reported previously,[3] the reaction involves four steps: coordination of aldehyde to aluminum alkoxide (11); alkoxide transfer (12); coordination of a second aldehyde molecule to the adduct (13); and hydride transfer (14).

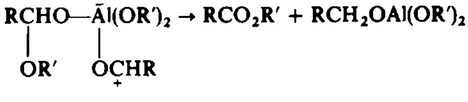
$$RCHO + Al(OR')_3 \rightleftharpoons R\overset{+}{C}HO{-}\overset{-}{Al}(OR')_3 \qquad (11)$$



$$R\overset{+}{C}HO{-}\overset{-}{Al}(OR')_3 \rightleftharpoons R\underset{\substack{|\\ OR'}}{C}HO{-}Al(OR')_2 \qquad (12)$$



$$R\underset{\substack{|\\ OR'}}{C}HO{-}Al(OR')_2 + RCHO \rightleftharpoons R\underset{\substack{|\\ OR'}}{C}HO{-}\underset{\substack{|\\ O\underset{+}{C}HR}}{\overset{-}{Al}}(OR')_2 \qquad (13)$$



$$R\underset{\substack{|\\ OR'}}{C}HO{-}\underset{\substack{|\\ O\underset{+}{C}HR}}{\overset{-}{Al}}(OR')_2 \rightarrow RCO_2R' + RCH_2OAl(OR')_2 \qquad (14)$$

The rate-determining step is an alkoxide transfer (12) for the aluminum isopropoxide-catalyzed reaction of acetaldehyde,[3] while the hydride transfer (14) determines the rate for the aluminum benzyloxide-catalyzed reaction of benzaldehyde,[4] since the latter reaction is second-order with respect to aldehyde. Therefore, the promoting effect affects mainly the hydride transfer step 14, though the equilibria 11, 12, and 13 are also affected.

EXPERIMENTAL

Materials. Commercial benzaldehyde was distilled under reduced N_2 atmosphere as described.[4] Aluminum benzyloxide and t-butoxide were prepared as described.[4] Benzene was purified by the ordinary method and dried (Na).

Rate measurements. In a typical run, benzaldehyde (2·1 g, 0·0198 moles), Ac_2O (0·01 ml, 0·000105 moles) as a promoter and 1,2-diphenylethane (0·100 g) as an internal standard for GLC were dissolved in benzene (10·0 ml) in a reaction tube. A benzene soln of aluminum benzyloxide was added at 20° and then the tube, filled with N_2 gas, was stoppered with silicone-rubber and thermostated. The reaction was followed by GLC as reported.[4] The second-order rate constant, k, was calculated from the ordinary second-order equation: $k = (1/t)[\{1/(a - 2x)\} - (1/a)]$. Here, a is the initial concentration of aldehyde and x the concentration of ester formed at time t.

The reaction of aluminum alkoxide with benzoic acid. Aluminum t-butoxide (0·5 g) was added to the soln of benzoic acid (0·5 g) in dry benzene (10 ml). The soln became viscous and gave ppt, which was washed with benzene, and dried under vacuum. The IR spectra (KBr) of benzoic acid, aluminum t-butoxide and the ppt were compared. Addition of excess NH_4OHaq to a soln of this material in conc HCl gave a ppt of $Al(OH)_3$.

The reaction of AcOH with aluminum t-butoxide also gave a very viscous soln, but no ppt was formed. The same is true for the reaction of benzoic acid with aluminum benzyloxide.

The GLC was carried out by a Yanagimoto gas chromatograph model GCG-220 and IR spectra were measured by a Perkin–Elmer grating IR spectrophotometer model 337.

REFERENCES

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

[2] I. Lin and A. R. Day, *Ibid.* **74**, 5133 (1943).

[3] Y. Ogata, A. Kawasaki and I. Kishi, *Tetrahedron* **23**, 825 (1967).

[4] Y. Ogata and A. Kawasaki, *Ibid.* **25**, 929 (1969).

[5] R. C. Mehrotra and K. C. Pande, *J. Inorg. Nuclear Chem.* **2**, 60 (1956);
K. C. Pande and R. C. Mehrotra, *Z. Anorg. Allgem. Chem.* **286**, 291 (1956).

[6] G. A. Razuvaev and L. P. Stepovik, *Zh. Obshch. Khim.* **35**, 1672 (1965); G. D. Razuvaev, L. P. Stepovik and E. V. Mitrofanova, *Ibid.* **35**, 1095 (1965); *Izv. Akad. Nauk SSSR, Ser. Khim.* 162 (1964).