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Reaction between Diethylaluminum *sec*-Butoxide and *n*-Butyraldehyde

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Reactions between diethylaluminum *s*-butoxide and *n*-butyraldehyde have been carried out at several temperatures from −65 to 40°C. The reaction mixtures were then treated with glacial acetic acid and subjected to vapor-phase chromatographic analysis (vpc). The products analyzed by vpc were methyl ethyl ketone, butanol-1, *s*-butyl *n*-butyrate, *n*-butyl *n*-butyrate, 2-ethyl-2-hexenal, and 2-ethyl-1, 3-hexanediol 1-*n*-butyrate. The last two compounds were formed only at reaction temperatures above 20°C, and methyl ethyl ketone was not formed below −40°C. The reaction of the ethylaluminum group with the aldehyde group was not observed. Finally, the interrelationship of the three reactions involving aluminum alkoxide and aldehyde, the *Meerwein-Ponndorf-Verley reduction*, the *Tishchenko reaction*, and the aldehyde polymerization, has been discussed.

The polymerization of aldehyde⁽¹⁾ by metal alkyl and metal alkoxide catalysts has been found by Natta *et al.*,⁽²⁾ by Vogl,⁽³⁾ and by the present authors.⁽⁴,⁵⁾ In our studies of the initiation mechanism of acetaldehyde polymerization by triethylaluminum, we have shown that diethylaluminum *s*-butoxide, $(C_2H_5)_2AlOC_4H_9$-*s*, is first produced in the reaction of triethylaluminum with acetaldehyde, and that this behaves as the real active species of the polymerization catalyst.⁽⁶⁾

Apart from the aldehyde polymerization, several synthetic reactions involving aluminum alkoxide and aldehyde are known. In a previous paper,⁽⁵⁾ we suggested a close relationship between some of these reactions and the polymerization, the *Meerwein-Ponndorf-Verley reduction (Oppenauer oxidation)* and

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1) Review of aldehyde polymerization, J. Furukawa and T. Saegusa, "Polymerization of Aldehyde and Oxides," John Wiley & Sons., New York (1963), pp. 43—123.

2) G. Natta, G. Mazzanti, P. Corradini and I. W. Bassi, *Makromol. Chem.*, **37**, 156 (1960).

3) O. Vogl, *J. Polymer Sci.*, **46**, 261 (1960).

4) J. Furukawa, T. Saegusa, H. Fujii, A. Kawasaki, H. Imai and Y. Fujii, *Makromol. Chem.*, **37**, 149 (1960).

5) J. Furukawa, T. Saegusa and H. Fujii, *ibid.*, **44/46**, 398 (1961).

6) H. Fujii, I. Tsukuma, T. Saegusa and J. Furukawa, *ibid.*, **82**, 32 (1965).

the *Tishchenko reaction* being referred to in the discussion of the polymerization mechansim.

In the present study, reactions between diethylaluminum *s*-butoxide and *n*-butyraldehyde in about equimolar amounts will be carried out at several temperatures, and the courses of the reactions will be examined by means of an analysis of the products. The results will then be discussed in relation to the polymerization reaction.

Experimental7)

Reagents. *n-Butyraldehyde.* A commercial reagent was treated with calcium carbonate, and with anhydrous sodium sulfate, and was then distilled through a 30-cm helices-packed column under a nitrogen atmosphere, bp 74.8°C.

Diethylaluminum s-Butoxide. Diethylaluminum *s*-butoxide was prepared by the reaction between equimolar amounts of triethylaluminum and butanol-2 in heptane; it was purified by fractional distillation under a reduced nitrogen atmosphere, bp 124—127°C/4 mmHg.

Reaction between Diethylaluminum *s*-Butoxide and *n*-Butyraldehyde. *n*-Butyraldehyde was stirred within a period of 5 min and under a nitrogen atmosphere, into a solution of diethylaluminum *s*-butoxide in 10 m*l* of heptane which had been kept at a desired reaction temperature. The reaction mixture was stirred for 1 hr at the desired temperature and then treated with an excess of glacial acetic acid. The product was subjected to the vapor-phase chromatographic (vpc) analysis. The alcohols, esters, ketone, and aldehyde were identified by vpc analysis using the respective authentic samples and determined by means of the calibration curve method, with toluene as the internal standard. The analytical procedure was verified by several reference runs with samples containing known amounts of the authentic compounds. By using diethylaluminum *s*-butoxide as a reference compound, it has also been established that, by after-treatment with acetic acid, the aluminum alkoxide species is fully converted into the corresponding alcohol and can be quantitatively analyzed by the vpc procedure. The gas evolved in the course of the reaction carried out at 20 and 40°C was identified by the vpc analysis as ethane; the amount was determined by gasometry.

Results and Discussion

The reaction between diethylaluminum *s*-butoxide and *n*-butyraldehyde was performed in *n*-heptane, and the reaction mixture was treated with glacial acetic acid. The product was then subjected to vpc analysis. Among the products obtained by the acid-treatment of the reaction mixture, methyl ethyl ketone, *s*-butyl *n*-butyrate, *n*-butyl *n*-butyrate, butanol-1, *n*-butyl acetate, *n*-butyraldehyde, butanol-2, *s*-butyl acetate, 2-ethyl-2-hexenal and 2-ethyl-1, 3-hexanediol 1-*n*-butyrate were the volatile compounds; they were analyzed by vpc. The formation of *n*- and *s*-butyl acetates may reasonably be ascribed to the

TABLE 1. REACTION OF DIETHYLALUMINUM *s*-BUTOXIDE WITH *n*-BUTYRALDEHYDE*1

	Reaction temperature, °C					
	−65	−40	−20	0	+20	+40
Reaction charge (mmol)						
$(C_2H_5)_2AlOC_4H_9$-*s*	14.20	17.20	19.30	15.50	13.62	16.76
n-C_3H_7CHO	13.80	16.00	16.00	16.75	12.48	13.30
Reaction products (mmol)						
$CH_3COC_2H_5$	0.00	trace	0.43	1.89	1.77	2.77
n-$C_3H_7CO_2C_4H_9$-*s*	1.43	2.26	3.16	2.74	1.80	0.61
n-$C_4H_9OH + CH_3CO_2C_4H_9$-*n*	1.26	2.18	3.39	4.59	3.67	4.41
n-$C_3H_7CO_2C_4H_9$-*n*	0.42	0.27	0.81	0.57	0.41	0.24
sec-$C_4H_9OH + CH_3CO_2C_4H_9$-*s**2	11.40	15.30	14.57	10.84	9.90	13.05
n-C_3H_7CHO*3	10.29	11.20	7.14	7.03	0.76	0.23
VIII	0	0	0	0	0.82	0.23
IX	0	0	0	0	trace	trace

*1 To a solution of diethylaluminum *s*-butoxide in 10 m*l* of heptane, *n*-butyraldehyde was added, and the mixture was stirred for 1 hr. The analytical procedure of the reaction mixture is given in the experimental section.

*2 The sum corresponds to the amount of the unreacted *s*-$C_4H_9OAl<$ group.

*2 *n*-Butyraldehyde comes from the unreacted species, and in the reactions at −40 and −65°C it comes also from the degradation of poly-*n*-butyraldehyde (see Text).

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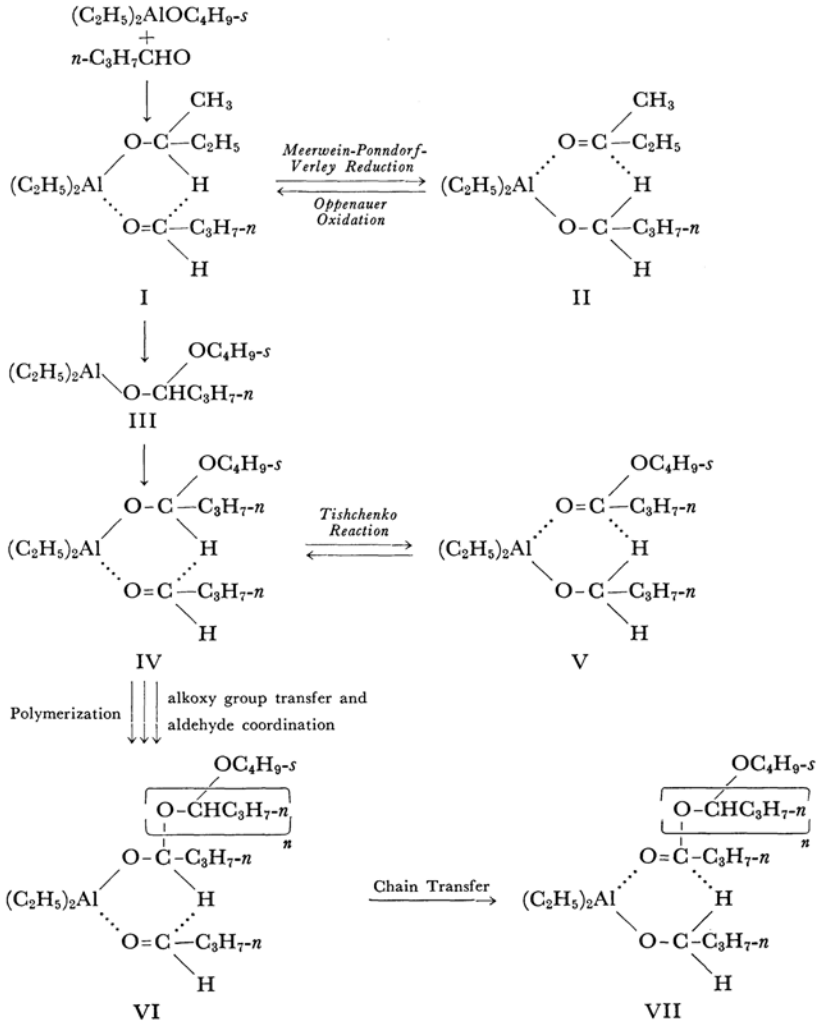
7) Vapor phase chromatograms were obtained using a Model 5 DH apparatus of the Yanagimoto Co. and a 3-m polyethleneglycol 20000 column at 75°C, under a flow rate of hydrogen of 60 m*l*/min. Compounds VIII and IX were determined at 200°C under a flow rate of 140 m*l*/min. Silicone D. C. 550 (3 m) and silica gel (3 m) columns were used for *s*-butyl *n*-butyrate (75°C) and ethane (at 10°C) respectively. The infrared spectra were taken on an IR-S spectrophotometer of the Japan Spectroscopic Co.



Scheme 1. Interrelationship of *Meerwein-Ponndorf-Verley Reduction*, *Tishchenko Reaction* and polymerization.

esterification of the two butanols with acetic acid. The fact that no trans-esterification between acetic acid and butyric acid esters of butanol-1 and butanol-2 occurs under the present reaction conditions has been established by a blank test, as well as by the finding that no butyric acid is detected in the vpc analysis. The sum of butanol-2 and *s*-butyl acetate corresponds to the amount of the unreacted *s*-$C_4H_9OAl<$ group. When the reaction was carried out at -40 and -65°C, the polymerization of butyraldehyde occurred, while *n*-butyraldehyde was regenerated by the acid-treatment of the butyraldehyde polymer. It has been reported by Kamio *et al.*[8] that the polymerization of *n*-butyraldehyde by a metal alkyl catalyst occurs only at temperatures below about -30°C.

In Table 1, the amounts of these compounds in several mixtures of reactions, carried out at different temperatures from -65 to 40°C, are shown. Methyl ethyl ketone, butanol-1, and *n*-butyl acetate are the products of the *Meerwein-Ponndorf-Verley reduction* (and the *Oppenauer oxidation)*, while the two esters of *n*-butyric acid are the products of the *Tishchenko reaction.*

The interrelationship of the *Meerwein-Ponndorf-Verley reduction*, the *Tishchenko reaction*, and the aldehyde polymerization has previously been discussed by us.[1,5] According to these relationships, the reactions of the present study involving *n*-butyraldehyde and diethylaluminum *s*-butoxide are interrelated as follows: Complex I is formed by the coordination of *n*-butyraldehyde with diethylaluminum *s*-butoxide. The coordination of aldehyde with aluminum alkoxide has been demonstrated by infrared studies, in which the shift of

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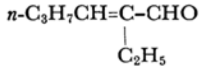
[8] K. Kamio, S. Kojima and H. Daimon, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 246 (1963).

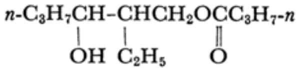
the $\nu_{C=O}$ band to a lower frequency was observed and was taken to indicate the coordination of the oxygen of the aldehyde carbonyl group with aluminum.9) The complex of this type plays an important role in reactions involving aldehyde and aluminum alkoxide. The hydride transfer from an alkoxy group to a carbonyl group in I produces the Complex II, consisting of diethylaluminum *n*-butoxide and methyl ethyl ketone; this reaction corresponds to the so-called *Meerwein-Ponndorf-Verley reduction.* The reverse reaction from II to I is the *Oppenauer oxidation.* In I, an alkoxy group instead of hydrogen can also be transferred to the carbonyl group to give a new aluminum alkoxide III, to which the second molecule of *n*-butyraldehyde coordinates to form a Complex IV. The hydride transfer reaction in IV gives *s*-butyl *n*-butyrate and diethylaluminum *n*-butoxide. The series of three successive processes, I→III→IV→V, corresponds to the *Tishchenko reaction.* On the other hand, the transfer of an alkoxy group in Complex IV will produce a higher aluminum alkoxide. The repetition of the two consecutive processes, the coordination of the aldehyde monomer to aluminum alkoxide, and the transfer of an alkoxy group, is the propagation of the aldehyde polymerization. Furthermore, the *Tishchenko reaction* starting from diethylaluminum *n*-butoxide in complexes II and V produces *n*-butyl *n*-butyrate.

In addition to the above reactions, the aldol condensation of *n*-butyraldehyde and the subsequent reaction of butyraldol (2-ethyl-3-hydroxyhexanal) become notable as the reaction temperature is raised. In the vpc analysis of the acid-treatment products of the reactions at 20 and 40°C, small amounts of several products with retention times longer than those of the simple products produced by the *Meerwein-Ponndorf-Verley reduction* and the *Tishchenko reaction* have been detected. These minor products may be assumed to be derived from butyraldol. Among them, 2-ethyl-2-hexenal VIII and 2-ethyl-1, 3-hexanediol 1-*n*-butyrate IX were identified by a comparison of their vpc retention times with those of the respective authentic samples.



$n\text{-}C_3H_7CH{=}\underset{\displaystyle C_2H_5}{\underset{|}{C}}\text{-}CHO$

VIII



$n\text{-}C_3H_7\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}CH_2O\underset{\displaystyle O}{\underset{\|}{C}}C_3H_7\text{-}n$

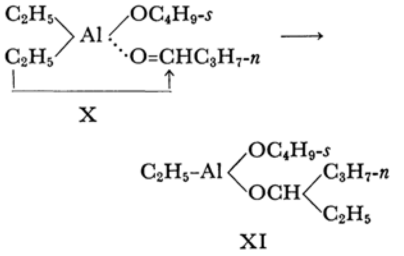
IX

The derivations of butyraldol to these two compounds may be readily understood; the former is produced by the dehydration of the aldol, and the latter, by the *Tishchenko reaction* between butyraldol and *n*-butyraldehyde. The dehydration of butyraldol by aluminum alkoxide has been reported by Häusermann.10)

Besides these two compounds, we may assume other products to be formed by other secondary reactions of butyraldol, involving other combinations of the butyraldol hydroxyl group (entering into reaction as aluminum alkoxide) and its aldehyde group. In the present study, the products of secondary reactions of butyraldol other than VIII and IX have not been identified.

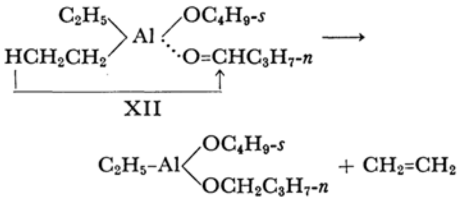
It may reasonably be assumed that the sum of VIII and IX in Table 1 is a minimum estimate of the actual extent of aldol condensation. In fact, considerable amounts of non-volatile materials were obtained when the ether extracts of the acid-treatment products of mixtures of the reactions performed at 20 and 40°C were subjected to vacuum evaporation at 100°C under 1 mmHg. The IR spectra of the non-volatile residues were shown to be composed of the absorption bands of the butyraldol and those assignable to the ether linkage. The formation of compounds having ether and acetal linkages as secondary reactions of aldol has been established by Späth *et al.*11,12) Ethane was evolved during the reaction between diethylaluminum *s*-butoxide and *n*-butyraldehyde at higher temperatures. The amount of ethane was 72.5 m*l* (NTP) at the reaction temperature of 40°C and 30 m*l* (NTP) at 20°C. The evolution of ethane may be ascribed, at least in part, to the reaction between the ethylaluminum group and the hydroxyl group of butyraldol.

In addition to the reactions hitherto discussed, there might occur the following two reactions between diethylaluminum *s*-butoxide and *n*-butyraldehyde, both reactions involving the ethylaluminum group:



X

XI



XII

XIII

However, it has been shown that the ethyl group transfer (the reaction from X to XI) does not

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9) H. Fujii, T. Saegusa and J. Furukawa, *ibid.*, **65**, 695 (1962).

10) M. Häusermann, *Helv. Chim. Acta,* **34**, 2172 (1951).

11) E. Späth and H. Schmid, *Ber.*, **74**, 859 (1941).

12) E. Späth, R. Lorenz and E. Freund, *ibid.*, **76,** 57, 513, 722 (1943).

TABLE 2. REACTION OF DIETHYLALUMINUM *s*-BUTOXIDE WITH *n*-BUTYRALDEHYDE. THE ACCOUNTS OF CHARGED, RECOVERED AND REACTED SPECIES*1

	Reaction temperature, °C					
	−65	−40	−20	0	+20	+40
$(C_2H_5)_2AlOC_4H_9$-*s*						
A Charged	100	100	100	100	100	100
B Recovered*2	80.3	88.8	75.5	69.9	72.6	77.9
C Reacted (total)	10.1	13.1	18.6	29.9	26.2	20.1
$CH_3COC_2H_5$	0	0	2.2	12.2	13.0	16.5
n-$C_3H_7COOC_4H_9$-*s*	10.1	13.1	16.4	17.7	13.2	3.6
D Balance [(B+C)/A]×100	90.4	101.9	94.1	99.8	98.8	98.0
n-C_3H_7CHO						
A Charged	100	100	100	100	100	100
B Recovered	74.5	70.0	44.6	42.0	6.1	1.7
C Reacted (total)	25.2	31.1	51.1	50.6	63.6	46.8
n-C_4H_9OH + $CH_3CO_2C_4H_9$-*n*	9.1	13.6	21.2	27.4	29.4	33.2
n-$C_3H_7COOC_4H_9$-*s*	10.0	14.1	19.8	16.4	14.4	4.6
n-$C_3H_7COOC_4H_9$-*n**3	6.1	3.4	10.1	6.8	6.6	3.6
n-$C_3H_7CH{=}C(C_2H_5)CHO$*3	0	0	0	0	13.2	5.4
D Balance [(B+C)/A]×100	99.7	101.1	95.7	92.6	69.7	48.5

*1 The amounts of recovered (unreacted) and reacted species are expressed on the basis of 100 of each charged species.

*2 Recovered as butanol-2 and *s*-butyl acetate.

*3 *n*-Butyl *n*-butyrate and 2-ethyl-2-hexenal are derived from two moles of *n*-butyraldehyde.

occur under the reaction conditions of the present study. In the acid-treatment products of the reaction mixtures, neither *n*-hexanol-3 nor ethyl *n*-propyl ketone was detected by vpc analysis. Furthermore, no indication of the reduction of aldehyde by hydrogen of the ethyl-aluminum group (the reaction from XII to XIII) was obtained. The gas evolved during the course of reaction was shown by vpc analysis to consist exclusively of ethane. Consequently, butanol-1 has been formed by the hydride transfer from aluminum alkoxide species, but not from the ethylaluminum group.

The material balances of the *n*-butyraldehyde and *s*-butoxy groups of diethylaluminum *s*-butoxide are given in Table 2. The amount of the initially-charged *s*-$C_4H_9OAl<$ group agrees quite well with the sum of the unreacted (determined as butanol-2 and *s*-butyl acetate) and the reacted (methyl ethyl ketone and *s*-butyl *n*-butyrate) species. The material balance of *n*-butyraldehyde is satisfactory in the reactions performed at temperatures below 0°C. At the reaction temperatures of 20 and 40°C, however, the amounts of *n*-butyraldehyde do not balance. The deficit may be caused, at least in part, by the aldol condensation and by the subsequent reactions of butyraldol.

The mode of the reaction of the *s*-butoxy group in Complex I varies with the reaction temperature. As has been discussed before, the *s*-butoxy group in I reacts in two ways, *i. e.*, hydride transfer reaction leading to the formation of methyl ethyl ketone (*Meerwein-Ponndorf-Verley reduction*), and butoxy group transfer leading to the formation of *s*-butyl *n*-butyrate (*Tishchenko reaction*). Figure 1 shows the change in the yields of the two products with the change in the reaction temperature. Here it is shown that the hydride transfer reaction in I does not occur at −40 and −65°C, but that it does occur at temperatures above −20°C. The extent of hydride transfer in I is expressed by the

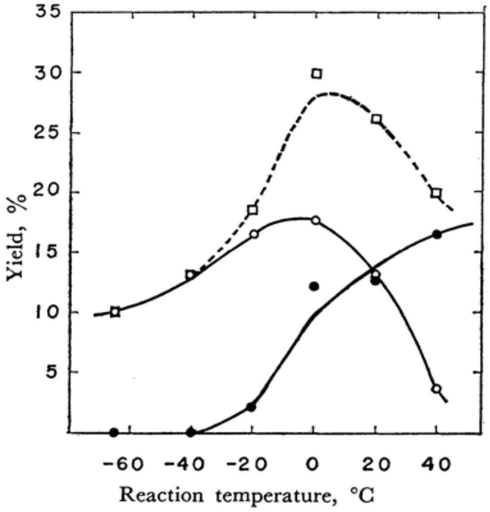

Fig. 1. Effect of the reaction temperature on the yields of methyl ethyl ketone and *s*-butyl *n*-butyrate.

● $CH_3COC_2H_5$ ○ *n*-$C_3H_7CO_2C_4H_9$-*s*

□ Total

Table 3. Accounts of oxidation and reduction

	Reaction temperature, °C					
	−65	−40	−20	0	+20	+40
Sum of species by oxidation (mmol)	1.85	2.53	4.40	5.20	3.98	3.62
Sum of species by reduction (mmol)	1.68	2.45	4.20	5.16	4.08	4.65

yield of methyl ethyl ketone, which gradually increases as the reaction temperature is raised. On the other hand, the formation of *s*-butyl *n*-butyrate, which is produced by *s*-butoxy transfer in I followed by the hydride transfer in Complex IV, does occur at temperatures as low as −65°C. According to Scheme 1, it follows that the reaction temperature required for the hydride transfer from aluminum alkoxide in I is higher than that required for the hydride transfer from the aluminum alkoxide in IV. As the reaction temperature is raised, the extent of the *Tishchenko reaction* (the formation of *s*-butyl *n*-butyrate) gradually increases, passes through a maximum at about 0°C, and finally falls off. It seems likely that, at higher temperatures, the reaction of the *s*-$C_4H_9OAl<$ group is hampered by aldol condensation. The extents of reaction have been given for the reaction time of 1 hr. A further prolongation of the reaction did not increase the yields of methyl ethyl ketone and *s*-butyl *n*-butyrate.

All the reaction products in Table 1 except VIII have been brought about by a process including the hydrogen transfer reaction. The hydrogen transfer reaction produces equal amounts of oxidized and reduced species. Table 3 shows the accounts of oxidation and reduction at several temperatures, where the sum of the amounts of methyl ethyl ketone, *s*-butyl *n*-butyrate, and *n*-butyl *n*-butyrate indicates the extent of oxidation, and the sum of the amounts of butanol-1, *n*-butyl acetate, and *n*-butyl *n*-butyrate indicates that of reduction. Here *n*-butyl *n*-butyrate is composed of the reduced species (the alcohol component) and the oxidized species (the carboxylate component), and is, consequently, counted in the two places. At reaction temperatures from −65 to 20°C, the accounts of oxidation and reduction correspond with each other. However, a considerable discrepancy is observed at 40°C, this may be due to the uncounted products formed by a secondary reaction of butyraldol.