CARBONYLATION OF ISOBUTYLENE, ITS OLIGOMERS, AND n-OLEFINS BY CARBON MONOXIDE IN THE PRESENCE OF BF_3 COMPLEXES WITH PROPIONIC, ACETIC OR CHLOROACETIC ACIDS

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It was shown previously in [1] that BF_3 complexes with acetic or propionic acids are highly active and stable catalysts of the carbonylation of branched olefins and tertiary alcohols. These catalysts are easily separated from the reaction products and can be used repeatedly without a reduction of activity.

The present paper describes the effect of the CO temperature and pressure, the molar ratio of catalyst to olefin, and the addition of water and solvents on the carbonylation of isobutylene, its oligomers, and n-olefins in the presence of complexes of BF_3 with C_2H_5COOH, CH_3COOH, and $CH_2ClCOOH$. The activity of the catalysts with repeated use has been studied.

Carbonylation of isobutylene (Table 1) carried out under optimum conditions [catalyst (Ct) $BF_3 \cdot 2C_2H_5COOH$, 80°C, p_{CO} 100 atm, a Ct: $i\text{-}C_4H_8$: water molar ratio 2 : 1 : 1] led to the formation of a mixture of acids with a mean yield of 95.2% after using the catalyst five times. In the presence of $BF_3 \cdot 2CH_3COOH$ at 80° the yield of acids was substantially unchanged but the content of trimethylacetic acid (TMAA) in the mixture decreased from 54.0 to 44.5%. It follows from Fig. 1 and Table 1 that the temperature rise, during carbonylation of isobutylene in presence of $BF_3 \cdot 2CH_3COOH$, causes an increase in the yield of carboxylic acids from 27.8% at 50° to 91.0% at 80°, and then a decrease to 35.0% at 125°. In this case, the TMAA content of the mixed acids decreased from 58.3% at 50° to 22.0% at 125°; the mean molecular weight (M_{av}) of the resulting acids mixture increased from 110 to 140-142.

Carbonylation of diisobutylene (DIB) without adding water, or adding it more slowly than the DIB, caused a lower yield of carboxylic acids (Table 2). Only simultaneous addition of equimolar quantities of water and DIB or, still better, its previous addition to the catalyst, increased the yield of acids. When DIB was carbonylated with n-hexane, chlorobenzene, or methyl acetate present, the yield of acids decreased from 99.6 to 92.1, 67.4, and 42.2%, respectively. In the presence of methanol, DIB forms, besides the branched acids, their methyl esters and methyl propionate, which latter is a component of the catalyst $BF_3 \cdot 2C_2H_5COOH$. This leads to an expenditure of catalyst and its deactivation.

With repeated use of the catalyst $BF_3 \cdot 2C_2H_5COOH$ under optimum conditions (80°; p_{CO} 100 atm; Ct: DIB:water molar ratio = 2 : 1 : 1) its activity is unchanged (Table 3, Fig. 2). The carboxylic acids formed after the first experiment are not completely extracted (about 85%), but afterwards are easily separated in subsequent experiments; quantitative extraction is achieved after the fifth trial, $BF_3 \cdot 2CH_3COOH$ also proved to be a highly active and stable catalyst for the carbonylation of DIB; the yield of acids was 93.4% after it had been used six times. The organic acids prepared in this case comprised 25% TMAA, 50% C_9 acids, 20% C_{13} acids, and 2-3% of C_6 and C_7 acids. The carboxylic acids formed from the (1 : 1) mixture of 2,4,4-trimethyl-1- and -2-pentenes or from the pure isomers had approximately the same qualitative and quantitative composition.

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*Deceased.

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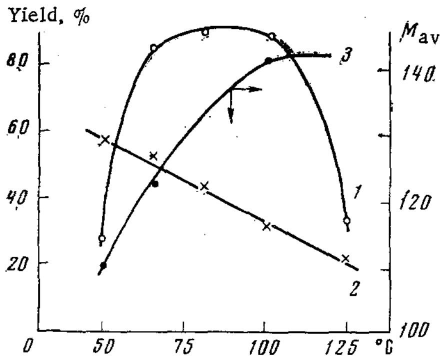

Fig. 1. Effect of temperature on carbonylation of isobutylene: 1) yield of acids; 2) trimethylacetic acid content in mixed acids; 3) mean molecular weight of mixed acids.

TABLE 1. Carbonylation of Isobutylene in the Presence of BF_3 Complexes with Acetic or Propionic Acid (p_{CO} 100 atm; Ct; i-C_4H_8: water molar ratio = 2 : 1 : 1; isobutylene feed rate 1.0-1.5 mole /h per mole of Ct)

Catalyst	T., °C	Yield of acids, % of theor.	Content of acid, % *						M_{av}
			trimethylacetic	2,2,4,4-tetramethylvaleric	3,3-dimethyl-2-isopropylbutyric	2-tert-butyl 3,5,5-trimethylcaproic	2,2,4,4,6,6-hexamethylenanthic	3,3,5-tetramethyl-2-isopropylcaproic	
$BF_3 \cdot 2C_2H_5COOH$	80	95,2 †	54,0	12,0	15,0	6,1	2,2	3,7	124,0
$BF_3 \cdot 2CH_3COOH$	50	27,8	58,3	15,9	12,3	3,7	1,9	2,2	110,0
The same	65	85,9 ‡	53,1	12,2	13,5	7,5	3,8	4,6	125,0
»	80	91,0 **	44,5	17,1	18,8	6,3	2,2	3,8	129,5
»	100	90,5	32,4	16,8	15,1	10,4	5,7	11,6	142,0
»	125	35,0	22,9	21,0	20,5	7,8	2,7	6,2	140,0

*In addition the mixtures of acids contained 1.0-2.0% of C_6 acids, 0.6-1.5% of C_7 acids, and 2-5% of a C_9 acid.

†Mean yield after using catalyst five times.

‡The same, after using four times.

**The same, after using twice.

Carbonylic acids have been prepared from triisobutylene (TIB) (Table 4) in 87-92% yield which comprised 40-50% TMAA, 30-40% C_9 acids, and only 10-15% of C_{13} acids. The variation of the Ct to olefin (DIB or TIB) molar ratio over the 2 : 1-1.1 range showed no significant effect on the reaction (see Table 4 and Fig. 2). It can be assumed, however, that the optimum ratio is 2 : 1, because it enables carbonylation to be carried out, not only producing carboxylic acids in high yield but also preserving the activity of the catalyst during its repeated use.

From TIB (a mixture of 2,2-dineopentylethylene and 2,2,4,6,6-pentamethyl-3-heptene) it was expected that 2,2-dineopentylpropionic acid would be formed through the intermediate tertiary carbonium ion A (on chart). However, the PMR spectrum showed the presence of another isometric acid – 2-tert-butyl-3,5,5-trimethylcaproic acid. This is evidently formed through carbonium ion B and is more probable under the reaction conditions mentioned. The formation of 2,2,4,4,6,6-hexamethylenanthic and 2-isopropyl-3,3,5,5-tetramethylcaproic acid probably occurs at the stage when the original TIB mixture isomerises to a mixture of 2,4,4,6,6-pentamethyl-1- and -2-heptenes, through the intermediate carbonium ions C and D, which are subsequently carbonylated (see Scheme 1).

1-Pentene and 2-petene did not react with CO in the presence of $BF_3 2C_2H_5COOH$ and $BF_3 \cdot 2CH_3COOH$ at 80-90° and 100 atm of CO (molar ratio Ct: olefin: water = 2 : 1 : 1). They were, however, quantitatively converted to mixtures

TABLE 2. Carbonylation of Diisobutylene (DIB) in the Presence of Various Solvents and Methods of Adding Water to $BF_3 \cdot 2C_2H_5COOH$ Catalyst (p_{CO} 100 atm; Ct:DIB:water molar ratio = 2 : 1 : 1; 80°; DIB feed rate 1.0-1.5 mole/h per mole of Ct)

Solvent, method of adding water to Ct	Yield of acids, % of theor.	Acid content, %*					
		trimethyl-acetic	2,2,4,4-tetramethyl-valeric	3,3-dimethyl-2-isopropylbutyric	2-tert-butyl-3,5,5-trimethylcaproic	2,2,4,4,6,6-hexamethyl-enanthic	3,3,5,5-tetramethyl-2-isopropylcaproic
Without added water	33,3	15,2	30,0	19,1	7,5	6,9	13,9
Water, addition rate half that of DIB	54,0	31,0	25,2	21,1	4,3	3,7	6,0
Water and DIB added simultaneously	89,2	28,1	26,8	24,2	6,2	3,5	4,9
Water added to Ct not more than DIB	99,6†	29,5	18,7	24,2	7,0	3,9	4,2
Water added to Ct not more than DIB and DIB added with equal volume of b-hexane	92,1‡	51,0	14,8	20,9	1,3	—	—
Water added to Ct not more than DIB and DIB added with equal volume of methyl acetate	42,2	18,7	24,2	16,9	9,4	7,2	15,5
Water added to Ct not more than DIB and DIB added with an equal volume of chlorobenzene	67,4	31,2	24,7	19,7	5,3	1,9	5,5
Methyl alcohol in molar ratio DIB: CH_3OH = 1: 1	56,0**	43,6	18,0	19,3	3,0	2,2	4,8

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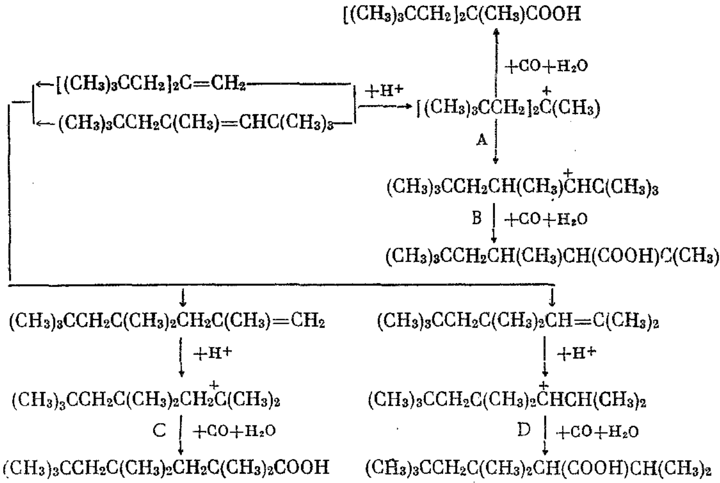
*In addition, the mixtures of acids contained 1.5-3.0% of C_6 acids, 1.0-2.5% of C_7 acids, and 5-6% of a C_9 acid. M_{av} for the mixtures of acids was 123-159.

†Mean yield after using catalyst ten times.

‡The same, after using twice.

**Methyl esters of propionic acid and branched acids were formed with total yield 27.3%.

of the normal, secondary, and tertiary amyl esters of propionic or acetic acid. Nevertheless, at 100° 1-pentene in the presence of $BF_3 \cdot 2CH_3COOH$ was already 21% converted to carboxylic acids.



Scheme 1

1-Hexene was converted in the presence of $BF_3 \cdot 2CH_3COOH$ at 100° to carboxylic acids with a yield of 84.0% (Table 5). When the more acid catalyst $BF_3 \cdot 1.65CH_2ClCOOH$ was present, 1-hexene at 80° was quantitatively converted to the C_7 carboxylic acids: 2,2-dimethylvaleric and 2-ethyl-2-methylbutyric acids. At 40° the yield of acids from 1-hexene was only 11.8% and in the mixture of acids, besides those mentioned, 19% of 2-ethylvaleric and 2-methycaptoic acids was present.

Carbonylation of n-olefins took place easily in the presence of the more active, and more conveniently converted, catalyst system $3BF_3 \cdot 2\,CH_2ClCOOH + BF_3 \cdot 2CH_3COOH$. Unlike $BF_3 \cdot 2CH_2ClCOOH$ it does not crys-

TABLE 3. Carbonylation of Diisobutylene in Presence of BF_3 Complexes with Acetic or Propionic Acid (p_{CO} 100 atm; Ct:DIB:water molar ratio = 2 : 1 : 1; 80°; DIB feed rate 1.0-1.5 mole/h per mole of Ct)

Catalyst	Yield of acids, % of theor.	Yield of acids, % of theor.					
		trimethyl acetic	2,2,4,4-tetramethyl-valeric	3,3-dimethyl-2-isopropylbutyric	2-tert-butyl-3,5,5-trimethyl-caproic	2,2,4,4,6,6-hexamethyl-enanthic	3,3,5,5-tetramethyl-2-isopropyl-caproic
Mixture (1 : 1) of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene							
$BF_3 \cdot 2C_2H_5COOH$, fresh	84,8	29,1	19,3	20,3	7,9	5,9	8,8
From expt. 1	105,5	28,8	16,9	20,8	8,1	7,0	9,9
The same	107,0	36,5	20,2	28,0	4,8	—	—
» 3	102,2	27,6	18,6	23,4	8,7	4,7	4,8
» 4	100,0	26,3	17,3	19,4	9,2	6,2	6,2
» 5	98,0	52,0	17,7	24,2	7,3	3,0	2,6
« 6	100,5	29,4	17,7	26,0	8,4	3,1	2,2
» 7	99,3	28,8	18,7	24,5	6,9	3,8	2,5
» 8	98,6	24,8	17,6	24,8	9,6	5,0	4,7
» 9	99,6	31,6	21,4	30,0	—	—	—
Mean	99,6	29,5	18,7	24,2	7,0	3,9	4,2
2,4,4-Trimethyl-1-pentene							
Fresh without added water	33,3	15,2	30,0	19,1	7,5	6,9	13,9
2,4,4-Trimethyl-2-pentene							
Fresh	97,3	31,9	19,4	20,2	5,5	5,4	10,6
2,4,4-Trimethyl-1-pentene							
Ct : DIB =2 : 1,5	98,4**	26,8	21,7	21,4	6,0	5,7	11,4
Ct : DIB =1 : 1	95,2**	23,2	21,6	20,6	7,1	7,0	13,9
$BF_3 \cdot 2CH_3COOH$	93,4***	25,1	22,8	23,3	8,2	4,5	6,5

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*In addition, the mixtures of acids contained 2.0-3.5% of C_6 acids, 2.0-3.5% of C_7 acids and 3-8% of C_9 acids. M_{av} for the mixtures of acids was 132-159.

†Mean yield after using catalyst three times.

‡The same, after six times.

TABLE 4. Carbonylation of Triisobutylene (TIB) in the Presence of BF_3 with Acetic or Propionic Acid (p_{CO} 100 atm; Ct:TIB:water molar ratio = 2 : 1 : 1; 80°; TIB feed rate 1.0-1.5 mole/h per mole of Ct)

Catalyst	Yield of acids, % of theor.	Acid content, %*					
		trimethyl-acetic	2,2,4,4-tetramethyl-valeric	3,3-dimethyl-2-isopropylbutyric	2-tert-butyl-3,5,5-trimethylcaproic	2,2,4,4,6,6-hexamethyl-enanthic	3,3,5,5-tetramethyl-2-isopropyl-caproic
Mixture (1 : 1) of 1,1-dineopentylethylene and 2,2,4,6,6-pentamethyl-3-heptane							
$BF_3 \cdot 2CH_3COOH$	87,8†	31,8	18,1	20,1	9,1	5,1	7,5
$BF_3 \cdot 2C_2H_5COOH$	92,5†	48,0	13,1	14,1	5,1	3,8	8,4
The same	90,5‡	44,9	13,4	14,4	7,6	4,6	7,8
$BF_3 \cdot 2C_2H_5COOH$ Ct : TIB = 2 : 1,5	90,3**	40,1	14,2	18,2	6,4	5,3	8,9
$BF_3 \cdot 2C_2H_5COOH$, Ct : TIB = 1 : 1	86,0**	41,1	11,0	10,9	5,3	7,0	12,5

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*In addition, the mixtures of acids contained 1.5-2.5% of C_6 acids, 2.0-1.5% of C_7 acids, and 3-7.5% of a C_9 acid. M_{as} from the mixtures of acids was 132-140.

†Mean yield after using catalyst five times.

‡At 70°.

**Mean yield after using catalyst three times.

tallize on standing. With a Ct:olefin:water ratio = 2 : 1 : 1, at 80°, and p_{CO} 100 atm, 1-pentene was 94.7% converted to acids. 1-Hexene and 1-heptene gave acids with an average yield of 93.8 and 92.6%, respectively, after the catalyst had been used ten times. The carboxylic acids formed from 1-heptene consisted of 92.5% of C_8 and 7.5% of C_{15} acids.

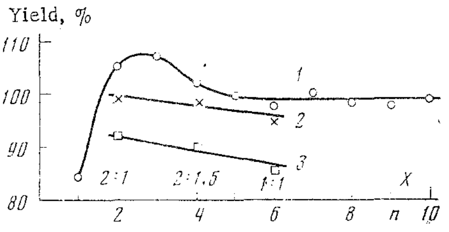

Fig. 2

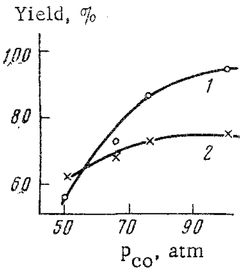

Fig. 3

Fig. 2. Effect of molar ratio of Ct to olefin (X) and number of repeat experiments (n) on yield of carboxylic acids: 1) from DIB with repeated use of Ct ($BF_3 \cdot C_2H_5COOH$); 2) from DIB with Ct to DIB molar ratios from 2 : 1 to 1 : 1; 3) from TIB with Ct to TIB molar ratios from 2 : 1 to 1 : 1.

Fig. 3. Effect of CO pressure on carbonylation of 1-pentene (Ct : $3BF_3 \cdot 2CH_2ClCOOH + BF_3 \cdot 2CH_3COOH$, 90°, Ct : 1-pentene : water molar ratio = 2 : 1 : 1). 1) Yield of acids; 2) 2,2-dimethylbutyric acid content.

TABLE 5. Carbonylation of n-Olefins in the Presence of BF_3 Complexes with CH_3COOH and $CH_2ClCOOH$ (p_{CO} 100 atm; Ct:olefin: water molar ratio = 2 : 1 : 1; olefin feed rate 1 mole/h per mole of Ct)

Olefin	T., °C	Yield of acids, % of theor	Acid content, %
			$BF_3 \cdot 2CH_3COOH$
1-Pentene	100	21,0	43.6 2,2,-dimethylbutyric; 11·2, 2,2-dimethylvaleric; 6.0, 2-ethyl-2-methylbutyric; 2.4, C_8 acids, 36.8, C_{11} acids
1-Hexene	100	84.0	43.3 2,2-dimethylvaleric; 56.7, 2-ethyl-2-methylbutyric
			$BF_3 \cdot 1.65CH_2ClCOOH$
"	40	11.8	37.6 2,2-dimethylvaleric; 43.4, 2-ethyl-2-methylbutyric; 19.0 of a mixture of 2-ethylvaleric and 2-methylcaproic
"	80	100.0	62.4 2,2-dimethylvaleric; 37.6, 2-ethyl-2-methylbutyric
			$3BF_3 \cdot 2CH_2ClCOOH + BF_3 \cdot 2CH_3COOH$
1-Pentene	90	94.7	75.3 2,2-dimethylbutyric; 21.5, 2-ethylbutyric and 3.2, 2-methylvaleric
1-Hexene	90	93.8*	47.8 2,2-dimethylvaleric; 52.2, 2-ethyl-2-methylbutyric
3-Hexene	90	96.0	29.8 2,2-dimethylvaleric; 45.4, 2-ethyl-2-methylbutyric; 18.0, 2-ethylvaleric; 7.1, 2-methylcaproic
1-Heptene	90	92.6*	Fraction 1, 92.5, C_8 acid: 42.3, 2,2-dimethylcaproic; 49.5, 2-ethyl-2-methylvaleric; 8.0, 2-ethylcaproic and 2-methylenanthic
1-Octene	90	93.5	52.0 2,2-dimethylenanthic; 48.0, 2-ethyl-2-methylcaproic

*Mean yield after using catalyst ten times.

The C_8-C_{15} olefins (1-octene, 1-nonene, 1-decene, 1-dodecene, and 7-pentadecene) were 90-98% converted exclusively to branched acids (neoacids) which contained one more carbon atom than the original olefin.

It can be seen from Fig. 3 that increasing the CO pressure from 50 to 100 atm gave an increase in the yield of acids from 1-pentene from 55.5 to 94.7% and the content of 1,1-dimethyl-butyric acid increased from 61.5 to 75.3%. It should be noted that the formation of amyl esters from acetic or propionic acids, found during the carbonylation of 1-pentene and 2-pentene in the presence of $BF_3 \cdot 2CH_3COOH$ and $BF_3 \cdot 2C_2H_5COOH$, is evidently connected with the inability of these complexes to activate the CO molecule to a sufficient extent. In confirmation of the last statement is the fact that a temperature increase from 90 to 100° causes carbonylation of 1-pentene to form acids in 21% yield. With the more acidic catalyst $BF_3 \cdot 1.65CH_2ClCOOH$ only 12% of 1-hexene was carbonylated at 40°, but at 100° the reaction was quantitative.

It is known from [2] that the protonating capability of acid catalysts at a higher temperature is greatly reduced, but, as is evident from the results quoted for 1-pentene and 1-hexene, the increased temperature has a good effect on the carbonylation reaction. This means that the reaction is independent of the protonation stage and is definitely dependent on the stage at which CO is added on to the carbonium ions which are formed.

From these results it can be suggested that the carbonylation of pentenes and lower olefins requires a higher level of CO activation than is needed in the carbonylation of 1-hexene. This is evidently associated with the lower stability and shorter life of the carbonium ions formed from the pentenes and other lower olefins, compared with the carbonium ions formed from 1-hexene and olefins with a longer carbon chain [3].

The high activity of the complexes $BF_3 \cdot 1.65\ CH_2ClCOOH$ and the system $3BF_3 \cdot 2CH_2ClCOOH + BF_3 \cdot CH_3COOH$ should evidently be ascribed to the considerable increase in the acidity of the lower carboxylic acids arising from complex formation with BF_3. The order of this acidity increase among complexes with BF_3 evidently matches the increase in the dissociation constants of the carboxylic acids and the extent of their saturation with BF_3. The acidity of the complexes increases in the order $BF_3 \cdot 2C_2H_5COOH < BF_3 \cdot 2CH_3COOH <$ system $3BF_3 \cdot 2CH_2ClCOOH + BF_3 \cdot 2CH_3COOH < BF_3 \cdot 2CH_2ClCOOH < BF_3 \cdot 1.65\ CH_2ClCOOH$.

Such halogen-substituted acids as CCL_3COOH and CF_3COOH do not form complexes with BF_3.

EXPERIMENTAL

Carbonylation of olefins under pressure with CO was carried out in a stainless-steel reaction vessel with a capacity of 0.3 liter. The vessel was fitted with two dripcocks and a stirrer with a screened motor. The temperature in the vessel was controlled by an ÉPV-01 instrument to an accuracy of ±1.0° and monitored by a thermocouple by means of a PP potentiometer. The stirrer rotation rate was 1400 rpm. Carbonylation was effected with the optimum ratio of Ct:olefin:water = 2 : 1 : 1, 80-100°, and 100-atm pressure. Equimolecular quantities of water were added to the catalyst before addition of the olefin. Carbonylation was effected by adding the olefin to the catalyst in 15-20 min. The carboxylic acids were extracted from the homogeneous reaction mixture with n-hexane (4 × 50 ml) and the separated catalyst was used again. With single use of the catalyst the carboxylic acids were isolated by diluting the reaction mass with water and further extraction of the diluted aqueous solution with benzene.

The catalysts were prepared as described in [1]: $BF_3 \cdot 2CH_3COOH$, d_4^{20} 1.366; $BF_3 \cdot 2C_2H_5COOH$, d_4^{20} 1.250; $BF_3 \cdot 1.65CH_2ClCOOH$, d_4^{20} 1.605; $BF_3 \cdot 2CH_2ClCOOH$, d_4^{20} 1.585, bp. 53-54°; system $3BF_3 \cdot 2CH_2ClCOOH + BF_3 \cdot 2CH_3COOH$, d_4^{20} 1.538. For the reaction isobutylene and normal olefins of purity ≥ 98% were used. The mixtures of di- and triisobutylene were prepared from isobutylene in the presence of 55-60% H_2SO_4 [4]. DIB (a 1 : 1 mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene), bp 102-104°, n_D^{20} 1.4133), was separated by distillation from TIB (a 1 : 1 mixture of 1,1-dineopentylethylene and 2,2,4,6,6-pentamethyl-3-heptene), bp 177-178°, n_D^{20} 1.4303). By fractional distillation of DIB pure fractions of 2,4,4-trimethyl-1-pentene (bp 101.3-101.5°, n_D^{20} 1.4085) and 2,4,4-trimethyl-2-pentene (bp 104.7-105.0°, n_D^{20} 1.4160) were isolated. 7-Pentadecene (bp 121.5-122.8° (7 mm), n_D^{20} 1.4408, d_4^{20} 0.7764) was synthesized from $n\text{-}C_7H_{15}MgCl$ and CO according to [5].

The composition of the acids was determined by gas–liquid chromatography [1,6]. An LKhP-5a preparative chromatograph, with an 8 m × 20 mm column, with 15% 20M Carbowax on 0.25-mm Chromaton at 160-175, was used to isolate pure specimens of the methyl esters of C_{13} acids from isobutylene and di- and triisobutylene.

The PMR spectra of the C_{13} acids methyl esters and of the acids were taken on a DA-60-IL spectrometer. From a fraction of C_{13} acids methyl esters [bp 84-86° (4 mm), n_D^{20} 1.4393], the methyl ester of 2-tert-butyl-3,5,5-trimethylcaproic, $C_{14}H_{28}O_2$, was isolated by preparative chromatography. It has bp 84.5-84.6° (4 mm), n_D^{20} 1.4389, d_4^{20} 0.8858. By its saponification 2-tert-butyl-3,5,5-trimethylcaproic acid, bp 145°, (12 mm), n_D^{20} 1.4529 was obtained. The PMR spectrum of the methyl ester (τ, ppm) was: 0.80 s (12H, $(CH_3)_3CCH_2CH(CH_3)$; 0.86 s (9H, $(C\underline{H}_3)_3CCH(COOCH_3)$; 0.93-1.89 m (4H, $C\underline{H}_2C\underline{H}(CH_3)C\underline{H}(COOCH_3)$; 3.50 s (3H, $COOCH_3$). The acid spectrum (τ, ppm) was: 0.835 s (12H, $(C\underline{H}_3)_3CCH_2CH(C\underline{H}_3)$; 0.94 s (9H, $(CH_3)_3CCH(COOH)$; 1.40-2.08 m (4H, $C\underline{H_2CH}(CH_3)C\underline{H}(COOH)$; 12.0 s (1H, $COO\underline{H}$). From the fraction with bp 85-85.6° (4 mm), n_D^{20} 1.4405) the methyl ester of 2,2,4,4,6,6-hexamethylenanthic acid, $C_{14}H_{28}O_2$, bp 85.3° (4 mm), n_D^{20} 1.4408, d_4^{20} 0.8879 was isolated by preparative chromatography. 2,2,4,4,6,6-Hexamethylenanthic acid was obtained by saponification of the latter. $C_{13}H_{26}O_2$ had bp 145° (12 mm), n_D^{20} 1.4516. The PMR spectrum of the methyl ester (τ, ppm) was: 0.79 s (9H, $(CH_3)_3$; 0.82 s 6H, $(CH_3)_3CH_2C(CH_3)_2$; 1.08 with accompanying signals at 1.0 and 1.1 (10H, $C\underline{H}_2C(CH_3)_2\underline{CH}_2C(C\underline{H}_3)_2COOCH_3$); 3.50 s (3H, $COOC\underline{H}_3$). The PMR spectrum of the acid (τ, ppm) was: 0.82–0.79 two unseparated singlets (15H, $(CH_3)_3CCH_2C(C\underline{H}_3)_2$); 1.08 s with accompanying signals at 1.06 and 1.17 (10H, $C\underline{H}_2C(CH_3)_2C\underline{H}_2C(C\underline{H}_3)_2COOH$); 12.4 s (1H, $COO\underline{H}$). From the same fraction the methyl ester of 3,3,5,5-tetramethyl-2-isopropylcaproic acid, $C_{14}H_{28}O_2$, was similarly isolated by preparative chromatography with bp 85.5° (4 mm), n_D^{20} 1.4409, d_4^{20} 0.8902. By its saponification 3,3,5,5-tetramethyl-2-isopropylcaproic acid $C_{13}H_{26}O_2$ was obtained with mp 101° (cf. [7]). The PMR spectrum of the methyl ester (τ, ppm) was: 0.775 s (15H, $(CH_3)_3CCH_2C(C\underline{H}_3)_2$; 1.0 s (8H, $CH_2C(CH_3)_2CH(COOCH_3)C(C\underline{H}_3)_2$); 1.16–2.38 m (2H, $C\underline{H}\cdot(COOCH_3)C\underline{H}(CH_3)_2$); 3.52 s (3H, $COOC\underline{H}_3$). The PMR spectrum of the acid (τ, ppm) was: 0.785 s (15H), $(CH_3)_3\cdot CCH_2C(C\underline{H}_3)_2$; 1.0–1.05 t (8H, $C\underline{H}_2C(CH_3)_2CH(COOH)CH(C\underline{H}_3)_2$; 1.32–2.1 m 1.64 ppm (2H, $C\underline{H}(COOH)C\underline{H}(CH_3)_2$; 12.25 s (1H, $COO\underline{H}$).

From 1-pentene were obtained C_6 neoacids, bp 186–186.4° (760 mm), n_D^{20} 1.4141 (here, and later on, the constants should be compared with [8]); from 1-hexene C_7 neoacids were obtained, bp 104–105° (15 mm), n_D^{20} 1.4218; from 1-heptene, fraction 1, C_8 neoacids were obtained in 92.5% yield, bp 105–110° (9 mm), n_D^{20} 1.4280 and from fraction 2 C_{15} neoacids, in 7.5% yield, bp 170–180° (9 mm), n_D^{20} 1.4505; from 1-octene C_9 neoacids with bp 117–120° (8 mm), n_D^{20} 1.4330; from 1-nonene C_{10} neoacids were obtained in 94.5% yield, bp 130–135° (8 mm), n_D^{20} 1.4368; from 1-decene at 100° C_{11} neoacids were obtained in 89.5% yield, bp 136–148° (7 mm), n_D^{20} 1.4392; from 1-dodecene C_{13} neoacids were obtained in 91.0% yield, bp 161, and from 7-pentadecene at 100° C_{16} neoacids were obtained in 98.0% yield, bp 173–178° (7 mm), n_D^{20} 1.4490.

CONCLUSIONS

1. Complexes of BF_3 with propionic, acetic, and monochloroacetic acid are highly active and stable catalysts for the carbonylation of isobutylene, its oligomers, and n-olefins at 80–100° and a CO pressure of 100 atm. The catalysts can be used repeatedly, up to ten or more times, without a reduction in activity.

2. Mixtures of carboxylic acids containing C_5, C_9, and C_{13} neoacids are formed from isobutylene and its oligomers in the presence of $BF_3\cdot 2C_2H_5COOH$ or $BF_3\cdot 2CH_3COOH$ under optimum conditions (80°, 100-atm CO) with 92–99% yield.

3. Olefins of normal structure in the presence of the catalytic system $3BF_3\cdot 2CH_2ClCOOH + BF_3\cdot 2CH_3\cdot COOH$, under the optimum conditions of 100-atm CO, 90–100° and catalyst:olefin:water molar ratio = 2 : 1 : 1, form carboxylic acids with a yield of 90–98%.

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