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TELOMERIZATION OF PROPYLENE WITH CARBOXYLIC ACIDS

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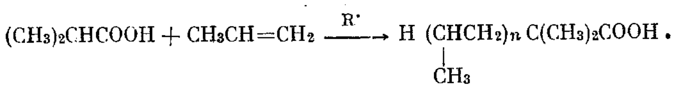
The telomerization of ethylene with propionic acid is accompanied by rearrangement of the radicals with a 1,5-migration of the H atom, and leads to the formation of α,α-dialkyl-substituted carboxylic acids. The partial chain transfer constants ($C_n = K_{tr_n}/K_{p_n}$) in such reactions are small (~0.1-0.2) and show comparatively little change with change in the chain length of the growing radical [1]. Together with a 1,5-migration of the H atom, a rearrangement of the radicals with a 1,3-migration of the hydrogen was detected in the telomerization of propylene with methyl chloroacetate [2]. A substantial increase in the partial chain transfer constants is observed here [3].

The telomerization of propylene with isobutyric and propionic acids was studied in the present paper.

The coupling of two types of rearrangements, with a 1,3- and a 1,5-migration of hydrogen, in one process leads to a substantial complication of the mixture of telomers and the formation of byproducts that especially contaminate the light fraction of the reaction products. Consequently, to identify the various types of telomers in the separate cases we resorted to the ^{13}C NMR spectra without isolating the individual telomers. The partial chain transfer constants were studied in the reaction of isobutyric acid with propylene, which goes without complications; the telomerization of propylene with propionic acid was studied qualitatively.

The telomerization of propylene with isobutyric acid, which has only one H atom α to the COOH group, gives one series of telomer homologs by the scheme:



$$(CH_3)_2CHCOOH + CH_3CH{=}CH_2 \xrightarrow{R^\cdot} H\,(\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2)_n\,C(CH_3)_2COOH\,.$$

The pure T_1 and T_2 telomers were isolated from the reaction mixture, and also a fraction that contained mainly T_3 (Table 1). Their structure was confirmed by the ^{13}C NMR spectra (Table 2). The T_2 spectrum (see Table 2) has two different signals of the α-$^{13}CH_3$ groups, which testifies to the nonequivalence of these groups with respect to the asymmetric center. A doubling of nearly all of the signals is observed in the T_3 spectrum in connection with the appearance of diastereomeric forms. The partial chain transfer constants (Table 3) have a value of ~1 and increase with increase in the chain length of the radical (from 0.36 for n = 1 to 1.4 for n = 2 and 3), which indicates the substantial effect exerted by the functional group on the reactivity of the first growing radical (n = 1). An increase in C_n when going from ethylene to propylene is apparently associated with the favorable coupling of the polar factors in the chain transfer step (the nucleophilic growing radical $CH_3\dot{C}HCH_2C(CH_3)_2COOH$ attacks the electrophilic center of the telogen molecule).

The telomerization of propylene with propionic acid (Table 4) goes with a rearrangement of the radicals, with a 1,3-, and possibly a 1,5-migration of the H atom by the scheme:

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2497-2501, November, 1975. Original article submitted December 16, 1974.

TABLE 1. Telomers Obtained from Propylene and Isobutyric Acid

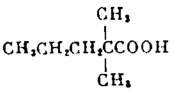
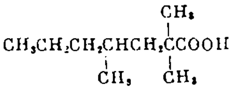
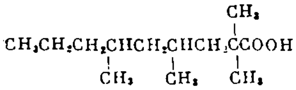
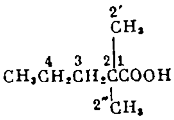
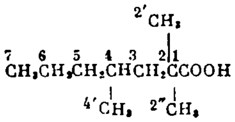
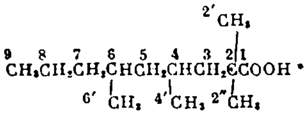
Compound	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR Found / Calc.	Empirical formula	Found / Calculated, %: H	Found / Calculated, %: C
 $CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}COOH$	61(3)	1,4205	0,9184	35,89 / 36,07	$C_7H_{14}O_2$	10,57 / 10,75	64,74 / 64,61
 $CH_3CH_2CH_2\underset{CH_3}{CH}CH_2\overset{CH_3}{\underset{CH_3}{C}}COOH$	92–93(2)	1,4344	0,8989	49,89 / 49,89	$C_{10}H_{20}O_2$	11,70 / 11,63	70,21 / 69,76
 $CH_3CH_2CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_2\overset{CH_3}{\underset{CH_3}{C}}COOH$ (fraction)	97–103(2)	1,4448	0,8839	—	$C_{13}H_{26}O_2$	—	—

TABLE 2. Data of ^{13}C NMR Spectra (δ, ppm from TMS)

Compound		$C-\underline{C}OO$	$\underline{C}H_3-C$	$\underline{C}H_3-CH$	$\underline{C}H_3-CH_2$	C	CH	CH_2
 $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{2'\,CH_3}{\underset{2''\,CH_3}{\overset{1}{C}}}COOH$	(T_1)	184,6(1)	24,9(2′, 2″)	—	14,5(5)	41,9(2)	—	18,1(4) 42,8(3)
 $\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{\underset{4'\,CH_3}{C}}H\overset{3}{C}H_2\overset{2'\,CH_3}{\underset{2''\,CH_3}{\overset{2\,1}{C}}}COOH$	(T_2)	185,1(1)	25,2 26,2(2′, 2″)	20,8(4′)	14,0(7)	41,9(2)	29,6(4)	19,8(6) 40,9(5) 48,0(3)
 $\overset{9}{C}H_3\overset{8}{C}H_2\overset{7}{C}H_2\overset{6}{\underset{6'\,CH_3}{C}}H\overset{5}{C}H_2\overset{4}{\underset{4'\,CH_3}{C}}H\overset{3}{C}H_2\overset{2'\,CH_3}{\underset{2''\,CH_3}{\overset{2\,1}{C}}}COOH$ * (fraction)	(T_3)	185,2(1)	24,9–25,1 26,3–26,5 (2′, 2″)	19,9(6′) 20,4(4′)	14,4(9)	41,6(2)	29,7(4,6)	19,3(8) 27,1(7) 46,1(5) 48,4(3)

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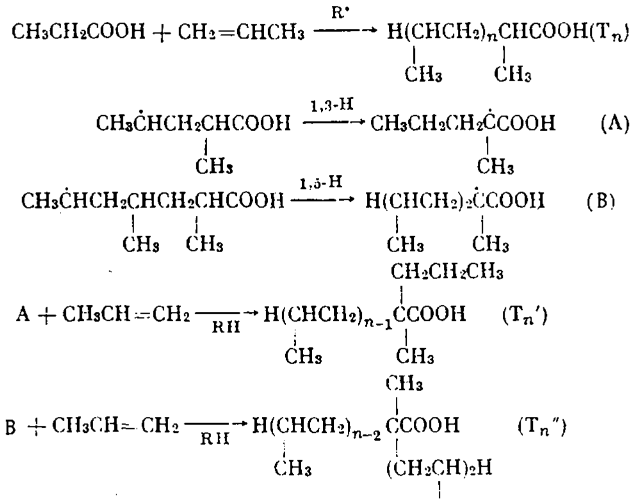
*The spectrum has unassigned signals that are much less intense, in particular, in the region of the double bond C atoms.



$$CH_3CH_2COOH + CH_2{=}CHCH_3 \xrightarrow{R^{\cdot}} H(\underset{CH_3}{CH}CH_2)_n\underset{CH_3}{CH}COOH(T_n)$$

$$CH_3\dot{C}HCH_2\underset{CH_3}{CH}COOH \xrightarrow{1,3\text{-}H} CH_3CH_2CH_2\underset{CH_3}{\dot{C}}COOH \quad (A)$$

$$CH_3\dot{C}HCH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}COOH \xrightarrow{1,5\text{-}H} H(\underset{CH_3}{CH}CH_2)_2\underset{CH_3}{\dot{C}}COOH \quad (B)$$

$$A + CH_3CH{=}CH_2 \xrightarrow[RH]{} H(\underset{CH_3}{CH}CH_2)_{n-1}\overset{CH_2CH_2CH_3}{\underset{CH_3}{C}}COOH \quad (T_n')$$

$$B + CH_3CH{=}CH_2 \xrightarrow[RH]{} H(\underset{CH_3}{CH}CH_2)_{n-2}\overset{CH_3}{\underset{(CH_2\underset{CH_3}{CH})_2H}{C}}COOH \quad (T_n'')$$

Three series of telomers are formed as a result, but only the T_n and T_n' series can be identified up to T_3, since the structure of T_3' and T_3'' coincides. Consequently, the question of the 1,5-migration of hydrogen is not considered in this paper.

The fractions of the telomers with two and three monomeric units were isolated from the reaction mixture and studied by the ^{13}C NMR method (Table 5). The spectral data and

TABLE 3. Telomerization of Propylene (M) with Isobutyric Acid (S)

Expt. No.	K_M*, %	$[M]_H$, mmoles	$[S]_H$, mmoles	[M]/[S] average	Amount of telomer homologes with n monomeric units, mole %				C_n		
					T_1	T_2	T_3	$\Sigma T_{>3}$	C_1	C_2	C_3
2	70,3	18,6	85,6	0,14	60,4	35,7	3,6	0,4	0,21	1,3	1,3
3	52,4	19,3	78,0	0,18	57,6	37,1	4,7	0,7	0,25	1,2	1,2
4	51,2	21,2	82,2	0,19	50,5	42,9	6,1	1,0	0,20	1,2	1,2
5	23,2	51,9	65,2	0,74	31,1	40,7	16,6	11,5	0,34	1,1	1,1
6	13,2	40,7	44,3	0,86	37,6	42,0	13,7	6,6	0,52	1,8	1,8
7	7,3	55,0	54,6	0,97	24,3	39,8	18,9	17,0	0,31	1,1	1,1
8	14,7	43,9	39,6	1,02	34,8	41,3	15,1	8,8	0,54	1,8	1,7
9	4,3	51,9	44,5	1,08	22,1	41,0	19,5	17,4	0,31	1,2	1,2
10	9,1	49,00	40,3	1,17	27,7	45,1	16,9	10,3	0,45	1,9	1,9
11	9,0	62,0	40,5	1,47	21,0	38,9	19,7	20,2	0,40	1,5	1,5
12	16,5	75,7	44,5	1,56	20,2	40,8	19,9	19,0	0,40	1,6	1,6
							Average	†C_n	0,36± ±0,04	1,40± ±0,09	1,40± ±0,09

*K_M is the monomer conversion.

†The arithmetical mean values of the partial chain transfer constants and the mean-square errors are given.

TABLE 4. Telomerization of Propylene (M) with Propionic Acid (S)

Expt. No.	K_M, %	$[M]_H$, mmoles	$[S]_H$, mmoles	[M]/[S] average	Yield of telomers when based on sum T_n, mole % n=1–3		
					T_1	$T_2 + T_2'$	T_3'
14	52,3	23,8	114,5	0,153	52,7	21,5	25,7
15	31,9	23,8	105,0	0,191	54,6	19,6	25,8
16	22,3	26,2	90,7	0,257	57,3	20,5	22,2
17	23,8	27,4	85,2	0,284	62,4	15,8	21,8

their comparison with those of the previously studied compounds of analogous structure [4, 5] make it possible to identify the compounds T_2 and T_2' (the amount of T_2' exceeds that of T_2), and T_3' (identical with T_3'') in these fractions (Table 6). The fact that the principal compound belongs to the T_n' series indicates that a 1,3-migration of the H atom also goes to a quite high degree in the given case.

EXPERIMENTAL METHOD

The ^{13}C NMR spectra were obtained on a Brüker HX-90 spectrometer, using CCl_4 solutions of the compounds and TMS as the standard. The chemical shifts are given relative to TMS.

Telomerization of Propylene with Isobutyric Acid

Expt. 1. Into a rotating 2-liter steel autoclave were charged 800 g of isobutyric acid and 25 g of tert-butyl peroxide (TBP); the initial propylene pressure at 150°C was 40 atm. The reaction time was 3 h. The yield of the mixed telomers was 150 g (18% when based on the acid). The mixture of telomer (108.5 g) was fractionally distilled into fractions. Further fractional distillation through a column gave a fraction with bp 59-62° (3 mm), from which by preparative chromatography on a PAKhV-02 chromatograph, using a 1.1 m × 15 mm column packed with 15% E-301 deposited on Chromatone N-AW (0.16-0.20 mm), at 180 and 190°, was isolated a telomer that corresponds to T_1 in composition, and fractions with bp 92-93° (2 mm) and 97-103° (2 mm), which correspond to T_2 and T_3 in composition. The structure and composition of the telomers was confirmed by the ^{13}C NMR spectra and the elemental analysis data (see Tables 1 and 2).

Expts. 2-12. The experiments were run in 10-ml steel test tube autoclaves as described in [3]. Distilled TBP at a concentration of ~1 mole % was used as the initiator. The experiments were run at 150° for 90 min. The experimental conditions and the obtained

TABLE 5. Telomers Obtained from Propylene and Propionic Acid

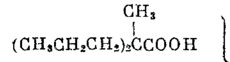
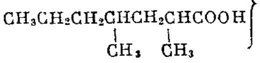
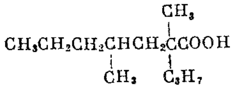
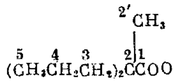
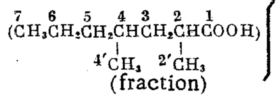
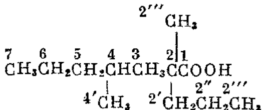
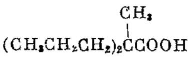
Compound	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR Found Calc.	Empirical formula	Found Calculated, % H	Found Calculated, % C
 $(CH_3CH_2CH_2)_2\overset{CH_3}{C}COOH$  $CH_3CH_2CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}COOH$	90—103(5)	1,4351	0,9137	45,16 45,21	$C_9H_{18}O_2$	11,20 11,39	69,51 68,35
 $CH_3CH_2CH_2\underset{CH_3}{CH}CH_2\overset{CH_3}{\underset{C_3H_7}{C}}COOH$	105—106(3)	1,4494	0,9050	46,84 45,21	$C_{10}H_{24}O_2$	11,00 12,00	71,32 72,00

TABLE 6. Data of ^{13}C NMR Spectra (δ, ppm from TMS)

Compound	C—COO	CH—COO	CH₃C—COO	CH₃—CH₂	CH₃CHC	C	CH	CH₂
 $(\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2)_2\overset{{}^{2'}CH_3}{\overset{2}{C}}\overset{1}{C}OOH$  $(\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\underset{{}^{4'}CH_3}{\overset{4}{C}H}\overset{3}{C}H_2\underset{{}^{2'}CH_3}{\overset{2}{C}H}\overset{1}{C}OOH)$ (fraction)	184,0	183,3	21,0(2') 20,5(2')	14,5(5) 13,8(7)	17,6(4')	45,2(2)	41,1—40,7(2) 30,3—30,1(4)	41,4(3) 17,6(4) 39,2—38,3(3) 37,0—37,1(5)
 $\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\underset{{}^{4'}CH_3}{\overset{4}{C}H}\overset{3}{C}H_3\overset{{}^{2'''}CH_3}{\underset{{}^{2'}CH_2\overset{2''}{C}H_2\overset{2'''}{C}H_3}{\overset{2}{C}}}\overset{1}{C}OOH$ (fraction)	184,7	(184,2)	21,2	15,0(2''') 14,2(7)	17,5(4')	46,8(2)	29,0(4)	20,0(2'') 19,7(6) 19,8(6) 45,4—45,1 43,2—42,1 41,1—40,1 (5, 3, 2')
 $(CH_3CH_2CH_2)_2\overset{CH_3}{C}COOH$ [5]	184,8	—	22,8	15,0	—	46,2	—	18,3 46,2

results are given in Table 3. The products were analyzed and identified by GLC on an LKhM-8MD chromatograph, using a 1 m × 4 mm column packed with 15% Carbowax deposited on Chromatone N-AW-DMCS (0.16-0.20 mm), a temperature of 180°, helium as the carrier gas, and detection based on the heat conductivity.

Telomerization of Propylene with Propionic Acid

Expt. 13. Into a rotating 0.5-liter steel autoclave that had been chilled were charged 200 g of propionic acid, 40 ml of propylene, and 5 g of TBP. Three experiments were run at 140°, and the reaction time was 3 h. The unreacted acid was distilled off, and the residues were combined (147.5 g) and fractionally distilled into fractions. Fractions with bp 90-103° (5 mm) and 105-106° (5 mm) were isolated by further fractional distillation through a column, from which by preparative chromatography on a PAKhV chromatograph (detection based on the heat conductivity, 1.1 m × 15 mm column packed with 15% E-301 deposited on Chromatone N-AW (0.16-0.20 mm), 180°) were isolated telomers that correspond to T_2 and T_3' in composition (see Table 5).

Expts. 14-17. The experiments were run the same as Expts. 2-12. The experimental conditions and obtained results are given in Table 4.

CONCLUSIONS

1. The telomerization of propylene with isobutyric and propionic acids were studied.

2. The partial chain transfer constants in the telomerization of propylene with isobutyric acid are substantially higher than in the reaction of carboxylic acids with ethylene.

3. The telomerization of propylene with propionic acid goes with rearrangement of the radicals, which includes a 1,3-migration of the H atom.

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