TELOMERIZATION OF ETHYLENE WITH ACETONITRILE AND CAPRONITRILE

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In [1] it was shown that rearrangement of the radicals by the scheme

 $\begin{array}{c} \begin{array}{c} \begin{array}{c} \text{Rearrangement} \\ \text{CH}_2\text$

occurs in the telomerization of ethylene with propionitrile. A measurement of the partial chain transfer constants (C_n) and relative isomerization constant (C_i) made it possible to conclude [2] that the efficiency of propionitrile as a chain transfer agent in the reaction with ethylene is close to that of methyl propionate. At the same time, the rearrangement of the radicals in the case of propionitrile is substantially less than in the reaction of ethylene with methyl propionate or propionic acid. A comparison of the behavior of the esters of carboxylic acids and their nitriles in telomerization was continued on the example of the reaction of ethylene with acetonitrile.

In the telomerization of ethylene with acetonitrile two series of telomer homologs $[3], H(CH_2CH_2)_n - CH_2CN$ (T_n) and $H(CH_2CH_2)_n - CHCN$ (T'n), were identified in the fraction of telomers that contain up to four

monomeric units in the molecule. The formation of the T'_n series can be explained by the rearrangement of the intermediately formed radicals $\dot{C}H_2CH_2CH_2CH_2CH_2CH_2CN$, with a 1,5-migration of the hydrogen atom analogous to Scheme (1) (R = H), and subsequent growth of the rearranged radical at the α -position to the nitrile group. The telomers of the T_n and T'_n series were identified by the GLC method, employing authentic specimens [3], and by the observance of a linear relationship between the logarithm of the retention times and the number of monomeric units in the molecule. The authentic telomers of the T'_n series (n = 3, 4) were also obtained by the telomerization of ethylene with capronitrile. The partial chain transfer constants (C_n) and the relative isomerization constant (C_i) were calculated as described in [1]. The experimental conditions and the obtained values of C_n and C_i are given in Table 1.

From the data on the C_n for the straight-chain series of telomers (T_n) it can be seen that the constants monotonically increase from C_1 to C_4 , while at the same time, if $C_2/C_1 \approx 2$, then $C_4/C_3 \approx 1.2$, i.e., the usual leveling out of the higher C_n is observed. The same as in the case of methyl acetate, all of the C_n values are very small (<0.1), which reflects the low efficiency of acetonitrile as a chain transfer agent in the reaction with ethylene. The relative isomerization constant in the reaction of acetonitrile with ethylene ($C_i \approx 0.9 \text{ mole}/liter$) is smaller than for propionitrile ($C_i \approx 2.9 \text{ mole}/liter$), i.e., the rearrangement of the radicals in the case of acetonitrile is substantially less than in the telomerization of ethylene with propionitrile. In the given case this relation is analogous to that observed in the corresponding carboxylic acid esters, and is apparently associated with the fact that the stability of the rearranged radicals $CH_3CH_2CH_2CRCN$ when $R = CH_3$ is higher than when R = H.

Previously we had shown that the rearrangement of the radicals in the telomerization of ethylene with propionitrile goes to less degree than for propionic acid and methyl propionate [2]. A similar tendency is also seen when the data on the C_i values are compared for acetonitrile (0.9) and methyl acetate

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к_и† , %	Mit. mmole		M/Si	A mount of telomer homologs with in monomeric units, mole %					C _n .10 ² ‡			
		sit. mmole		T ₁	T,	$\frac{T_{3}'}{T_{3}}$	$\frac{T_4'}{T_4}$	$\left \frac{\Sigma T_{n>4}}{\Sigma T_{n>4}} \right $	C1	C ₂	C ₃	C4
28,3	11,1	343	0,030	28,97	16,72	$\frac{17,88}{10,76}$	$\frac{2,98}{5,46}$	$\frac{10,60}{6,63}$	1,2	2,2	2,7	2,5
32,0	14,6	344	0,037	24,88	13,98	$\frac{16,35}{13,98}$	$\frac{3,55}{8,53}$	$\frac{10,42}{8,29}$	1,2	1,7	3,1	3,8
15,0	15,0	340	0,042	22,02	16,52	$\tfrac{14,28}{14,14}$	$\frac{3,87}{9,97}$	$\frac{9,83}{9,37}$	1,2	2,1	3,1	4,5
13,5	15,7	338	0,045	19,19	15,93	$\frac{13,17}{13,82}$	$\frac{3,41}{9,11}$	$\frac{11,70}{13,65}$	1,1	2,0	2,8	3,0
24,0	18,6	344	0,050	19,21	14,49	$\frac{12,28}{13,07}$	$\frac{3,46}{8,03}$	$\tfrac{15,46}{14,01}$	1,2	2,1	3,0	2,9
25,4	21,8	344	0,058	16,36	15,14	$\frac{9,16}{14,04}$	$\tfrac{3,66}{12,09}$	$\tfrac{12,82}{16,72}$	1,1	2,0	2,8	4,2
23,0	36,8	344	0,100	9,49	16,86	$\frac{5,64}{15,69}$	$\tfrac{2,65}{12,67}$	$\tfrac{11,82}{25,15}$	1,0	3,2	4,1	5,0
29,0	50,0	342	0,130	8,53	14,51	$\frac{4,34}{13,76}$	$\left \frac{2,17}{12,19} \right $	$\frac{13,17}{31,34}$	1,2	3,3	4,1	5,1
11,0	44,3	302	0,140	8,45	14,25	$\left \frac{4,95}{12,63}\right $	$\left \frac{2,47}{12,29} \right $	$\frac{15,69}{29,26}$	1,3	3,7	4,3	5,9
	$C_i \approx 0.9 \text{ mole/lite}$								$^{1,2\pm}_{\pm 0,03}$	2,5+ $\pm 0,2$	$3,3\pm \pm 0,2$	4,1+ $\pm 0,3$
	C_n^{total} 10 ² **						*	1,2	1,5	3,4	3,2	

TABLE 1. Telomerization of Ethylene with Acetonitrile (150°, tertbutyl peroxide)*

*The experiments were run in 10-ml stainless steel autoclaves.

 $^{\dagger K}M$ is the monomer conversion; M_i and S_i are the initial charges of monomer and telogen,

#See [1] for the calculation equations and experimental procedure.

**Data for the "total" series, obtained by adding the yields of the telomers with the same number of monomeric units in the molecule,

(1.5) [4]. It is quite probable that the difference in the polar characteristics of the functional groups and the corresponding radicals plays a definite role here.

A low degree of rearrangement has a substantially smaller effect on the character of the change in C_n^{total} with increase in n for the total series of telomers * (cf. [1]) (see Table 1). In this case a minimum is not observed when n = 2, but only a retardation in the growth of C_n^{total} from C_1^{total} to C_2^{total} .

$$(C_2^{\text{total}}/C_1^{\text{total}} = 1.2; C_3^{\text{total}}/C_2^{\text{total}} = 2.3)$$

The telomerization of ethylene with capronitrile goes in a complex manner and gives a series of secondary products; this reaction was studied only qualitatively. From the mixture of telomers by fractional distillation we isolated and characterized the telomers $H(CH_2CH_2)_nC(C_4H_9)HCN$ with n = 1, 2 (Table 2). Their structure was confirmed by the data of the ¹³C NMR spectra (Table 3). The ¹³C NMR spectra of the fraction, containing mainly the telomers with n = 3, revealed that it contains two types of telomers, $H(CH_2CH_2)_nC(C_4H_9)HCN$ (T'_n , n = 3) and $H(CH_2CH_2)_nC(C_4H_9)_2CN$ (T''_m , m = 1). The appropriate assignments of the signals were made employing the ¹³C NMR spectra that were taken without suppressing the coupling with the protons, and also by analogy with the assignment of the signals in the spectra of the carboxylic acids and their esters [5], whose structure is close to that of the studied nitriles (see Table 3). The presence of a CH₃CH₂ group in series with a quaternary carbon atom ($\delta_{13}CH_3-CH_2 = 8.4$ ppm) is characteristic for the T''_m compounds (m = 1) (see Table 3, compound 6a), whereas the signal of the carbon of the $^{13}CH_3$ - CH₂ group, adjacent to a tertiary carbon atom (see Table 3, compound 4), has $\delta_{13}CH_3-CH_2 = 11.3$ ppm; the signal of the carbon of the $^{13}CH_3(CH_2)_3$ group is found further downfield ($\delta_{13}CH_3(CH_2)_3 = 13.7-13.9$ ppm), and its chemical shift is independent of the character of the carbon atom to which the CH₃(CH₂)₃-group is attached.

The presence of compounds of the $T_m^{"}$ type in the mixture of telomers (in the case of capronitrile) shows that rearrangement of the radicals, with a 1,5 migration of the hydrogen atom [analogous to Scheme (1), $R = C_4 H_9$], also occurs here.

*This series was obtained by adding the yields of telomers with the same molecular weight.

	Ba °C (n mm	Yield when			Found	,%	Calculated,%	
Telomer	of Hg)	based on sum of T_1 - T_3 ,%*	d_4^{20}	²⁰ nD	∽ c	н	Ċ	н
$T_1 \\ T_2 \\ T_3' + T_3''$	80 (9) 100 (2) 102 (2) 108 (2)	41,7 23,0 20,5	0,8245 0,8335 —	1,4204 1,4298 	77,15 77,88	11,93 12,36	76,80 78,43	12,00 12,41

TABLE 2. Telomerization of Ethylene with Capronitrile

*The unidentified products constitute 14.8% of the sum of the T_n products, n = 1-3.

TABLE 3. Data of ¹³C NMR Spectra

		8 ₁₃ CN			δ ₁₃₍	C-CN	δ ₁₃ _{GH₃-(CH₂)_n-ζ-}		δl3CH2	
No.	Nitriles	-C-CN	>CH-CN	-CH2-CN	-CH<	CH2	$\begin{bmatrix} \mathbf{C}\mathbf{H}_3 - \mathbf{C}\mathbf{H}_2 \\ (n = 1) \end{bmatrix}$	$\frac{\mathrm{CH}_{\mathrm{s}}(\mathrm{CH}_{\mathrm{s}})_{n}}{(n \ge 3)} -$	CH2-CH3	-CH2-
1	CH₃CH₂CN	_	-	120,7		10,5	10,3	_		_
2	CH ₃ (CH ₂) ₂ CH ₂ CN	· _ `		119,2	_	21,7		13,0	16,4	27,3
3	CH ₃ (CH ₂) ₃ CH ₂ CN		-	119,2	—	21,8	_	13,5	16,6	$25,1\\30,6$
4	CH3(CH2)3CHCN CH2CH3		121,1		33,0	-	41,3	13,7	25,6 (Et) 22,2 (Bu)	29,2 $31,6$
5	CH3(CH2)3CHCN (CH2)3CH3		120,5 (120,9)		31,3			13,7	22,1	29,1 31,9
6	(CH ₂) ₃ CH ₃	122,6					8,4		26,3 (Et)	27,0
	a) $CH_3(CH_2)_3C-CN$							13,8	22,7(Alk)	28,7 29,1
	b) CH3(CH2)5CHCN (CH3)5CH3 (fraction)		120,9		33,9			13,9		31,9 35,3 35,8

A relation between the shielding of the ¹³C nuclei of the nitrile group and the structure of the hydrocarbon radical attached to it was observed when the chemical shifts of the signals of the nuclei of the ¹³C atoms of the investigated compounds were examined.* The total range of change in the ¹³CN chemical shifts is ~6 ppm. Here the ¹³CN signal is successively shifted downfield with increase in the branching of the α -carbon atom (see Table 3, Nos. 3-6). In general, a similar phenomenon is characteristic for compounds of the R-X type (X = ¹³CN, ¹³COO [5], ¹³CH₃ [8]) and, as a result, can be used to identify these derivatives in mixtures. The deshielding of the α -carbon atom of the discussed compounds proceeds in a similar manner with increase in the number of added radicals (see Table 3, compounds 1-3 and 4-6).

EXPERIMENTAL METHOD

The 13 C NMR spectra were taken on a Bruker-Physik HX-90 instrument, on the δ -scale from TMS.

<u>Telomerization of Ethylene with Acetonitrile.</u> The telomeric mixtures were analyzed and identified by the GLC method, employing authentic specimens, and by the observance of a linear relationship between the logarithms of the retention times and the molecular weight; the results are given in Table 1. The chromatograms were calculated by the internal normalization method without making any corrections; we used a 2-m column, 20% of the liquid phase SKTPT-50 deposited on Chromosorb W (80-100 mesh), helium as the carrier gas, and both heat-conductivity and flame-ionization detection.

Telomerization of Ethylene with Capronitrile. Into a rotated 0.5-liter steel autoclave were charged 200 g of capronitrile and 8 g of tert-butyl peroxide. The ethylene pressure was 40-50 atm. The autoclave was heated at $145-150^{\circ}$ for 2 h. The ethylene was pumped in as it was absorbed. Two experiments were run in a similar manner. The capronitrile was distilled off (up to 56 deg/10 mm), and the residues were combined (68.8 g) and fractionally distilled through a column; the results are given in Table 2.

^{*}The obtained results are in agreement with the measurements given in [6]. However, the data given in [7] are found to contradict both our data and those given in [6]. The signals of these groups were also initially identified by the $J_{13}C_{-H}$ value, which is 130-135 Hz and, as a result, is noticeably different from the value that is characteristic for the ordinary alkyl chain (125-126 Hz).

CONCLUSIONS

1. The telomerization of ethylene with acetonitrile and capronitrile goes with a rearrangement of the radicals and a 1,5 migration of the hydrogen atom.

2. A measurement of the partial chain transfer constants and the relative isomerization constant in the telomerization of ethylene with acetonitrile revealed that the rearrangement goes to less degree in the given reaction than in the reactions of ethylene with methyl acetate, propionitrile, and methyl propionate.

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