TELOMERIZATION OF ETHYLENE BY METHYL METHOXYACETATE

N. S. Ikonnikov, N. I. Lamova,
A. B. Terent'ev, and R. Kh. Freidlin

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The radical telomerization of ethylene by telogens of the type XCH_2CO_2R (X = H, CH_3, C_4H_9, Cl; R = H, CH_3) is achieved by the rupture of the α-C–H bond and is accompanied by the regrouping of radicals involving the 1,5-migration of a H atom. To an appreciable extent, the nature of the substituent X determines the relative reactivity of the telogens and the radicals formed from them, as well as the structure and distribution of the final telomerization products [1]. It was of interest to extend the boundaries of research using as telogens carboxylic acids and their derivatives containing X substituents of a different type, including, in particular, a heteroatom at the α-C atom of the telogen. The present investigation deals with a study of the peroxide-initiated telomerization of ethylene by methyl methoxyacetate (MMA) (I) (Table 1).

After telomerization individual compounds having both linear and branched hydrocarbon chains were isolated from the reaction mixture and identified (see Table 1). A series of straight-chain telomers T_n (IV)-(VI) is formed according to a general telomerization scheme, including the rupture of the α-C–H bond of the telogen, the growth of the radicals formed, and chain transfer by the growing radicals:

$$CH_3OCH_2CO_2CH_3\,(S) + (CH_3)_3CO^{\cdot} \rightarrow CH_3O\dot{C}HCO_2CH_3\,(A)$$
$$\phantom{CH_3OCH_2CO_2CH_3\,(S) + (CH_3)_3CO^{\cdot}} \rightarrow \dot{C}H_2OCH_2CO_2CH_3\,(B)$$

$$2A \rightarrow \underset{(VIII)}{\begin{matrix} CH_3OCHCO_2CH_3 \\ | \\ CH_3OCHCO_2CH_3 \end{matrix}}$$

$$A + nCH_2{=}CH_2\,(M) \rightarrow \dot{(}CH_2CH_2)_n\underset{}{\overset{OCH_3}{\overset{|}{C}}}HCO_2CH_3\,(C_n)$$

$$C_n + CH_3OCH_2CO_2CH_3 \rightarrow CH_3O\dot{C}HCO_2CH_3 + H(CH_2CH_2)_n\underset{\underset{OCH_3}{|}}{C}HCO_2CH_3\,(T_n)$$

To a comparatively small extent (up to 1.9 mole %), the direction of the reaction is also determined by the rupture of the C–H bond in the α-methoxy group, which leads to the formation of methyl propoxyacetate (II):

$$B + CH_2{=}CH_2 \xrightarrow{S} (II)\,(T_1^M)$$

A series of α-methoxy-substituted branched telomers (X) and (XIII) is formed as a result of the regrouping of the radicals C_2, involving the 1,5-migration of a H-atom:

$$\dot{C}H_2CH_2CH_2CH_2\overset{OCH_3}{\overset{|}{C}}HCO_2CH_3 \xrightarrow{1,5\text{-}H} CH_3CH_2CH_2CH_2\overset{OCH_3}{\overset{|}{\dot{C}}}CO_2CH_3\,(D)$$

$$D + (n-2)CH_2{=}CH_2 \xrightarrow{S} CH_3CH_2CH_2CH_2\overset{OCH_3}{\overset{|}{\underset{\underset{(CH_2CH_2)_{n-2}H}{|}}{C}}}CO_2CH_3\,(T_n')$$

A particular feature of the given system is that the regrouped radicals D are fixed both in the form of telomers in the series T_n' and products from the recombination with the radicals A, which reflects a fairly prolonged lifetime for the radicals D and indicates the high stabilizing effect of the methoxy group:

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TABLE 1. ^{1}H and ^{13}C NMR Spectral Data and Elemental Analysis Methoxyacetate

Compound	NMR spectrum	COO	CH_3O	C
$CH_3^{3}OCH_2^{2}CO_2^{1}CH_3^{1'}$ (S) (I)	^{1}H		3,39 s (1′) 3,38 s (3)	–
	^{13}C	170,0	50,3 (1′) 58,4 (3)	
$CH_3^{5}CH_2^{4}CH_2^{3}O^{2}CH_2^{1}CO_2^{1'}CH_3$ (T_1^M) (II)	^{1}H		3,67 s (1′)	–
	^{13}C	169,5	50,6	
$CH_3CH_2CH_2CH_2CH_2OCH_2CO_2CH_3$ (T_2^M) (III)	^{1}H		3,74 s (1)	–
	^{13}C	169,7	50,7	
$CH_3CH_2CHCO_2CH_3$ (T_1) OCH_3 3′ (IV)	^{1}H		3,72 s (1′) 3,32 s (3′)	–
	^{13}C	171,4	50,7 (1′) 57,3 (3′)	
$CH_3CH_2CH_2CH_2CHCO_2CH_3$ (3′ OCH_3) (T_2) (V)	^{1}H		3,70 s (1′) 3,32 s (3′)	–
	^{13}C	171,6	50,7 (1′) 57,3 (3′)	
$CH_3CH_2CH_2CH_2CH_2CH_2CHCO_2CH_3$ (3′ OCH_3) (T_3) (VI)	^{1}H		3,67 s (1′) 3,29 s (3′)	–
	^{13}C	171,6	50,7 (1′) 57,3 (3′)	
$CH_3CH_2CHCO_2CH_3$ $OCH_2^{3'}CH_2^{4'}CH_3^{5'}$ (T'_2) (VII)	^{1}H		3,68 s	–
	^{13}C	171,7	50,6	
$CH_3OCHCO_2CH_3$ $CH_3OCHCO_2CH_3$ (D_S) (VIII)*	^{1}H a)		3,70 s (1′) 3,37 s (3)	–
	^{13}C a)	168,2	51,2 (1′) 58,4 (3)	
	^{1}H b)		3,71 s (1′) 3,37 s (3)	–
	^{13}C b)	168,5	51,3 (1′) 58,7 (3)	
$CH_3CH_2CH_2CH_2C(CO_2CH_3)(CH_2^{3'}CH_3^{4'})(CH_2CH_3)$ (T_4^e) (IX)	^{13}C	175,6	50,6	49,1
$CH_3CH_2CH_2CH_2C(CO_2CH_3)(OCH_3^{3''})(CH_2CH_3)$ (T_3') (X)	^{1}H		3,66 s (1′) 3,16 s (3″)	–
	^{13}C	172,9	50,7	82,3
$CH_3CH_2CH_2CH_2C(CO_2CH_3)(OCH_3^{3''})(CH_2CH_3)$ (XI) $CH_3OCHCO_2CH_3$ (5′ 3′ 4′ 4″) (D′)*	^{1}H		3,76 s (4″) 3,70 s (1′) 3,29 s (3″) 3,47 s (5′)	
	^{13}C a)	170,1 168,5	50,9 51,1 (1′, 4″) 58,5 (5′) 54,6 (3″)	86,1
	^{1}H b)		3,67 s (1′, 4″) 3,38 s (5′) 3,24 s (3″)	
	^{13}C b)	170,8 168,7	51,0 51,3 (1′, 4″) 58,9 (5′) 51,8 (3″)	85,0
$(CH_3CH_2CH_2CH_2)_2C(CO_2CH_3)(CH_2^{3'}CH_3^{4'})$ (T_5^e) (XII) †	^{13}C	176,0	50,6	48,9
$(CH_3CH_2CH_2CH_2)_2C(CO_2CH_3)(3'\ OCH_3)$ (T_4') (XIII)		173,2	50,8 (1′) 50,6 (3′)	82,2
$CH_3OCHCO_2CH_3$ $CH_3OCHCO_2CH_3$ (D_S) (VIII)		168,5 168,7	51,3 (1′) 58,2 58,6 (3)	–

*Data are presented for the individual compounds a) and b).
†Compounds (XII), (XIII), and (VIII) are presented in the

of the Products from the Telomerization of Ethylene by Methyl

CH	$CH_3\underline{CH_2}$	CH_2	Found / Calc., % C	Found / Calc., % H
–	–	3,97 s 69,1	46,43 46,15	7,87 7,74
– –	0,94 t 10,3	3,92 s (2), 3,40 t (3), 1,53 m (4) 72,8 (2), 67,6 (3), 22,7 (4)	– –	– –
–	0,97 t 13,8	4,00 s (2), 3,51 t (3), 1,48 m (4, 5, 6) 71,2 (2), 67,7 (3), 28,1 (4) 29,2 (5), 22,3 (6)	60,22 59,97	10,03 10,07
3,70 m	0,89 t	1,67 m	–	–
81,2	9,3	25,8		
3,70 m	0,90 t	1,40 m	–	–
80,1	13,7	32,3 (3), 27,1 (4), 22,2 (5)		
3,67 m	0,89 t	1,28 m	63,63 63,79	10,78 10,71
80,1	13,8	32,6 (3), 24,9 (4), 28,8 (5), 31,5 (6), 22,4 (7)		
3,65 m 79,8	0,94 t (4, 5') 9,5 (4), 10,5 (5')	1,65 m (3, 4'), 3,34 m (3') 71,6 (3'), 25,9 (3), 22,8 (4')	–	–
3,96 s	–	–		
80,9	–	–		
4,07 s	–	–	46,45 46,60	6.89 6,84
80,8	–	–		
–	8,2 (4'), 13,8 (6)	33,3 (3), 26,3 (3'), 26,0 (4), 23,0 (5)	–	–
0,80 t (4') 0,92 t (6)				
–	13,8 (6), 7,3 (4')	1,66 m (3; 3'), 1,29 m 33,0 (3), 26,3 (3'), 25,1 (4), 22,8 (5)	63,30 63,79	10,84 10,71
4,01 s	0,89 t	1,63 m (3), 1,22 m	54,91 54,94	8,46 8,47
84,2	13,7	35,7 (3), 25,6 (4), 22,6 (5)		
4,09 s	0,91 t	1,70 m (3), 1,28 m		
83,8	13,8	30,6 (3), 25,2 (4), 22,7 (5)		
–	8,1 (4'), 13,7 (6)	33,7 (3), 26,4 (3'), 26,0 (4), 23,0 (5)		
–	13,7	33,5 (3), 25,1 (4), 22,8 (5)		
80,9 81,0	–	–		

form of fractions.

TABLE 2. Experimental Data and Chain Transfer Constants (C_n) in the Telomerization of Ethylene by Methyl Methoxyacetate (150°C, 0.01 mole % of TBP, 20 min)

Expt. No.	S_H (mmoles)	M_H (mmoles)	K_S (%)	K_M (%)	Yield of telomers from sum of react. products, %	Average [M]/[S]	Content of telomer homologs having n monomeric units, mole% ‡													C_n							
							T_1	T_2	T_4^0	$\frac{T_3'}{T_3}$	T_5^0	$\frac{T_4'}{T_4}$	T_6^0	$\frac{T_5'}{T_5}$	D′	T^0_7	$\frac{T_6'}{T_6}$	$\sum_{n\geq 8} T_n^0$	$\frac{\sum_{n\geq 7} T_n'}{\sum_{n\geq 7} T_n}$	C_1	C_2	C_3'	C_3	C_4'	C_4	C_5'	C_6
1 *	145,63	85,71	15,1	54,8	21,7	0,46	46,3	12,4	2,4	$\frac{3,5}{6,7}$	1,3	$\frac{2,1}{4,3}$	0,7	$\frac{1,1}{2,2}$	9,7	0,3	$\frac{0,5}{0,9}$	0,3	$\frac{0,3}{0,6}$								
2	67,53	8,57	0,3	3,5	0,4	0,12	71,7	11,0	2,1	$\frac{3,3}{3,4}$	0,7	$\frac{1,6}{1,5}$	—	—	4,7	—	—	—	—	0,30	0,27	0,25	0,27	—	—	—	—
3	66,85	14,64	0,4	3,4	0,6	0,21	57,2	13,3	3,1	$\frac{4,7}{6,0}$	1,6	$\frac{2,7}{3,5}$	0,7	$\frac{0,9}{1,0}$	5,0	—	—	—	—	0,28	0,26	0,27	0,26	—	—	—	—
4	68,01	22,86	0,6	4,1	1,0	0,33	46,7	14,2	3,5	$\frac{5,5}{8,0}$	2,4	$\frac{2,9}{4,4}$	0,9	$\frac{1,5}{2,2}$	4,0	0,3	$\frac{0,7}{1,0}$	0,2	$\frac{0,7}{0,9}$	0,29	0,29	0,31	0,31	0,33	0,35	0,35	0,38
5	66,85	28,21	0,7	4,4	1,2	0,41	39,0	14,1	2,7	$\frac{5,2}{9,1}$	2,7	$\frac{4,0}{5,7}$	1,0	$\frac{2,0}{3,2}$	4,0	0,4	$\frac{1,0}{1,7}$	0,5	$\frac{1,5}{2,2}$	0,26	0,26	0,23	0,29	0,36	0,33	0,33	0,34
6	67,05	33,57	0,6	3,2	1,1	0,49	32,6	13,0	3,4	$\frac{6,2}{9,2}$	2,9	$\frac{4,2}{5,9}$	1,0	$\frac{2,6}{4,2}$	2,2	0,6	$\frac{1,7}{2,6}$	1,0	$\frac{2,4}{4,3}$	0,24	0,24	0,28	0,27	0,31	0,26	0,31	0,30
7	66,76	40,71	0,8	4,2	1,6	0,60	29,9	14,4	2,2	$\frac{5,3}{10,5}$	2,0	$\frac{3,6}{7,3}$	0,8	$\frac{2,3}{4,7}$	2,5	0,4	$\frac{1,5}{3,0}$	0,8	$\frac{3,4}{5,4}$	0,26	0,28	0,29	0,31	0,30	0,33	0,28	0,33
8	66,86	45,00	1,0	5,4	1,9	0,66	26,7	13,2	1,7	$\frac{5,9}{10,0}$	1,6	$\frac{3,4}{7,3}$	0,8	$\frac{2,6}{5,5}$	1,4	0,4	$\frac{1,8}{3,8}$	1,1	$\frac{3,2}{9,6}$	0,24	0,24	0,35	0,25	0,30	0,25	0,34	0,27
9	71,18	57,14	1,5	7,4	3,0	0,78	23,0	13,6	1,0	$\frac{4,1}{10,8}$	1,2	$\frac{3,2}{8,5}$	0,5	$\frac{2,4}{6,0}$	1,2	0,4	$\frac{1,8}{4,5}$	0,8	$\frac{4,9}{12,1}$	0,23	0,25	0,26	0,27	0,27	0,29	0,28	0,29
																				† 0,26± ±0,03	0,26± ±0,02	0,28± ±0,04	0,28± ±0,02	0,31± ±0,03	0,30± ±0,04	0,31± ±0,03	0,32± ±0,04

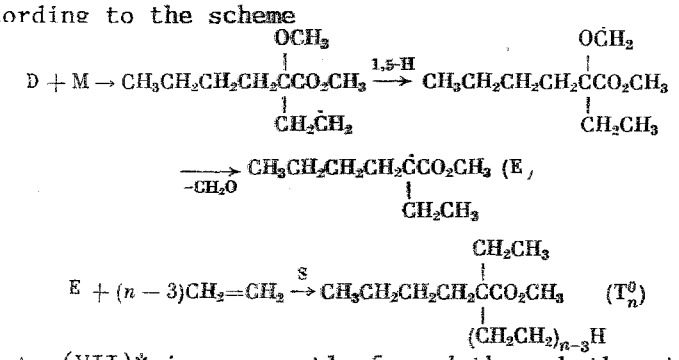
*Content of T_1^M = 1.9 and T_2' = 2.5 mole %.

†The mean arithmetic values and the mean square errors are presented.

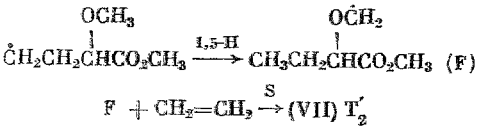
‡ T_n—$H(CH_2CH_2)_nCH(OCH_3)CO_2CH_3$; T'_n—$H(CH_2CH_2)_{n-2}C(C_4H_9)(OCH_3)CO_2CH_3$; T^0_n—$H(CH_2CH_2)_{n-3}C(C_2H_5)(C_4H_9)CO_2CH_3$.

$$D + A \longrightarrow (XI)$$

Another important feature of the telomerization of ethylene by MMA is the formation of products having a branched structure and not containing the methoxy group at the α-C atom [T_n^0, (IV), (XII)] according to the scheme



Methyl 2-propoxybutanoate (VII)* is apparently formed through the stage of 1,5-migration of the H atom from the methoxy group to the radical C_1 but without subsequent fragmentation:



The general reaction scheme suggested on the basis of the results obtained provided the possibility of comparing the reactivity of the radicals at the chain growth and transfer stages. The particular chain transfer constants for non-regrouped (C_n) and regrouped (C_n') radicals are presented in Table 2. The given system is the first example in a series of studies of the telomerization of ethylene by the methyl esters of carboxylic acids [1], where the values of C_n and C_n' are virtually constant, irrespective of the chain length of the radical. The contrast between the results obtained with data on the telomerization of ethylene by methyl chloroacetate is very clear, where the C_n values increase with an increase in n: $C_1 = 0.07$; $C_2 = 0.13$; $C_3 = 0.18$; $C_4 = 0.18$. A similar variation in C_n was always observed for other examples of telomerization. It is caused by a decrease in the polar effect of the functional group and the substituent on the reactivity of the radicals at the chain transfer stage.

Thus, based on the constancy of the values of C_n for the telomerization of ethylene by MMA, it can be considered that in radicals of the type $CH_2CH_2(CH_2CH_2)_{n-1}CR(OCH_3)COOCH_3$ (R = H, alkyl) the α-methoxyl substituent compensates the polar effect of the carbomethoxyl group.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra of the compounds isolated (~20% solutions in CCl_4, TMS) were recorded on Hitachi-Perkin-Elmer R-12 (60 MHz) and Bruker WP-200 (50.31 MHz) instruments. Analytical GLC: a 2000 × 3 mm stainless steel column containing 20% SKTFT-50 on 80-100 mech Chromosorb W; temperature programming from 100°C at a rate of 4 deg/min; helium flow rate 55 ml/min; katharometer. The weight content of the unreacted telogen and reaction products was calculated from the peak areas of the corresponding components by the internal standard method (methyl propionate for the telogen, methyl pentoxyacetate for the reaction products) followed by normalization. Preparative GLC: stainless steel columns: 1) 1300 × 9 mm containing 20% SKTFT-50 on Chromaton N-AW, 0.16-0.20 mm, 100, 140°C; 2) 2600 × 9 mm, the same phase, 152°C; helium flow rate 120 ml/min, katharometer.

Telomerization of Ethylene by Methyl Methoxyacetae (MMA). The experiments to determine the chain transfer constants C_n (calculated from the Mayo equation [2]) were conducted with 10-ml stainless steel autoclaves by the procedure described in [3]. The experimental conditions and the GLC analytical data are presented in Table 2. The telomerization products were produced in 28-ml stainless steel autoclaves. In an experiment we used 15 g MMA, 2.4 g ethyl-

*Other pathways can be suggested for the formation of compounds of the type T_n^0 and methyl 2-propoxybutanoate, e.g., from the radicals C by a combination of the stages of chain growth and transfer, fragmentation, and regrouping. However, the absence in the reaction mass of intermediate products from the stabilization of radicals – esters of the lower acids of linear structure, and esters of 2-ethylbutanoic and 2-ethylhexanoic acids – permits the schemes indicated above to be considered as most probable.

ene, and 1.0 g tert-butyl peroxide (TBP); 140°C, 4 h. The reaction masses of five experiments were combined, and after distilling of the unreacted telogen 18 g of the product mixture was separated into narrow fractions (residue 2.3 g), from which the individual products were isolated by preparative GLC (see Expt. 1).

Analysis of the ^{13}C NMR Data. For all the compounds in the T_n series signals from the CH_3O group at the α-C atom (53.7 ppm) and the α-C atom itself (80.1-81.2 ppm) are characteristic, and a signal from the CH_3CH_2 group at the tertiary C atom is also characteristic for T_1 (9.3 ppm).

Besides linear products, we identified the branched products (X) and (XIII) containing the CH_3O, CH_3CH_2 (7.3 ppm), and C_4H_9 groups (X) and CH_3O and two C_4H_9 groups (XIII) at the quaternary α-C atom, which enabled us to assign structures T_3 and T_4, respectively, to them. In the structurally similar compounds (IX) (T_4^0) and (XII) (T_5^0) C_2H_5 is found in (IX) instead of the fragment CH_3O, while in (XII) the C_4H_9 group is found. Compound (XI) would seem to consist of fragments of two components. On the one hand, this is a radical of the initial telogen [cf. (VIII) in Table 1] and, on the other, it is a grouping of (X), including the CH_3COO, CH_3O, and C_4H_9 groups at the quaternary α-C atom. Component (VII) contains CH_3CH_2 (9.5 ppm) and $CH_3CH_2CH_2O$ [cf. (II) in Table 1] at the tertiary α-C atom and is methyl 2-propoxybutanoate.

CONCLUSIONS

1. The telomerization of ethylene by methyl methoxyacetate takes place principally as a result of the rupture of the α-C—H bond in the telogen and is accompanied by regrouping of the radicals (involving the 1,5-migration of the H atom), cross-recombination, and fragmentation, as a result of which six types of reaction products are formed.

2. The absence of a polar effect from the methoxycarbonyl group on the reactivity of radicals of the type $CH_2CH_2(CH_2CH_2)_{n-1}CR(OCH_3)COOCH_2$ (R = H or alkyl) is caused by the compensating effect of the α-methoxyl substituent.

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