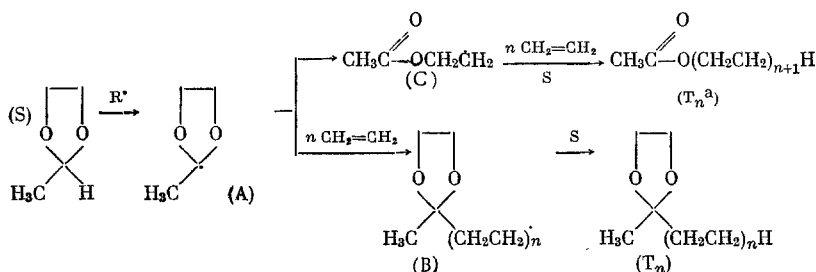


TELOMERIZATION OF ETHYLENE WITH
2-METHYL-1,3-DIOXOLANE

V. P. Nayanov, D. L. Rakhmankulov,
S. S. Zlotskii, and A. B. Terent'ev

UDC 66.095.2:547.313.2

The action of radical initiators or UV light on 1,3-dioxanes that have a hydrogen atom in the 2 position leads to the cleavage of a hydrogen atom from the 2 position; the thus formed radical can add to an unsaturated compound to give a 2-alkyl-1,3-dioxane [1]. This radical can also be isomerized to give, after hydrogen cleavage, the ester (analogous to that shown in the scheme). In the present paper we examined the possibility of telomerizing ethylene with 2-methyl-1,3-dioxolane. Substitution of the dioxolane in the 2 position excludes involvement of the second hydrogen atom in the reaction. The telomerization of ethylene with 2-methyl-1,3-dioxolane was run in the presence of either tert-butyl peroxide (TBP) at 150°C or benzoyl peroxide (BP) at 90°. Two series of telomers were identified in the reaction mixture, namely 2-methyl-2-alkyl-1,3-dioxolanes (T_n) and alkyl acetates (T_n^a) (S = telogen). The formation of the



The formation of the acetates T_n^a is associated with opening of the ring in radical A and subsequent reaction of the isomeric radical C with ethylene. The alkyl dioxolanes T_n are obtained by the usual telomerization scheme. The telomers T_n ($n = 1-3$) and acetates T_n^a ($n = 2-4$) were identified in the reaction mixture by GLC employing two phases of different polarity and authentic specimens, which were obtained by reacting ethylene glycol with the appropriate methyl ketones. The higher telomers of both series were identified via the fact that the linear relation $\log \tau - n$ was obeyed. The amount of acetates increases with increase in the reaction temperature. Up to 5% of acetates T_n^a , when based on the sum of all of the telomers, is formed at 90°, while at 150° their yield reaches 20%. The yield of T_n^a also increases with increase in the monomer conversion. However, at close monomer-telogen ratios the distribution of the telomers by molecular weight is but slightly dependent on the reaction temperature.

The partial chain transfer constants for the dioxolane series ($C_n = k_{tr}/k_{pn}$, where k_{tr} and k_{pn} are the rate constants of the chain transfer and growth reactions for the radical with n monomeric units) were calculated from the data of the experiments where the yield of acetates did not exceed 5-10% (Tables 1 and 2). The monomer-telogen ratio was varied by 6-7 times. The degree of filling the autoclave was 80-90%, and the monomer conversion did not exceed 30%.

From Tables 1 and 2 it can be seen that C_n is small (~ 0.2) for all of the growing radicals and shows little change either with increase in the chain length of the telomer radical or when the reaction temperature is increased from 90 up to 150°.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 594-597, March, 1975. Original article submitted June 10, 1974.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Telomerization of Ethylene with 2-Methyl-1,3-Dioxolane (90°, Benzoyl Peroxide 0.5%)*

Expt. No.	SH, immoles	MH, immoles	K _M , mole %	(M/S) _{av}	Amount of telomer homologs with n monomeric units, mole %					C ₁	C ₂	C ₃	Yield of acetates, %†
					T ₁	T ₂	T ₃	T ₄	T _{n>4}				
					1	78.4	13.0	25.0	0.15				
2	85.6	41.0	33.6	0.40	25.9	20.4	16.5	9.8	27.3	0.24	0.16	0.18	5.1
3	74.0	35.0	11.0	0.50	37.3	24.6	14.4	8.0	15.5	0.30	0.32	0.30	2.8
4	77.5	45.0	18.4	0.55	25.7	19.9	14.3	10.3	29.5	0.19	0.20	0.20	3.7
5	70.0	40.0	9.8	0.56	38.0	26.0	10.7	8.3	17.0	0.34	0.38	0.24	2.3
6	88.8	70.0	31.0	0.70	17.4	18.8	12.4	10.9	40.4	0.15	0.20	0.17	5.0
C_{av}										0.23±0.04	0.28±0.04	0.22±0.04	

*M_H and S_H are the initial charges of monomer and telogen; K_M is the monomer conversion.

†Based on the sum of the products.

TABLE 2. Telomerization of Ethylene with 2-Methyl-1,3-Dioxolane (150°, tert-Buyl Peroxide 0.007-0.02%)

Expt. No.	SH, immoles	MH, immoles	K _M , mole %	(M/S) _{av}	Amount of telomer homologs with n monomer units, mole %					C ₁	C ₂	C ₃	Yield of acetates, %*
					T ₁	T ₂	T ₃	T ₄	T _{n>4}				
					7	80	10.0	30	0.10				
8	84	17.0	32	0.20	47.4	24.9	12.3	7.7	7.6	0.18	0.18	0.17	9.9
9	90	20.0	40	0.20	55.2	23.3	10.8	5.5	5.2	0.24	0.20	0.20	10.5
10	80	20.0	25	0.25	44.5	23.4	11.3	7.4	13.3	0.20	0.17	0.15	8.7
11	75	27.0	28	0.36	46.5	22.5	11.2	8.0	11.0	0.30	0.26	0.23	8.8
12	84	33.0	27	0.40	32.6	20.6	13.4	10.0	13.4	0.19	0.17	0.16	8.6
13	70	33.0	20	0.48	30.2	19.8	14.4	11.1	27.2	0.20	0.18	0.19	7.9
14	60	30.0	28	0.50	33.0	19.0	14.0	10.1	16.9	0.21	0.16	0.16	8.9
15	70	38.0	27	0.54	35.7	20.5	14.3	10.4	19.1	0.29	0.24	0.25	8.8
16	60	40.0	32	0.67	29.2	18.3	14.2	11.4	26.3	0.27	0.22	0.24	10.0
C_{av}										0.23±0.01	0.19±0.01	0.19±0.01	

*Based on sum of products.

TABLE 3. Telomerization of Ethylene with 2-Methyl-1,3-Dioxane (150°, Duration of Experiments 0.5 h)

Expt. No.	TBP, mole %	(M/S) _{av}	Ethylene conversion, %	Yield, in mole % of		Amount of telomer homologs with n monomeric units (dioxolanes/acetates)				
				dioxolanes	acetates	T ₁	T ₂	T ₃	T ₄	T _{n > 4}
17	0,23	0,34	83	81,3	18,7	51,2	25,2	11,0	5,9	6,7
						42,3	22,3	8,9	6,7	19,8
18	0,23	0,42	85	83,6	16,3	41,2	21,7	15,2	9,0	12,8
						41,5	24,4	15,9	8,5	9,8
19	0,30	0,80	90	73,9	26,1	42,4	21,5	14,7	9,3	12,8
						43,4	21,7	17,0	8,7	9,2
20	0,30	1,10	86	77,5	22,2	31,3	20,9	19,4	12,3	16,2
						37,1	25,1	22,7	11,2	3,1

2-Methyl-1,3-dioxolane in its efficiency as a chain carrier in the reaction with ethylene is close to the carboxylic acids and their esters [2]. The small C_n values show that the growing radicals react more easily with ethylene than with the telogen. The fact that C_n is not dependent on n shows that the reactivity of the growing radicals is close, i.e., even the first growing radical B (n = 1) fails to experience the substantial polar effect of the dioxolane ring.

EXPERIMENTAL METHOD

Experiments 1-16 were run in stainless steel autoclaves with a capacity of ~10 ml. Prior to experiment the telogen was freed of traces of O₂ by the "freezing-evacuation-thawing" method. The autoclaves after charging with the reactants, the amount of which was determined by weighing with an accuracy of 0,01 g, were heated in a bath and rotated at a speed of 8 rpm. The C_n values were calculated using the Mayo equation [3, 4]. The experimental conditions are given in Tables 1 and 2.

Experiments 17-20 were run under the conditions of Experiments 1-16, but up to 90% monomer conversion (Table 3).

Experiments 22-23 were run in a rotated 0,5 liter steel autoclave. Into the autoclave were respectively charged 176.6 g (180.1 g) of 2-methyldioxolane and 0.75 g (0.79 g) of BP, the system was purged with N₂, and then ethylene was added up to a pressure of 40 at [735.5 mm of Hg] (at the experiment temperature), after which the autoclave was heated at 90° for 5 h, pumping in ethylene as it was absorbed. The increase in the weight of the reaction mixture was 17.6 g (8.7 g); after distilling off the starting dioxolane the weight of the mixture of telomers was 19.6 g (7.9 g). The mixture of telomers from a number of experiments was combined and fractionally distilled through a column. Here we isolated the telomer fractions T₁ (49° (10 mm), weight 6.2 g), T₂ [80° (10 mm), 18.4 g], and T₃ [123° (8 mm), 2g], which contained 80-85% of the given telomer. The GLC analysis conditions were: column length 2 m, 10% PEGA deposited on Chromosorb, at either 60 or 80°, and 10% SKTPT deposited on Chromosorb, at either 80 or 120°.

CONCLUSIONS

1. The telomerization of ethylene with 2-methyl-1,3-dioxolane proceeds with the formation of 2-methyl-2-alkyldioxolanes and alkyl acetates.

2. The partial chain transfer constants (C_n) were measured at 90 and 150°. The C_n values are practically independent of the reaction temperature and the chain length of the growing radical.

LITERATURE CITED

1. S. S. Zlotskii, Dissertation [in Russian], Moscow (1973).
2. R. Kh. Freidlina, A. B. Terent'ev, N. S. Ikonnikov, and M. A. Churilova, Dokl. Akad. Nauk SSSR, 208, 1366 (1973).
3. F. R. Mayo, J. Am. Chem. Soc., 70, 3689 (1948).
4. V. Ya. Katsobashvili, E. D. Safronenko, and I. B. Afanas'ev, Vysokomolekul. Soedin., 8, 282 (1966).