these samples gave the percentages of undeuterated, monodeuterated, and dideuterated material as a function of time. A scan of the mass spectra from m/e 30 to 150 at 15 e.v. showed that there was less than 2% of other volatile material. The results are plotted in Figure 1. Using an Electronic Associates, Inc., TR 20 analog computer programmed for two consecutive, first-order reactions, the curves were fitted to the data (Figure 1) and the rate constants $k_1 = 4.63 \pm 0.05 \times 10^{-4}$ and $k_2 = 2.18 \pm 0.05 \times 10^{-4}$ were compiled. The computer was used to synthesize the rate of disappearance of the protons at the 2- and 6-positions which is the rate observed by n.m.r. The k_{calcd} of 2.25×10^{-4} sec.$^{-1}$ agrees reasonably well with the k_{obsd} of 2.05×10^{-4} sec.$^{-1}$.

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Liquid-Phase and Vapor-Phase Reactions of Ethylene with Carbon Tetrachloride[1]

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The telomerization of ethylene and carbon tetrachloride, initiated by t-Bu_2O_2, has been studied at 140° in the liquid phase in carbon tetrachloride, n-octane, and methanol as solvents, and in the vapor phase at total pressures of 0.3–28 atm. The objective was to determine the effects of solvent change and phase change on the variation with n of the transfer constants of the radicals $Cl_3C(C_2H_4)_n\cdot$. In the liquid phase, kinetic chain lengths are in the thousands and normal telomers are nearly the sole products. In the vapor phase, chain lengths fall between about 10 and 200. Unexpectedly, intramolecular chain-transfer reactions of hydrogen and chlorine atoms in the 5-positions in the radicals become dominant at low pressures, leading to so much of numerous isomers of normal telomers and of 1-hexene that normal telomers become minor products. Rate constants for these rearrangements have been evaluated in terms of the rate constants for normal chain propagation and intermolecular chain transfer and then applied to chain branching in polyethylene. Except for the intrusion of intramolecular reactions of free radicals at low concentrations, there are no important differences between liquid-phase and vapor-phase telomerizations, and the effects of polar solvents are small. Comparison of these liquid-phase results at 140° with literature data at 70° shows that the activation energies for chain transfer with carbon tetrachloride and for chain propagation with ethylene are about the same for each of the radicals involved.

Introduction

This research originally had two objectives. One was to further some general comparisons of vapor-phase and liquid-phase reactions of free radicals. A more specific objective was to determine the effects of solvent and phase change on the transfer constants in the telomerization of ethylene with carbon tetrachloride. When we carried out our first vapor-phase experiments, a wholly unexpected problem arose: how to identify and account for the large number of new products and isomers formed.

In the polymerization of a vinyl monomer, E (here ethylene), the transfer constant of a solvent (here carbon tetrachloride) is the ratio of the rate constants for chain transfer and chain propagation as shown in eq. 4 (eq. 1 to 3 are in Chart I).

When n is large, C is constant and is a convenient measure of the reactivity of a solvent in chain transfer. However, when n is small and the solvent is carbon tetrachloride, C_n is sensitive to chain length with ethylene,[3,4] higher alkenes,[5] or styrene.[6] C_1 is usually much smaller than C_2, which means that the 1:1 telomer is hard to obtain in good yield (except in short-chain reactions in a large excess of carbon tetrachloride), but that the 2:1 product is easier to obtain, and so on. In the instances cited, the transfer constant increases regularly from C_1 up to about C_3 and thereafter remains nearly independent of chain length. More recently Robb and co-workers[7,8] have examined the reactions of styrene and methyl methacrylate with bromotrichloromethane. They found that the transfer constant goes through a maximum when n is 3 or 4 and that high telomers are therefore obtained only at very low $BrCCl_3$ concentrations. With alkenes or styrene and carbon tetrachloride, the effect of chain length on C_n has been ascribed to polar effects[5]: a nearby Cl_3C– group retards reaction of the free radical with carbon

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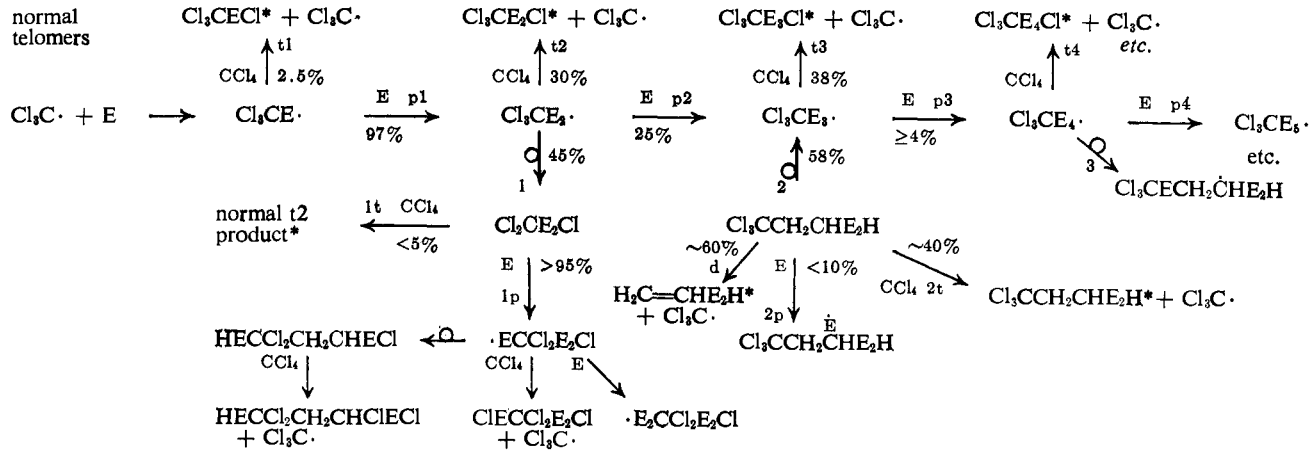
Chart I. Some Gas-Phase Chain Reactions of Ethylene (E) and CCl_4 at 140°[a]



[a] Illustrated by expt. 10 in Table I. Molecules required for the indicated reactions and the proportion of radical reacting by that route are noted at the tails of the arrows. Identified products are noted by an asterisk. Arrows with loops indicate rearrangements. Reactions p1 and t1 are normal reactions of the $Cl_3CE\cdot$ radical, etc., reactions 1p and 1t are propagation and transfer reactions following rearrangement 1, etc.

tetrachloride more than it affects addition of the radical to the double bond.[6] However, the work cited with bromotrichloromethane[7,8] indicates that the rate constant for chain propagation rather than for chain transfer is affected by the Cl_3C group. In an effort to throw some light on these effects, which are apparently transmitted through as many as six carbon atoms, we undertook a study of the reaction of ethylene and carbon tetrachloride at 140°, a temperature suitable for study of both liquid-phase and gas-phase reactions, with di-*t*-butyl peroxide as initiator.

$$\frac{k_t \text{ for } Cl_3C\text{-}E_n\cdot + CCl_4 \longrightarrow Cl_3C\text{-}E_n\text{-}Cl + Cl_3C\cdot}{k_p \text{ for } Cl_3C\text{-}E_n\cdot + E \longrightarrow Cl_3C\text{-}E_{n+1}\cdot} = C_n \quad (4)$$

Experimental

Materials. C.P. grade *ethylene* was obtained from the Matheson Co. Most of the oxygen and other noncondensable impurities were removed by freezing the storage tank with liquid nitrogen and evacuating to 2 mm. of mercury. After this purification the induction period before beginning of noticeable reaction in expt. 10 (Table I(b)) was less than 6 in contrast to 50 min. with the original ethylene. An experiment identical with 7 with research grade ethylene (Matheson Co., >99.9%) yielded the same rates and products as the treated C.P. ethylene.

Baker Analyzed reagent grade carbon tetrachloride was used without further purification. In expt. L12, synthetic *n-octane* from Matheson Coleman and Bell was used, and Baker's Analyzed reagent methanol in L8-11.

Experimental Procedures. Liquid-phase telomerizations were run in heavy-walled, sealed glass ampoules of 6.7-ml. volume. Oxygen was removed by three times freezing the reaction mixture with liquid nitrogen, evacuating, and then warming up to about −110° under a nitrogen atmosphere. The ampoules were then heated in a steel bomb filled with methanol and pressurized sufficiently by nitrogen (*ca.* 500 atm. in the case of the experiments without a solvent. An equimolar liquid mixture of C_2H_4 and CCl_4 as in L5 exhibits a total pressure[3] of *ca.* 300 atm. at 140°).

Special care was taken to ensure that the ampoules contained little vapor space above the liquid. In the experiments with solvents (L7-L12) tube fillings could be predicted moderately well from literature data[9] on the densities of carbon tetrachloride, methanol, and *n*-octane under the reaction conditions and from taking the partial density of ethylene as 0.5 g./ml. at 140° and 100 atm. In these experiments, the liquid level could be observed at 10°. From the thermal expansion and compressibility[9] of the solvents and CCl_4, we estimated that tubes were more than 90% full during reaction.

The densities of liquid mixtures of CCl_4 and ethylene without a solvent were not known. Therefore six experiments were carried out with fillings increasing by 10–20% from run to run. Experiment L5 in Table I(a) probably represents a tube more than 85% full of liquid. A similar glass tube with a still higher filling burst despite an external pressure of 500 atm. Experiments with less material than L5 yielded higher transfer constants, apparently because the concentration of ethylene in the liquid phase was depleted. Transfer constants from L5 are too high by no more than 10% due to incomplete filling with liquid.

Vapor-phase telomerizations were carried out either in a 1-l., Pyrex, round-bottom flask with a capillary opening leading to a stopcock or in a 100-ml. sealed glass tube of 2.8 cm. i.d. The actual volume of the 1-l. flask was 1066 ml., but the stated concentrations in Table I(b) have been corrected to 1000 ml. For the low-pressure runs in this flask, oxygen was removed from the CCl_4–*t*-butyl peroxide mixture by repeated freezings and evacuations before distilling the mixture into the flask containing the ethylene. This flask was then heated in an oil bath. The rate of diffusion of the evaporated CCl_4 in the unagitated gas phase of the large reaction flask was checked by g.l.c. analyses of samples drawn at different times from different points in the flask. About 6 min. after introducing 4 mmoles of liquid CCl_4 into the flask containing 38 mmoles of C_2H_4 at 100° no significant differences in CCl_4 concentrations could be detected.

(9) G. Damkohler, *Z. physik. Chem.*, **31B**, 449 (1936); J. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 440 (1909–1910); E. A. Kelso and W. A. Felsing, *J. Am. Chem. Soc.*, **62**, 3133 (1940).

Table I. Reactions of Ethylene and Carbon Tetrachloride for 3 Hr. at 140°

Expt. no.	Reactants, mM: C_2H_4/CCl_4	C_2H_4	CCl_4	t-Bu_2O_2	Products, mM: n in Cl_3CE_nCl: 1	2	3	4	5	>5[a]	1-C_6H_{12}	Cl_3CCH_2-$CHClE_2H$	C_2H_4, mM: Consumed	Identified	C_2H_4/R·[b]	Transfer constants[c]: C_1	C_3	C_3	C_4	C_1/C_2H_4[d] l./mole
(a) Liquid-phase experiments in 6.7-ml. bulb (concentrations assume full bulb																				
L5	1	5220[e]	5250[e]	0.0052	51.8	220	74.6	17.1	2.5	0.3	<<1		~700	800	150,000	0.157	2.24	3.6	5.9	0.030
L12	2.6	4600	1750	0.015	4.7	34.3	23	11.2	3.0	1			~270	210	14,000	0.17	2.3	3.9	7.2	0.037
	(2.74 M n-octane)																			
L7	0.1	313	3050	0.520	<1	<1							10	3	<1					
	(7.0 M $PhNO_2$)																			
L8	1	2220	2150	2.15	161	456	79	10	1.3	0.17			1160	1210	550	0.23	4.0	5.4	~6	0.10
	(10.8 M MeOH)																			
L9	2.5	4480	1770	0.090	34.5	236	119	34	6.3	1.5				1040	12,000	0.21	3.5	6.9	10	0.047
	(10.8 M MeOH)																			
L11	2.5	4500	1720	0.084	20.1	144	68	23	4.9				640	640	7,600	0.22	3.8	6.0	9.3	0.048
	(10.8 M MeOH)																			
(b) Low-pressure gas-phase experiments in 1066-ml. flask																				
14	19.5	35	1.80	0.12	0.0052	0.025	0.0097	0.0004			0.049	~0.004	1.42[f]	0.270	11.8	0.4	6.7			~11
13	9.8	35	3.56	0.12	0.0080	0.057	0.0212	0.0006			0.050	0.010	1.63[f]	0.368	13.6	0.25	6.9			7.1
10	4.9	35	7.1	0.06	0.0130	0.100	0.0315	0.0010			0.030	~0.018	1.30[f,o]	0.456	21.2	0.19	6.1			5.4
11	4.9	35	7.1	0.12	0.0170	0.132	0.039	0.0015			0.039	0.023[a]	1.93[f]	0.590	16.1	0.19	5.8			5.4
7	4.9	35	7.1	0.22	0.0232	0.165	0.045	0.0021			0.045	0.027	2.68[f]	0.713	11.7	0.21	5.8			6.0
26	4.9	35	7.1	0.50	0.031	0.222	0.049	0.0025			0.050	~0.030	3.90[f]	0.872	7.8					
20[h]	4.9	35	7.1	0.12	0.0090	0.073	0.0205	0.0008			0.028	0.016[a]	0.90[f,h]	0.350	18	0.18	5.1			5.1
22	4.9	17.6	3.62	0.12	~0.0062	0.052	0.0100	<0.0005			0.0183	0.0060	1.01[f]	0.218	8.4	0.13	6.9			7.4
12	2.43	35	14.4	0.12	0.050	0.308	0.056	0.0054			0.029	0.044	2.48[f]	1.080	20.7	0.19	5.5	13		5.4
15	1.47	35	23.8	0.12	0.130	0.600	0.091	0.0054			0.020	0.059	3.00[f]	1.860	25	0.18	5.0	16		5.1
42	0.74	17.5	23.8	0.06	0.160	0.475	0.031	0.0014			0.005	0.019	~1.80[f]	1.280	30	0.16	6.1	12		9.2
43	0.37	8.8	23.8	0.06	0.188	0.298	0.0090	<0.0005			~0.0012	~0.006[a]	~1.15[f]	0.833	19	0.16	6.9			18
															Av.	0.19	6.0	14		7.6
(c) High-pressure gas-phase experiments in 102-ml. bulb																				
39	10.4	763	73.0	0.017	0.390	0.660	0.284	0.133	0.048	0.040	~0.020			3.34	196	3.0	11.8	12.2	15	4.0
33	9.8	372	38.0	0.270	0.530	1.700	0.830	0.284	0.095	0.028	~0.030		8.9	8.04	33	1.4	9.8	14.5	17	3.8
41	10.0[i]	196	19.6	0.280	0.190	0.760	0.320	0.044	~0.0056					2.88	~15	1.06	11.8	(36)		5.4
38	5.0	380	76.5	0.017	0.900	0.700	0.194	0.060	0.015	~0.004	~0.015		~2	3.20	200	4.0	10.8	10.3	14	10.5
32	5.0	374	74.6	0.270	5.040	3.840	1.180	0.395	0.120	0.034	~0.080		26	18.6	100	4.1	9.4	9.0	11	10.9
35	2.5	191	75.8	0.280	1.780	2.820	0.940	0.180	0.035	0.004	0.040		17.5	11.15	63	0.98	5.1	9.1	10	5.1
															Av.		9.8	11.0	13	6.6
40	400	3150	7.9	0.13	(10-hr. reaction time)								123		500	C for long chains 18				

[a] Estimated. [b] Number of ethylene molecules consumed per radical, assuming that in 3 hr. half the t-Bu_2O_2 has decomposed to give two radicals/molecule (half-life = 2.9 hr. according to L. Batt and S. W. Benson, *J. Chem. Phys.*, 36, 875 (1962). However some g.l.c. determinations of recovered t-Bu_2O_2 indicate up to 50% more (and therefore some induced) decomposition. [c] Gas-phase values are calculated from yields of Cl_3CE_nCl, 1-hexene, and Cl_3C-CH_2CHClE_2H, corrected for rearrangement of $Cl_3CE_2\cdot$, $Cl_3CE_3\cdot$, and $Cl_3CE_4\cdot$, assuming $k_1/k_{t2} = 0.01$ and $k_2k_{t3} = k_3/k_{t4} = 0.014$ mole/l. [d] See Discussion. [e] Estimated total pressure, 300 atm. [f] Calculated from total pressure decrease during reaction, corrected for formation of acetone and cyclohexene and approximately for partial condensation of high telomers. [g] From this value and the chlorine content of the telomer mixture, 0.31 mmole of CCl_4 was consumed. [h] Reaction time was 1.0 hr. [i] Also contained 580 mM ethane.

In the high-pressure experiments, the charged, 100-ml. reaction tube was cooled three times with liquid nitrogen and evacuated to 0.01 mm. with intermittent warming to −110°. These tubes were heated in a pressurized steel bomb filled with methanol.

Ethylene consumption in the high-pressure, gas-phase and in the liquid-phase experiments was determined by measuring its volume and pressure as a gas before and after the reaction. In the low-pressure, gas-phase runs the 1-l. flask was connected to a mercury manometer through a stopcock. The total pressure of the reaction mixture at 140° was read intermittently. The decrease in total pressure yields directly the ethylene consumption, except that corrections were applied for formation of 1-hexene and acetone, as determined by g.l.c.

Chromatographic Analyses of Products. Because of the thermal instability of the products at the temperatures necessary to pass the telomers through the gas chromatographic columns, g.l.c. analyses presented some difficulties. An Aerograph dual-column gas chromatograph Model A350B was used with temperature program. On most columns every telomer except the lowest boiling (Cl_3CECl) gave two peaks, one of the parent compound and one of the dehydrohalogenated telomer. Between the two peaks, the trace usually did not return to the baseline, indicating some decomposition of the telomer while it passed through the column.

A 180-cm. brass column packed with 30% of a fluorosilicone oil (QF 10065) on Chromosorb W provided clean separation of the regular telomers, Cl_3CE_nCl, up to the pentamer, without significant decomposition on the column at up to 230°. This column was therefore used in most of this work. The column temperature was usually constant at 45° for the first 6 min. and at 230° after 28 min. and was increased continuously between these times. Most of the dehydrohalogenation occurred in the first 2 cm. of the column which was in contact with the injector (*ca.* 240°) and therefore much hotter than the rest of the column. By introducing 12 cm. of an empty stainless steel capillary tube between injector and column, overheating of the column packing material was avoided and the peak areas of the dehydrohalogenated telomers were usually smaller than 20% of those of the parent compounds (for a typical chromatogram see Figure 3). The peaks of the dehydrohalogenated compounds were taken into account for the determination of a telomer.

QF 10065 columns were affected by the liberated HCl and therefore had a limited life. The following other column packings were used successfully to determine some by-products and to check whether usual peaks covered some peaks of by-products: diethylene glycol succinate, Halcomid, DC 710 (a silicone oil), and Apiezon M. The latter column permitted a clean separation of the linear dimer Cl_3CE_2Cl from the rearranged trimeric side product $Cl_3CCH_2CHClE_2H$, not possible with the QF 10065 column.

Because of the large number of by-products and the tendency of the higher telomers to lose HCl, our g.l.c. data may be subject to errors of up to 10% in the liquid-phase and high-pressure, vapor-phase reactions and up to 20% in low-pressure vapor-phase runs.

Telomers, Cl_3CE_nCl. The procedure used by Joyce, Hanford, and Harmon[10] in their "large-scale" experiment was employed with 1.8 moles of CCl_4, 2.6 mmoles of dibenzoyl peroxide, and 16 moles of H_2O in an 800-ml. rocking autoclave pressurized with ethylene to 100–140 atm. at 90–130°. After removal of water and CCl_4, the reaction product was distilled in a spinning-band column. Telomers containing one to four ethylene units were obtained in purities of about 96% and about 80% for the pentamer. By g.l.c., the impurities were mostly the next lower or higher analogs.

Telomerization of 1-Hexene with CCl_4. The three liquid-phase experiments in Table II at 140° yielded the 1:1 adduct of CCl_4 to hexene as the major product.

Table II. Telomerization of 1-Hexene with CCl_4 at 140°

Expt. no.	C_6H_{12}–CCl_4 mole ratio Initial	Av.	t-Bu_2O_2–CCl_4 mole ratio	Conversion of C_6H_{12}, %	Ratio of 1:1 to 2:1 peak areas	C_{1h}[a]
H 1	0.30	0.18	0.0001	85	27	4.9
H 2	3.30	3.0	0.000009	3	1.5	4.5
H 3	3.30	3.2	0.00016	12	1.1	3.5
					Av.	4.1

[a] Calculations assume that concentrations are proportional to peak areas; the first value of C_{1h} may err in using an average value of C_6H_{12}/CCl_4, the others in neglecting higher telomers.

The only significant by-product was much higher boiling and is assumed to be the 2:1 adduct, $Cl_3CCH_2CH(E_2H)CH_2CHClE_2H$. Calculation of the transfer constant, C_{1h}, for the $Cl_3CCH_2\dot{C}HE_2H$ radical yields fairly consistent values averaging about 4.1. This calculation assumes that the dimer radical has a still higher transfer constant so that only negligible amounts of higher telomers are formed.

Results and Calculations

Liquid-Phase Telomerizations. Reactions in the liquid phase were first run in bulk without solvent (Table I(a)). Because expt. L5 was run in the most nearly full tube (see Experimental), it gives the most reliable results for the transfer constants, C_n. C_n for a telomer radical with n ethylene ($-CH_2-CH_2-$) units, was calculated from the yields of Cl_3CE_nCl and of all higher species, $Cl_3CE_{>n}Cl$, and from the average ratio of C_2H_4 and CCl_4 concentrations during the experiment.[6] The

$$C_n = \frac{k_{tn}}{k_{pn}} = \frac{[C_2H_4]}{[CCl_4]} \cdot \frac{[Cl_3CE_nCl]_f}{[Cl_3CE_{>n}Cl]_f} \quad (5)$$

subscripts, f, indicate the final concentrations of products formed during reaction. Under the conditions of expt. L5, over 200,000 molecules of ethylene were consumed per molecule of t-Bu_2O_2 decomposed, and the gas chromatograms showed practically no other peaks besides those of CCl_4 and the linear telomers Cl_3CE_nCl.

A few experiments were carried out in more or less polar media. Transfer constants in n-octane are very similar to those obtained without a solvent in expt. L5. All transfer constants in methanol are about 50% larger than those in bulk or in octane. Nitrobenzene com-

(10) R. M. Joyce, W. E. Hanford, and J. Harmon, *J. Am. Chem. Soc.*, 70, 2529 (1948).

Table III. Analyses of Products of Experiments 26–31

Fraction				G.l.c. analyses								Elemental analyses				
No.	B.p.,[a] °C.	Pressure, mm.	Weight, mg.	CCl_4, mg.	Cl_3CECl, mg.	Cl_3C-E_2Cl, mg.	Cl_3C-E_3Cl, mg.	Cl_3C-E_4Cl, mg.	Cl_3C-E_5Cl, mg.	Hexene, mg.	Unidentified, wt. %	C, %	H, %	Cl, %	C_2H_4/CCl_4[b]	N.m.r. analyses Primary CH,[c] %
1	Up to 130	760	4000	~4000	1	2	<0.1	<0.01	<0.01	~25						
2	Up to 100	20	1200	~1000	3.2	1.8	<0.1	<0.01	<0.01							
3	100–130	20	537	1.6	22	102	6	<0.01	<0.01		75	41.08	6.06	51.16	4.3	21.6
4	90–112	2	324	0.5	1.0	140	17	0.02	<0.01		51	39.45	5.55	53.88	3.8	16.7
5	115–138	1.8	165	<0.3	0.3	46	28	0.12	<0.04		55	41.36	5.94	51.49	4.3	13.6[d]
6	100–140	0.2 to 0.05	196	<0.1	<0.05	11.5	14.1	1.9	<0.2		86	44.22	6.12	48.60	4.9	19.6[d]
7	Undistilled (dark brown)		158	<0.1	<0.05	1.0	1.5	0.12	<0.06		98	48.99	6.03	41.26	6.8	
	Total		6600	5000	27	304	67	2.2	<0.3	25					4.7	
	Result from Table I(b) for total of V26–31				36	297	74	4		27						

[a] These are bath temperatures at which fractions were removed at the indicated pressures and are higher than actual boiling points. [b] Based on four Cl atoms per molecule. In the heavier fractions, the C–H ratio increases, when it should decrease slightly for pure telomers. This trend suggests some dehydrochlorination. [c] The number of methyl groups per 100 combined C_2H_4 is $^4/_3$ times this number. [d] 19.6 for fractions 5–7 combined.

pletely inhibits all reactions, even at fairly high initiator concentrations.

Gas-Phase Telomerizations at Low Pressures. Telomerizations of ethylene and CCl_4 in the gas phase, at about 1 atm. (Table I(b)), yielded more by-products than regular telomers, in both numbers and yields. Although not all the by-products have been identified, nearly all seem to arise by intramolecular transfer of hydrogen and/or chlorine within the telomer radicals. At these low concentrations of ethylene and CCl_4, unimolecular rearrangements of radicals can outrun their bimolecular reactions. Relative rates of the most important rearrangements were estimated, and it was then possible to estimate normal transfer constants even under the least favorable conditions.

1. Material Balance. This section shows that normal analyses of low-pressure, gas-phase telomerization products accounted for only 20–35% of the reacted ethylene, depending on the feed ratio. Modified procedures showed that nearly all of the missing ethylene is present in isomers of telomers which decompose during gas chromatography.

Table I(b) summarizes several telomerizations with 35 mmoles of ethylene/l. (1.2 atm.) and 1.8 to 24 mmoles CCl_4/l. Fifteen to 60 moles of ethylene were consumed per mole of initiator decomposed. At this relatively low ethylene pressure only a small fraction of the ethylene consumed appears in the expected telomers, Cl_3CE_nCl, and in known by-products. For example, Table I(b) and Figure 1 show that in expt. 26 only 16% of the ethylene consumed was found in known normal telomers, 4% in 1-hexene, and 2% in one telomer isomer. The two major peaks on each side of the Cl_3C-ECl peak in Figure 1 fail to account for much of the missing ethylene. The several marked peaks, mostly small, are not associated with ethylene since they also appear in similar quantities on heating t-Bu_2O_2 with CCl_4 in the absence of ethylene. Experiment 26 contained a high proportion of initiator; after 1 half-life of t-Bu_2O_2 (3 hr. for a purely thermal decomposition)[11] 0.25 mmole/l. of termination products should have formed. Even if they contained 1 mmole/l. of ethylene, they would account for only 26% of the ethylene consumed. Experiment 10 contained only one-eighth as much initiator, but still only 35% of the consumed ethylene is accounted for.

(11) See Table I, footnote *b*.

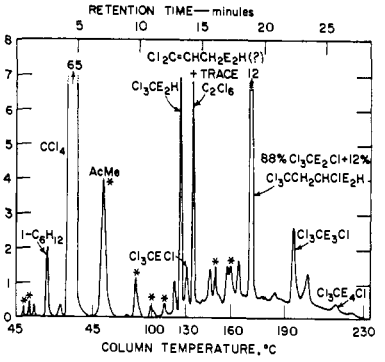


Figure 1. Gas chromatogram of products from low-pressure, gas-phase telomerization (expt. 26) in column QF 10065. The asterisks indicate peaks arising from t-Bu_2O_2 and CCl_4 without ethylene.

In a search for the missing ethylene, the products from six experiments like 26 (26–31) were collected, combined, and fractionally distilled below 140° to avoid decomposition. There was very little undistillable residue. Table III shows that the normal telomers found in the several fractions agree well with the data for expt. 26 in Table I(b) but that only 2–49% of the fractions can be identified by gas chromatography. By elementary analyses, these fractions approximate normal telomers in average composition (see Table III footnote *b*), but the n.m.r. data indicate the presence of 20–30 methyl groups per 100 C_2H_4 units present. Thus extensive intramolecular transfer of hydrogen has occurred in the growing radicals. Since these isomeric compounds do not appear in Figure 1 and since the base line has obviously drifted, they must have decomposed in the column with loss of hydrogen chloride. Thus most of the "missing" ethylene is in isomers of the linear telomers Cl_3CE_nCl (n = 3 to 6). Further evi-

dence will be given later. The most important rearrangement reactions which can lead to such isomers will now be considered.

2. *Possible Reactions.* As a basis for further discussion, Chart I indicates what chain reactions can occur in the gas-phase reaction of ethylene and carbon tetrachloride and our estimates of their relative importance in expt. 10. Chart I also indicates which of the expected products have been identified. The normal reactions of substituted alkyl radicals with ethylene (eq. p1, p2, etc.) and carbon tetrachloride (eq. t1, t2, etc.) need not be considered here, but the ratios of the rate constants ($k_{t1}/k_{p1} = C_1$, etc.) will be considered later.

3. *Intramolecular Hydrogen Transfer.* Intramolecular chain transfer of the 5-hydrogen atoms in primary alkyl radicals is well known to produce side-chain butyl groups in polyethylene.[12,13] In our system, the trimer radical, $Cl_3CE_3\cdot$, is the shortest which can rearrange to produce a butyl branch (reaction 2). The $Cl_3CCH_2\dot{C}HE_2H$ radical can then add ethylene (reaction 2p), or produce 1-hexene by loss of $Cl_3C\cdot$ (reaction d), or $Cl_3CCH_2CHClE_2H$ by transfer with CCl_4 (reaction 2t). A similar rearrangement, reaction 3, applies to $Cl_3CE_4\cdot$.

The importance of rearrangement reaction 2 may be gauged by comparing it with reaction t3 with CCl_4, the principal reaction of the same radical. The ratio, k_2/k_{t3}, may be obtained from the following reactions. 1-

$$\frac{k_2}{k_{t3}} = ([1\text{-}C_6H_{12}]_f + [Cl_3CCH_2CHClE_2H]_f + [\text{products of } Cl_3CCH_2CH(E_2H)E\cdot]_f)\,[CCl_4]/[Cl_3CE_3Cl]_f \quad (6)$$

Hexene and $Cl_3CCH_2CHClE_2H$, which is also the 1:1 adduct of CCl_4 to 1-hexene (see Experimental), have actually been found in considerable quantities as shown in Table II. Possible products from $Cl_3CCH_2CH(E_2H)E\cdot$ were not identified or determined by g.l.c. They apparently do not form in significant amounts under these reaction conditions since column 3 of Table IV shows that the ratios

$$([1\text{-}C_6H_{12}]_f + [Cl_3CCH_2CHClE_2H]_f)\,[CCl_4]/[Cl_3CE_3Cl]_f\ (\simeq k_2/k_{t3})$$

are fairly constant, indicating that hexene and $Cl_3CCH_2CHClE_2H$ are the only major products from $Cl_3CCH_2\dot{C}HE_2H$. If products of $Cl_3CCH_2CH(E_2H)E\cdot$ were important, increasing the concentration of CCl_4 at constant concentration of ethylene should decrease the calculated value of k_2/k_{t3} in Table IV; if there is a trend it is in the reverse direction. Further, participation of $Cl_3CCH_2\dot{C}HE_2H$ in termination seems to be unimportant because k_2/k_{t3} is not affected by change in the kinetic chain length (expt. 7 and 9). We conclude that the calculated values of k_2/k_{t3} in Table IV are good approximations.

The average value of k_2/k_{t3}, 0.014 mole/l. from Table IV, means that with 0.014 *M* CCl_4 at 140° (0.48 atm.) as many $Cl_3CE_3\cdot$ radicals rearrange (reaction 2) as react with CCl_4 (reaction t3). Using $C_3 = k_{t3}/k_{p3} = 14$ from Table I(b), $k_2/k_{p3} = 0.20$ mole/l. Thus 0.20 *M* ethylene (6.8 atm.) is required for even competition of reactions p3 and 2.

From the values in the last column of Table IV, the ratios of the rates of formation of hexene (reaction d) and $Cl_3CCH_2CHClE_2H$ (reaction 2t) can be compared

(12) M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).
(13) J. C. Woodbrey and P. Ehrlich, *ibid.*, **85**, 1580 (1963).

Table IV. Products of Reaction of $Cl_3CE_3\cdot$ Radicals[a]

Expt. no.	C_2H_4/CCl_4	k_2/k_{t3}[b] $\times 10^3$	k_d/k_{2t}[c] $\times 10^3$
14	20	9.9	...
13	10	10.0	~15
9[d]	5	10.8	12.6
7	5	11.4	12.0
22	5	8.8	11.1
12	2.4	18.9	9.3
15	1.5	20.7	9.1
42	0.74	19.0	7

[a] Details are in Table I(b). [b] k_2/k_{t3} calcd. from $([1\text{-}C_6H_{12}]_f + [Cl_3CCH_2CHClE_2H]_f)[CCl_4]/[Cl_3CE_3Cl]_f$ with concentrations in mole/l., neglecting [products of $Cl_3CCH_2CH(E_2H)E\cdot$] in eq. 6. [c] $k_d/k_{2t} = [1\text{-}C_6H_{21}]_f[CCl_4]/[Cl_3CCH_2CHClE_2H]_f$ with concentrations in mole/l. [d] Run like expt. 10.

(eq. 7). This ratio in turn can be used to obtain some

$$k_d/k_{2t} = [CCl_4][1\text{-}C_6H_{12}]_f/[Cl_3CCH_2CHClE_2H]_f = 0.011 \text{ mole/l.} \quad (7)$$

information on the telomerization of 1-hexene with CCl_4 ($C_{1h} = k_{2t}/k_{ph} = 4.1$ from Experimental). These two ratios give rate of decomposition of $Cl_3CCH_2\dot{C}HE_2H$/rate of addition to $1\text{-}C_6H_{12} = k_d/k_{ph}[1\text{-}C_6H_{12}] = 0.05/[1\text{-}C_6H_{12}]$. Thus loss of $Cl_3C\cdot$ from this radical at 140° will be important only at low concentrations of 1-hexene (and carbon tetrachloride).

Intramolecular 5-hydrogen abstraction (reaction 3) of the tetramer radical, $Cl_3CE_4\cdot$, and longer radicals presumably proceeds at about the same rate as with the trimer radical or a little faster. However, the resulting products can contribute little to the total product because so few radicals reach the $Cl_3CE_4\cdot$ stage without previous transfer or rearrangement,

Rearrangement by hydrogen abstraction should ordinarily produce both methyl groups and tertiary hydrogen atoms. N.m.r. peaks which may be due to tertiary hydrogen atoms are present but could not be identified with certainty. By n.m.r., the total content of methyl groups in expt. 26–31 (Table III) is much higher than corresponds to the $Cl_3CCH_2CHClE_2H$ and $Cl_3CECH_2CHClE_2H$ present. Some of the other methyl groups may arise from the initiator, $t\text{-}Bu_2O_2$. However, the product of expt. 10, which had only one-eighth as much initiator as expt. 26–31, contains about as many (23) methyl groups per 100 molecules of C_2H_4. The high methyl content suggests complex rearrangements of the dimer radical, $Cl_3CE_2\cdot$, to produce a compound such as $HECCl_2CH_2CHClECl$.

4. *Intramolecular Chlorine Transfer.* Reaction 1 is the most important intramolecular chain transfer of chlorine. The $Cl_3CE_2\cdot$ radical is apparently the only straight-chain radical with a trichloromethyl group suitably located for chlorine transfer. From the preponderance of butyl groups over propyl groups in polyethylene,[12,13] 5-hydrogen transfer is negligible in this radical. To estimate the importance of chlorine transfer, we first estimate the transfer constant for this radical, $C_2 = k_{t2}/k_{p2}$, from expt. 10. C_2 we find to be 6.1 by multiplying the E/CCl_4 ratio (4.9) by the yield of Cl_3CE_2Cl (0.100 mmole) and dividing it by the yield of all known products in expt. 10 containing three or more E units (0.081 mmole). (We can correct for reaction 3 by assuming that its relative importance is the same as reaction 2, but so few high telomers are formed that

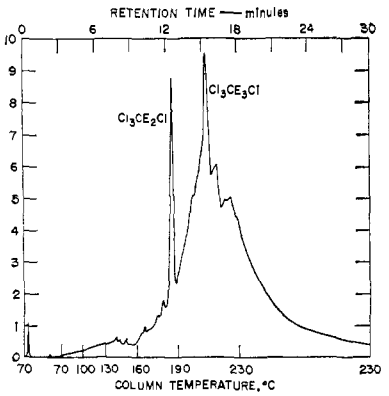


Figure 2. Gas chromatogram of high-boiling fraction 6 from experiments 26–31.

the correction is trivial.) Other values of C_2 in Table I(b), calculated in the same way, are about the same. These values of C_2 are a little smaller than the value found (10) at higher concentrations of reactants (Ic) where much less rearrangement occurs. We conclude that the *known* products with three or more E units in Table I(b) represent essentially *all* the products of reaction p2 (otherwise our estimate of C_2 should be too high).

Nevertheless, all the identified products in expt. 10 account for only 35% of the ethylene reacted and 53% of the CCl_4 reacted (0.164 of 0.310 mmole). If all the unidentified CCl_4 units (0.146 mmole) are associated with rearrangement of $Cl_3CE_2\cdot$ radicals, then we can calculate relative rates of reactions 1, p2, and p3:

$$\frac{k_1}{k_{p2}} = \frac{[Cl_2\dot{C}E_2Cl \text{ products}]_f[E]}{[Cl_3\dot{C}E_3\cdot\text{products}]_f} \simeq \frac{0.146}{0.081}\cdot 0.035 = 0.06 \text{ mole/l.} \quad (8)$$

$$\frac{k_1}{k_{t2}} = \frac{[Cl_2\dot{C}E_2Cl \text{ products}]_f[CCl_4]}{[Cl_3\dot{C}E_2Cl]_f} \simeq \frac{0.146}{0.100}\cdot 0.0071 = 0.010 \text{ mole/l.} \quad (9)$$

Since the method of calculation puts all the unknown products in the numerators of these equations, the ratios found are more likely to be high than low. Tending in the other direction is the fact that one of the possible products of the rearranged dimer radical, $Cl_2\dot{C}E_2Cl$, is the *regular* telomer, Cl_3CE_2Cl. Therefore, this reaction cannot be detected directly. If it were important, then the transfer constant, C_2, after correction for rearrangements, should increase as $[CCl_4]/[C_2H_4]$ increases. Since Table I shows no indication of such a trend, we conclude that $k_{1t}/k_{1p} < 0.2$.

Investigation and identification of the main products from rearranged dimer radical is difficult because compounds like $ClECCl_2E_2Cl$ and $HECCl_2CH_2CHClECl$ seem to decompose with loss of HCl during gas chromatography above 130°. Instead of producing sharp peaks, these compounds raise the baseline of the chromatogram at column temperatures between 130 and 230°. In gas chromatograms of the original dilute solutions of the products in CCl_4, this shift in baseline is hardly perceptible (Figure 1), especially since the baseline could not be expected to remain at zero over a temperature range of 100°. However, when the bulk of the CCl_4 is first removed and more telomeric material is used per injection, the shift in the base line becomes very striking (Figure 2).

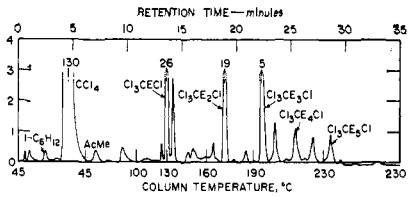


Figure 3. Gas chromatogram of products from high-pressure, gas-phase telomerization (expt. 32).

5. *Transfer Constants.* We can now estimate values for transfer constants of normal telomer radicals in the gas phase, even in experiments like 10 where the normal telomers Cl_3CE_nCl constitute only a minor fraction of the total products. For calculation of C_1, we used the amount of Cl_3CECl found and the yield of all higher products. For expt. 10, this yield was easily obtained from the total amount of CCl_4 consumed plus the yield of 1-hexene. In the other experiments, the yield of higher products came from the known yields of higher products and the yields of unknown products calculated from k_1/k_{t2} (eq. 9).

We obtained C_2 from the yields of Cl_3CE_nCl (n = 2 to 5), of $Cl_3CCH_2CHClE_2H$ and of 1-hexene. The rearrangement of the dimer radical does not affect the determination of C_2. In experiments where $Cl_3CCH_2CHClE_2H$ had not been determined by gas chromatography (in all runs not listed in Table IV) a correction for its formation was made using eq. 6 and 7. A correction for 5-hydrogen abstraction of the radical $Cl_3CE_4\cdot$ was applied in all cases, assuming that eq. 7 applies.

High-Pressure, Gas-Phase Telomerization. In order to obtain more reliable values for gas-phase transfer constants, we attempted to reduce extents of rearrangements. We had some success at low C_2H_4 pressures by using high CCl_4 concentrations; thus in expt. 15, 42, and 43 (Table I(b)), 60–70% of the ethylene consumed was found in the regular telomers Cl_3CE_nCl. A more efficient means of suppressing rearrangements was to raise both ethylene and CCl_4 concentrations as high as the volatility of the latter would permit. Under the reaction conditions in Table I(c), 60–95% of the ethylene reacted was in regular telomers. Formation of 1-hexene was negligible. Figure 3 shows that the gas chromatographic peaks of the other by-products are much smaller than at low ethylene pressures. Greater kinetic chain lengths and lower initiator concentrations at higher reactant concentrations also contribute to the simpler chromatograms. Transfer constants in Table I(c) were calculated from the yields of the regular telomers in the high-pressure, gas-phase experiments with only minor corrections for rearrangements.

Experiment 40 (Table I(c)) used a large excess of ethylene at 100 atm. to determine the average (and presumably uniform) transfer constant of longer polyethylene radicals. Some condensation probably occurred before the reaction mixture was cooled. The waxy product was brought to a constant weight after several days at room temperature and 0.01 mm. Gas chromatograms then showed that nearly all the Cl_3CE_4Cl and lower telomers (containing 6.4% of the initial CCl_4) were in the volatile fraction, containing 0.05 mmole of reacted CCl_4 and 0.12 mmole of

ethylene. The 405 mg. of nonvolatile fraction contained 12.56% Cl (45.3% of the initial CCl_4) and therefore 0.36 mmole of CCl_4 and 12.5 mmoles of ethylene. From the relations in ref. 6, ^{14}C for long chains is about 18.5.

Discussion

Liquid-Phase Transfer Constants. Table V summarizes our own and literature determinations of transfer constants. Since the liquid-phase results agree quite well among themselves and since they are subject to fewer complications, they are most reliable. Our own resulted from special efforts to use full reaction vessels and thus known concentrations of ethylene. Transfer constants C_1–C_4 obtained in CCl_4 solution are essentially the same as those in *n*-octane. Comparison with literature values at 70° shows that changes in transfer constant with chain length tend to level out at the higher temperature. There is little difference between the activation energies for chain transfer and propagation for the radicals, but $Cl_3CE\cdot$ seems to have a measurably higher activation energy for transfer than for propagation, 1.5 kcal./mole according to David and Gosselain.[4b]

Table V. Transfer Constants for the Reaction of C_2H_4 and CCl_4

Reaction conditions, temp., °C.	C_1	C_2	C_3	C_4
	Liquid phase[a]			
0[b]	0.051			
27[b]	0.067	3.0	9.7	18
65[b]	0.084			
70[c]	0.08	1.9	~3.2	
	0.105	2.5	5.1	6.0
140	0.16	2.2	3.6	6
140, in *n*-octane	0.17	2.3	3.9	7
140, in methanol	0.22	3.8	6.1	9
	Vapor phase			
140, 1.2 atm. C_2H_4	0.18	6.0	13	
140, 12 atm. C_2H_4	3	10	11	~14

[a] No solvent except CCl_4, except as noted. [b] See ref. 4b. [c] See ref. 3 and 4a.

All transfer constants in methanol are uniformly larger than in the nonpolar media at 140°. Apparently methanol stabilizes the more polar activated complex for chain transfer with carbon tetrachloride a little more than the activated complex for addition to ethylene. This effect applies equally to $Cl_3CE_1\cdot$ and $Cl_3CE_2\cdot$, although the former was supposed to be more susceptible to polar effects.

Vapor-Phase Transfer Constants. The low- and high-pressure transfer constants agree poorly, but the low-pressure values for C_1 and C_2 agree better with the liquid-phase values and the low-pressure C_3 value is somewhat uncertain. To the extent that the products are cleaner and fewer estimates and approximations regarding side reactions are needed, the high-pressure results are more reliable than the low-pressure results. Nevertheless, the differences between the C_1 values are surely significant and between C_2 values, probably significant. Condensation of telomers, which occurs in at least some high-pressure runs, is probably responsible for at least part of the difference. Thus, during part of an experiment, part of the telomerization occurs in the liquid phase which is relatively rich in carbon tetrachloride. Reaction in solution leads to excessive formation of 1:1 and 2:1 telomers and high values of C_1 and C_2. While this explanation is less than satisfactory, we have no better one. Details on the possible influence of condensation on the change of C_1 with pressure and on some alternative explanations are considered in the next four paragraphs.

Partial condensation of CCl_4 and reaction products was observed in several high-conversion runs at low pressures and probably occurred in all high-pressure runs but not in low-pressure runs. Supporting the idea that this condensation is responsible for abnormally high value of C_1 and C_2 are the agreement of the low-pressure and liquid-phase transfer constants and the tendency of the vapor-phase values of C_1 to be lowest when the concentration of both CCl_4 and higher telomers (n = 5 or more) are lowest (expt. 41) and highest when both these concentrations are highest (expt. 32), and some rate phenomena. Against the importance of condensation are (1) the fact that C_1 and C_2 in expt. 32 and 38 do not show the expected increase with conversion and accumulation of liquid, (2) our failure to find by g.l.c. new compounds expected by telomerization of ethylene telomers, and (3) results of expt. 34. This experiment was identical with expt. 32 except that it contained 2.5 times as much CCl_4 (187 mmoles/l.), 30% more than would evaporate at 140° into 1 l. of free space. This run gave C_1 = 3.0, C_2 = 22.9, C_3 = 7.2, and C_4 = 8.4 (calculated as usual as for a homogeneous gas reaction). With this large proportion of liquid phase, the value of C_1 is not unusually large for a "high-pressure" run although the value of C_2 is.

The available conversion data show that the high-pressure runs are difficult to interpret without invoking some unknown factor, possibly condensation. At low pressures, the rate of reaction (as measured by $C_2H_4/R\cdot$ in Table I) is close to half order in peroxide (expt. 7, 10, 11, and 26), less than first order in ethylene (42 and 43), between zero and one-half order in carbon tetrachloride (11–15), and, at the same E/CCl_4 ratio, nearly proportional to the total pressure (11 and 22). These results are reasonable. On the other hand, at high pressures the rate appears higher than first order in carbon tetrachloride (32 and 33; 35 and 41), about one-fourth order in peroxide (32 and 38), and irregular with respect to ethylene (32, 35, 38, and 39).

Other possible explanations for the differences in vapor-phase values of C_1 have been considered and excluded. (a) The increase of C_1 is not due simply to higher total gas pressures since addition of excess ethane in expt. 41 does not affect C_1. (b) A nonradical addition of CCl_4 to ethylene is not involved. Experiments like 32 gave no reaction in the absence of *t*-butyl peroxide even with addition of 0.3 m*M* hydrogen chloride. (c) Walls and size of the reaction vessel have

(14) From eq. 8 in ref. 6, total product, and average concentrations of E and CCl_4, C = 17.58. From the integrated and more accurate eq. 19, C is slightly higher, 18.4. From eq. 8, substituting 4 + 1 for 1, and with $d[E]/d[CCl_4]$ based on nonvolatile material only, C = 17.65, essentially the same as for total product. An accurate integrated equation would presumably again give a slightly higher value of C (about 18.5), but eq. 19 is not applicable.

little effect on C_1. An additional experiment like 10 (Table I(b)) carried out in the 102-ml., 2.8-cm. i.d. tube used for high-pressure experiments instead of the usual 1-l. flask, yielded the same transfer constants.

If we exclude any significant effects of condensation on C_1, we can reconcile the different values of C_1 in the high- and low-pressure runs by dividing each value of C_1 by the concentration of ethylene. These ratios are shown in the last column of Table I. If they are really constant, then the reactions of $Cl_3CE\cdot$ are proportional to the concentration of carbon tetrachloride but independent of the concentration of ethylene. We can account for such behavior if CCl_4 reacts appreciably only with a Cl_3C–ethylene complex or hot radical while ethylene reacts with the stabilized radical. The weakness of this interpretation is the implausible restriction that it must not apply at the lowest ethylene pressures (expt. 22, 42, and 43), or in the liquid phase, but only in higher pressure experiments where condensation is most probable.

Comparison of Liquid- and Vapor-Phase Results. Although the absolute values of the transfer constants are similar in the liquid phase and at low pressure (Table V), the ratios C_2/C_1 and C_3/C_1 are two to three times as large for the vapor-phase reactions. This result could mean that polar effects in chain transfer are greatest with $Cl_3CE\cdot$ and that solvation favors this reaction most. On the other hand, the absolute values of C_2 and C_3 for the low-pressure, vapor-phase experiments are closer to those in methanol than to those in less polar solvents. We are unable to account for this difference and we are not sure that it is beyond experimental error. In any event, our data show surprisingly little effect of drastic changes in reaction medium on relative reactivities of carbon tetrachloride and ethylene toward the family of radicals, $Cl_3CE_{1-3}\cdot$, and therefore contribute little to understanding this effect. David and Gosselain[4b] have recently attributed the effect to changes in the entropy of activation of the propagation reaction.

Comparison of Intermolecular and Intramolecular Chain-Transfer Reactions. If we assume that $k_{p2} = k_{p3}$, then from $k_1/k_{p2} = 0.06$ mole/l. and from $k_2/k_{p3} = 0.20$ mole/l., $k_2/k_1 = 3.3$. Thus the pair of 5-hydrogen atoms in $Cl_3CE_2\cdot$ is 3.3 times as reactive as the trio of chlorine atoms in $Cl_3CE_2\cdot$. In contrast to this relation, in liquid-phase bimolecular chain transfer at 70° the trichloromethyl group in 1,1,1-trichloroethane ($C = 0.05$)[3] is 5.5 times as reactive as all five pairs of secondary hydrogen atoms in heptane ($C = 0.009$).[15] Thus the relative reactivity of chlorine compared with hydrogen is significantly less in intramolecular chain transfer. The difference may be due to the large loss of entropy when the free rotation of the trichloromethyl group is lost during intramolecular chain transfer. Our previous discussion indicated that the effect of temperature on the normal transfer constants is small.

In our telomerizations with carbon tetrachloride, intramolecular transfer competed noticeably with intermolecular transfer and chain propagation only in vapor-phase reactions. Intramolecular transfer has been recognized for some time in the high-temperature, high-pressure polymerization of ethylene. Small proportions of such rearrangements have recently been reported also in cyclohexane solution[16a] at 157–237°, and large proportions in glacial acetic acid[16b] at 140°. Since these solvents are much less reactive than carbon tetrachloride in chain transfer, they have some properties of an inert diluent.

Intramolecular Hydrogen Transfer and Chain Branching in Polyethylene. This section is an effort to relate, through several assumptions, our evaluation of k_2/k_{p3} at about 1 atm. to chain branching in the polymerization of ethylene at 1000 atm. We estimate that there should be at least ten times as much branching in the polymer as is observed. We do not know whether the discrepancy is due to an error in our estimates, to the effect of high pressure, or to phase separation.

For this estimate we assume that the relative values of the rate constants for chain propagation and intramolecular transfer of hydrogen are independent of pressure and of the chain length of the reacting radical and that the rate of chain propagation is proportional to the fugacity of ethylene. The fugacity of ethylene[17] at 1000 kg./cm.^{2} and 140° is 600 kg./cm.^{2} and so the effective concentration of ethylene is 600 times that at 1 kg./cm.^{2} (0.0296 M at 140°). Then the rate of rearrangement divided by the rate of chain propagation is $0.20/(600 \times 0\ 0296) = 0.0113$. Thus we should expect to find 1.13 butyl (and methyl) groups per 100 molecules of ethylene reacting.

Woodbrey and Ehrlich[13] found, however, that polyethylene prepared under these conditions contained only 0.16 methyl group per 100 ethylene units. Since many ethyl groups as well as butyl groups have been observed by infrared,[18] and since still other types of rearrangement may occur (especially abstraction of tertiary hydrogen at previous branching points), less than one-tenth of the expected intramolecular transfers of 5-hydrogen atoms were observed.

Acknowledgments. Drs. S. W. Benson and Dale G. Hendry have assisted us in useful discussions, Mr. William C. Anderson, Jr., in n.m.r. determinations.

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