(3) Cardenas, J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 883.
(4) Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1976**, *9*, 302.
(5) Ross, R. T.; Laurence, R. L. *AIChE Symp. Ser.* **1976**, *No. 160*, 74.
(6) Schmidt, A. D.; Ray, W. H. *Chem. Eng. Sci.* **1981**, *36*, 1401.
(7) Marten, F. L.; Hamielec, A. E. *ACS Symp. Ser.* **1979**, *No. 104*, 43.
(8) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(9) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339.
(10) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(11) Brooks, B. W. *Proc. R. Soc. London, Ser. A* **1977**, *357*, 183.
(12) High, K. A.; Lee, H. B.; Turner, D. T. *Macromolecules* **1979**, *12*, 332.
(13) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(14) North, A. M. "The Collision Theory of Chemical Reactions in Liquids"; Wiley: New York, 1964.
(15) Bird, R. B.; Armstrong, R. C.; Hassager, O. "Dynamics of Polymeric Liquids"; Wiley: New York, 1977; Vol. I, p 71.
(16) Fujita, H.; Kishimoto, A.; Matsumoto, K. *Trans. Faraday Soc.* **1960**, *56*, 424.
(17) Middleman, S. "Fundamentals of Polymer Processing"; McGraw-Hill: New York, 1977; p 362.

Radical Reactions of Highly Polar Molecules. Hydrocarbons as Chain-Transfer Agents in Fluoro Olefin Telomerizations†

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ABSTRACT: Hydrocarbons act as chain-transfer agents to provide telomeric products in the radical polymerization of tetrafluoroethylene. At 125 °C, linear alkanes (hexane, nonane, and decane) participate by transferring more than one hydrogen; by contrast, cyclopentane and cyclohexane do not. Methylcyclohexane is attacked only at the tertiary hydrogen. For comparison, the chain transfer of nonane with hexafluoropropene and chlorotrifluoroethylene as well as with tetrafluoroethylene was studied.

Although there is considerable literature on the abstraction of hydrogens by halogen atoms[1-4] and various other radicals,[5] there is little information on the reactivity of hydrocarbons as chain-transfer agents,[6] particularly for fluorinated olefins. In earlier papers we described the relative reactivities of halogenated olefins,[7] the chloromethanes,[8] and several other halocarbons[9] with tetrafluoroethylene and the use of chain-transfer constants to correlate reactivity on radical abstraction reactions to bond energy.

We have now examined the reactivity of a few hydrocarbons as chain-transfer agents in telomerization with tetrafluoroethylene and also compared the reactivity of nonane with telomer chains of tetrafluoroethylene, hexafluoropropene, and chlorotrifluoroethylene.

Experimental Section

Reaction of Hexane with Tetrafluoroethylene. A mixture of 20 g of hexane, 1.6 g of benzoyl peroxide, and 60 g of 1,1,2-trichloro-1,2,2-trifluoroethane was charged to a 300-cm^3 autoclave.[10] The autoclave was closed, cooled in a dry ice–acetone bath, and evacuated to below 50 mm, and 20 g of tetrafluoroethylene[11] was added. More than the desired 20 g of tetrafluoroethylene was charged, so the excess was bled off after the autoclave had warmed slightly. The mixture was stirred and heated. It required 1 h to reach 125 °C, where it was held for an additional hour. After the mixture cooled, unreacted tetrafluoroethylene was bled into a dry ice–acetone-cooled trap and the remaining material was distilled to separate unreacted hexane and fluorocarbon solvent. The residue was a waxy solid, mp 27–32 °C.

Elemental analyses of carbon and fluorine were used to calculate the average molecular weight and average degree of telomerization $\bar{n}$. The values agree within about 2%.

$$\bar{n} = [\%\ \mathrm{C} \times (\text{mol wt of telogen}) - 1201.1 \times (\text{no. of C in telogen})]/[2402.2 - \%\ \mathrm{C} \times (\text{mol wt of } C_2F_4)]$$

$$\bar{n} = [\%\ \mathrm{F} \times (\text{mol wt of telogen})]/[4 \times 18.998 \times 100 - \%\ \mathrm{F} \times (\text{mol wt of } C_2F_4)]$$

$$\text{mol wt of telomer} = (\text{mol wt of telogen}) + \bar{n} \times (\text{mol wt of } C_2F_4)$$

The concentrations of reactants in the liquid phase were estimated by noting the total pressure and estimating partial pressures of telogen and solvent based on the vapor pressures and relative concentrations. The difference of pressure was assumed to be due to tetrafluoroethylene.

$$P_{C_2F_4} = P_{\text{total}} - (P_{\text{telogen}} + P_{\text{solvent}})$$

The amount of tetrafluoroethylene in the vapor phase was then estimated by the gas equation, where the volume was that volume above the liquid phase. From this the concentration of tetrafluoroethylene in the liquid phase could be calculated.

$$C_2F_{4\,\text{soln}} = C_2F_{4\,\text{total}} - C_2F_{4\,\text{vapor}}$$

The chain-transfer constant was calculated by the method of Walling.[12]

$$C = \frac{1}{\bar{n}} \frac{[C_2F_4]}{[\text{telogen}]}$$

NMR spectra of the telomer residues were obtained with a Varian HA-100 spectrometer to indicate the extent of branching and, where possible, the position of attack.

Since in the linear alkanes there was more than one telomer chain initiated per molecule of hydrocarbon, a second chain-transfer constant was calculated as $\bar{n}' = \bar{n}/(\text{no. of branches})$. This is designated as C' in Table I and is used for comparisons in the Discussion.

The results of the experiments are presented in Table I and the NMR results are presented in the Discussion.

Discussion

Normal Alkanes. The reactivity to hydrogen abstraction by fluoroalkyl radicals increases with increasing chain length of the normal alkanes as noted in Table I. The reactivity is on a molar basis because the primary and secondary hydrogens were not sufficiently resolved in the NMR spectra. Thus the reactivities of these two types of hydrogen could not be distinguished. The reactivity is compared on the basis of the number of telomer chains formed. The normal alkanes did not give only one fluo-

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† Work done at Union Carbide Corp.

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Table I
Chain Transfer of Hydrocarbons with Tetrafluoroethylene

telogen structure	telogen, mol	TFE, mol	TFE recovered, mol	telomer amt, g	telomer $\bar{n}$	chain-transfer constant[a] C[a]	chain-transfer constant[a] C'[b]	no. of branches per telomer molecule[c]
hexane	0.232	0.200	0.080	10.0	1.153	0.4989	0.5488	1.1
nonane	0.156	0.200	0.100	15.0	1.907	0.3252	0.5854	1.8
decane	0.141	0.200	0.080	20.0	1.968	0.3978	0.6365	1.6
cyclopentane	0.285	0.200	0.050	17.0	1.050	0.4694	0.4694	1.0
cyclohexane	0.238	0.200	0.050	23.0	1.093	0.5010	0.5010	1.0
methylcyclohexane	0.204	0.600	0.410	22.0	3.963	0.4732	0.4732	1.0
hexane[d]	0.232	0.200	0.080	11.0	3.255	0.2859	0.6290	2.2
nonane[e]	0.156	0.200[e]	0.100[e]	11.0	2.297			2.3
nonane[f]	0.156	0.200[f]	0.133[f]	8.0	3.45	0.7087	2.3387	3.3

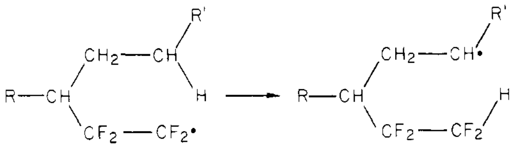
[a] Chain-transfer constant calculated by the method of Walling. [b] Chain-transfer constant using the same equation but $\bar{n}' = \bar{n}$/(no. of branches). [c] Determined by NMR spectroscopy. [d] This experiment was at 185 °C using di-*tert*-butyl peroxide as the catalyst. [e] Hexafluoropropene was used in place of tetrafluoroethylene in this experiment. [f] Chlorotrifluoroethylene was used in place of tetrafluoroethylene in this experiment.

Table II
Relative Reactivity[a]

hydrocarbon	abstracting radical $-CF_2CF_2\cdot$[b]	$C_6H_2Cl_3$-$(CH_3CO)N\cdot$[c]	$CCl_3\cdot$[d]	$CCl_3SO_2\cdot$[e]	$CH_3\cdot$[f]	$CH_3\cdot$[g]
hexane	1.0	0.96				1.00
heptane		1.0			1.0	
nonane	1.06					
decane	1.16	1.36				1.95
cyclopentane	0.86		1.57	1.0		1.02
cyclohexane	0.92	1.66	1.0	1.0	1.0	1.01
methylcyclohexane	0.86	3.32				

[a] The relative reactivities are compared within each column and not between the different radicals. [b] This work. [c] Chlorination with 2,4,6-trichloro-*N*-chloroacetanilide catalyzed by benzoyl peroxide at 85 °C.[22] [d] Bromination with $CBrCl_3$ catalyzed by benzoyl peroxide at 80 °C.[16] [e] Chlorination with CCl_3SO_2Cl catalyzed by benzoyl peroxide at 80 °C.[25] [f] Methyl radical formation from acetyl peroxide decomposition at 55 and 85 °C.[23] [g] Methyl radical formation from *tert*-butyl peracetate decomposition at 110 °C.[24]

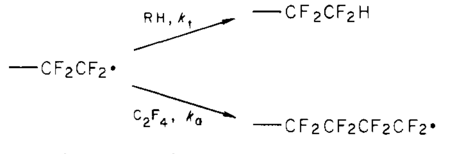
rocarbon chain per alkane molecule but, apparently by a "back-biting" mechanism, introduced more chains (eq 1).



(1)

This was true for the linear alkanes but not for the cyclic alkanes; therefore it is not a random attack.[13] Further evidence on this reaction relating to the conformation of the telogen is that the radical reaction of chlorotrifluoroethylene with ethyl ether gives "branched" telomers but with tetrahydrofuran it does not.[14]

The effect of temperature was noted in the reaction of tetrafluoroethylene with hexane. The chain-transfer constant is 0.629 at 185 °C and 0.569 at 125 °C. The activation energy difference and Arrhenius factor ratio are indicated in eq 2.



(2)

chain-transfer constant = k_t/k_a
$E^{\ddagger}_t - E^{\ddagger}_a = 0.8$ kcal/mol
$\log (A_t/A_a) = 0.19$ (L s^{-1} mol^{-1})

The differences of the attacking fluorocarbon radicals from various monomers was indicated by carrying out the telomerization of nonane with chlorotrifluoroethylene as well as with tetrafluoroethylene. Comparison of these results indicated increasing chain-transfer constants in the order $C_2F_4 < C_2ClF_3$.

$$-CF_2CF_2CF_2CF_2\cdot \xleftarrow[k_{a1}]{C_2F_4} -CF_2CF_2\cdot \xrightarrow[k_{t1}]{RH} -CF_2CF_2H$$

$$-CF_2CClFCF_2CClF\cdot \xleftarrow[k_{a2}]{C_2ClF_3} -CF_2CClF\cdot \xrightarrow[k_{t2}]{RH} -CF_2CClFH$$

Thus $k_{t1}/k_{a1} = 0.585 = C'$ and $k_{t2}/k_{a2} = 2.34 = C'$. The constants are functions of both the ease of chain transfer and the ease of polymerization of the monomers. Comparison of hydrogen abstraction reactivity thus can only be made with reference to relative rates of polymerization. In copolymerization, Bruk[15] found that chlorotrifluoroethylene and tetrafluoroethylene were of about equal reactivity. Thus, if $k_{a1} = k_{a2}$, then for comparative ease of hydrogen abstraction, $-CFCl\cdot = 4.0$ and $-CF_2\cdot = 1.0$.

Cyclic Alkanes. Cyclopentane is slightly *less* reactive than cyclohexane on a molecular basis but *more* reactive on the basis of the hydrogens available. This second order is that noted for the reactivity to several radicals including trichloromethyl,[16] trichloromethanesulfonyl,[17] and trifluoromethyl.[18,19]

The tertiary hydrogen of methylcyclohexane is much more reactive than are the hydrogens of cyclopentane or cyclohexane. Analysis of the NMR spectra indicated no attack (less than the 3% sensitivity of the NMR instrument) at any hydrogen except the tertiary hydrogen in methylcyclohexane. In bromination studies of methylcyclohexane, the selectivity to attack at the tertiary hydrogen was 64% at 23 °C and 86% at 100 °C.[20] Our value of >97% at 125 °C is not out of line with these results, although the greater selectivity at higher temperatures would not necessarily be expected.

General. The reactivities of the alkanes in telomerization with tetrafluoroethylene at 125 °C are all nearly the same. The trend of change in the linear alkanes is the same as that observed for photochlorination[21] and for benzoyl peroxide catalyzed chlorination with 2,4,6-trichloro-*N*-chloroacetanilide.[22] The reactivity of the cycloalkanes is less than that expected on the basis of the chlorination results with 2,4,6-trichloro-*N*-chloroacetanilide but about the same as expected from the reactivity with methyl radicals[23,24] and from chlorination with trichloromethanesulfenyl chloride.[25] The comparison of these results is given in Table II.

References and Notes

(1) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; pp 180–199.
(2) Sosnovsky, G. "Free Radical Reactions in Preparative Organic Chemistry"; Macmillan: New York, 1964; pp 282–296.
(3) Fuller, A. E.; Hickenbottom, W. J. *J. Chem. Soc.* **1965**, 3228.
(4) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; pp 348–396.
(5) Trotman-Dickenson, A. F. In "Advances in Free Radical Chemistry"; Williams, G. H., Ed.; Academic Press: New York, 1965, Vol. 1, pp 1–38.
(6) Walling, C. *loc. cit.*, pp 148–161, 256–259.
(7) Moore, L. O. *J. Phys. Chem.* **1970**, *74*, 3603.
(8) Moore, L. O. *J. Phys. Chem.* **1971**, *75*, 2075.
(9) Moore, L. O. *Can. J. Chem.* **1971**, *49*, 666.
(10) The reaction vessel was a Parr Magnedash autoclave of 316 stainless steel.
(11) Tetrafluoroethylene was purchased from Peninsular Chem-Research Inc. It is sold as 99.9% purity containing 1% α-pinene as an inhibitor. The inhibitor was removed by vaporizing the tetrafluoroethylene from the cylinder.
(12) Walling, C. *loc. cit.*, p 150.
(13) Similar metathesis of rearrangement within a molecule in the telomerization of ethylene with methyl chloroacetate has been reported: Friedlina, R. Kh.; Terent'ev, A. B.; Ikonikov, N. S. *Dokl. Akad. Nauk SSSR* **1970**, *193* (3), 605.
(14) Dedek, V.; Fikar, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 3769.
(15) Bruk, M. A.; Abkin, A. D.; Khomikovskii, P. M.; Gol'der, G. A.; Chu, Hsiang-Ling *Dokl. Akad. Nauk SSSR* **1964**, *157* (6), 1399.
(16) Huyser, E. S.; Schimke, H.; Burham, R. L. *J. Org. Chem.* **1963**, *28*, 2141.
(17) Davidson, R. S. *Q. R., Chem. Soc.* **1967**, *21*, 259.
(18) Stefani, A. P. *Fluorine Chem. Rev.* **1971**, *5*, 140.
(19) Jones, S. H.; Whittle, E. *Int. J. Chem. Kinet.* **1970**, *2*, 479.
(20) Agaev, U. Kh.; Movsumzade, A. A.; Rzaeva, A. Z.; Mekhtiev, Zh. M.; Smirnova, V. P. *Azerb. Khim. Zh.* **1968** (2), 8; *Chem. Abstr.* **1969**, *70*, 77397*n*.
(21) Colebourne, N.; Stern, E. S. *J. Chem. Soc.* **1965**, 3599.
(22) Boocock, J. R. B.; Hickenbottom, W. J. *J. Chem. Soc.* **1963**, 1234.
(23) Antonovskii, V. L.; Berezin, I. V.; Shevelkova, L. V. *Dokl. Akad. Nauk SSSR* **1960**, *134*, 621; *Chem. Abstr.* **1962**, *56*, 4592*d*.
(24) Pryor, W. A.; Fuller, D. L.; Stanley, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1632.
(25) Kloosterziel, H. *Recl. Trav. Chim., Pays-Bas* **1963**, *82*, 497.

Radical Reactions of Highly Polar Molecules. Acetic Acid and Related Compounds as Chain-Transfer Agents in Tetrafluoroethylene Telomerization[†]

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ABSTRACT: The relative reactivities of the hydrogens in acetic acid and ethyl acetate to abstraction by fluoroalkyl radicals at 125 °C have been determined as follows: $H-CH_2COOH$, 0.029; $H-CH_2COOCH_2CH_3$, 0.019; $H-CH_2CH_2OCOCH_3$, 0.019; $H-CH(CH_3)OCOCH_3$, 0.10. A separate series of experiments provided less precise reactivities for the abstraction of hydrogen and chlorine from acetonitrile and the chlorinated acetonitriles. The nitrile group stabilizes the intermediate radicals, leading to extensive coupling.

In previous papers we have examined the relative reactivities of halogenated olefins,[1] the chloromethanes,[2] some halofluorocarbons,[3] and several alkanes[4] with tetrafluoroethylene. We now extend the study to a group of compounds related to acetic acid.

The chain-transfer constant for acetic acid is 0.029 and for ethyl acetate 0.039 as calculated by the method of Walling.[5] The relative reactivities of the various hydrogens are as follows: $H-CH_2COOH$, 0.029; $H-CH_2COOCH_2CH_3$, 0.019; $H-CH_2CH_2OCOCH_3$, 0.019; $H-CH(CH_3)OCOCH_3$, 0.10.

The determination of reactivity followed a method previously reported for chloromethanes,[2] using tetrafluoroethylene as taxogen so that the abstraction is essentially all by fluoroalkyl radicals. The protons in the products from ethyl acetate telomerization were determined by proton NMR, with assignments of peaks as follows (chemical shift values indicated are δ relative to $(CH_3)_4Si$):

$$\underset{5.8}{H}-(CF_2CF_2)_n-\underset{3.55}{CH_2}-COO-\underset{4.05}{CH_2}-\underset{1.2}{CH_3}$$

$$\underset{1.95}{CH_3}-COO-\underset{5.4}{CH}(\underset{1.4}{CH_3})-(CF_2CF_2)_n-\underset{5.8}{H}$$

$$\underset{1.95}{CH_3}-COO-\underset{4.8}{CH_2}-\underset{2.75}{CH_2}-(CF_2CF_2)_n-\underset{5.8}{H}$$

The areas of the peaks in the NMR spectra provided a measure of the amounts of each product. The relative reactivities per proton are then estimated by the distribution[6]

$$(3C_\alpha + 2C_1 + 3C_2)/8 = C = 0.039$$

$$C_\alpha = C_2 = {}^{3}\!/_{16}C_1 \text{ (from NMR area)}$$

where $C = 0.039$ = average chain-transfer constant observed, $C_\alpha = 0.019$ = constant for $H-CH_2COOCH_2CH_3$, $C_1 = 0.10$ = constant for $H-CH(CH_3)OCOCH_3$, and C_2 =

[†] Work done at Union Carbide Corp.

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