

Radiation-induced Chain Reaction in Solutions of Tetrachloroethylene in n-Pentane

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THE presence of olefins, even at dilute concentrations, is known to alter the nature and distribution of the products in the radiolysis of saturated compounds.

We report a rather unusual chain reaction

between tetrachloroethylene, a poor radical scavenger,¹ and radiolytically generated pentyl radicals.

Solutions of freshly distilled tetrachloroethylene in n-pentane were deaerated under vacuum and irradiated with ⁶⁰Co γ -rays at room temperature.

TABLE
Major products of radiolysis of solutions of tetrachloroethylene in *n*-pentane

C ₂ Cl ₄ mmole	Scavenger mmole	<i>G</i> (C ₅ H ₁₁ Cl) ^a	<i>G</i> (C ₂ Cl ₃ H) ^b	<i>G</i> (C ₇ H ₁₁ Cl ₃) ^a	<i>G</i> (HCl) ^a	$\frac{G(C_5H_{11}Cl) + G(HCl)}{G(C_2Cl_3H) + G(C_7H_{11}Cl_3)}$
30.5		0.8	2.3	1.50	3.4	1.09
61		1.0	2.9	2.9	5.7	1.13
122		1.4	3.5	5.9	7.6	0.96
245		1.5	3.8	11.6	11.4	0.90
368		1.6	3.9	16.9	16.5	0.88
490		1.9	4.0	21.8	21.4	0.90
980		2.3	4.4	33.8	32.5	0.91
500	SF ₆ 100			18.0	21	
500	N ₂ O 200			21.4	22	
500	C ₆ H ₆ 200			20.7	21	
500	C ₅ H ₁₀ 400			2.2	3.5	
500	I ₂ 200			<0.2	≈ 3	

^a Total dose 7.2 10¹⁹ eV ml.⁻¹

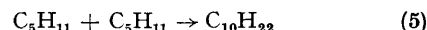
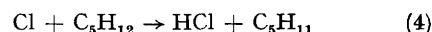
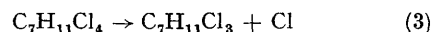
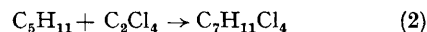
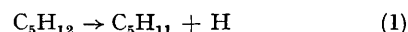
^b Total dose 4.5 10¹⁸ eV ml.⁻¹

Liquid products were determined chromatographically and identified by mass-spectrometric and infrared analysis. Hydrogen chloride was analysed coulometrically.

The yields of the major products, trichloroethylene, chloropentanes, hydrogen chloride and pentyltrichloroethylene (C₇H₁₁Cl₃) are shown in the Table. The structure of the last compound was also confirmed by combustion analysis. The chlorine balance based on the products found was satisfactory. Thus no chlorine-containing products of any importance are produced besides those determined. The yields of chloropentanes and trichloroethylene increase only slightly with growing concentrations of tetrachloroethylene. On the other hand, the formation of C₇H₁₁Cl₃, and to a lesser extent of HCl, was found to increase almost linearly with the concentration of the solute. At the lower concentration range of solute, it is clearly seen that the yield of HCl is larger than that of C₇H₁₁Cl₃. Thus at least a part of HCl yield is most probably associated with the formation of trichloroethylene. The high *G*-values for the formation of C₇H₁₁Cl₃ and HCl, 33.8 and 32.5, respectively, in the presence of 0.98 M-tetrachloroethylene would suggest that these products are formed by a chain-reaction mechanism. The fact that *G*(C₄Cl₆) was less than 0.5 at 0.5 M-concentration of C₂Cl₄ and that no C₂Cl₂ could be detected would also preclude the possibility that C₇H₁₁Cl₃ is formed, to any significant extent, by the combination of pentyl and trichlorovinyl radicals. In order to elucidate the nature of the chain mechanism the effect of several electron and radical scavengers on the yield of C₇H₁₁Cl₃ and HCl was tested. The results of these experiments are shown in the Table. N₂O and SF₆, both of which compounds are known to

be highly efficient electron scavengers,² had no effect on the yields of C₇H₁₁Cl₃ and HCl. Benzene, which is known to be an effective agent in reducing the radiolytic decomposition of hydrocarbons, by supposedly acting as an excitation-energy acceptor,³ left the yields of C₇H₁₁Cl₃ and HCl unchanged. The yields of these last two products were, however, drastically reduced when either iodine or pent-1-ene was added to the solution of tetrachloroethylene in *n*-pentane. Both iodine and pent-1-ene can be expected to act as very efficient radical scavengers.

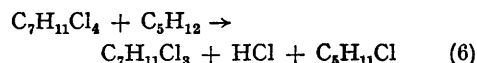
On the basis of the foregoing, the following scheme is suggested for the chain reaction:



There exists a possibility that steps (2) and (3), the chain initiation, may occur through the interaction of tetrachloroethylene with any alkyl radicals or with hydrogen atoms. In view of the fact that C₂Cl₄ is known to exhibit very low reactivity toward hydrogen atoms⁴ and alkyl radicals¹ the reaction with the long-lived pentyl radical would seem to be much more likely. Step 3, the splitting off of a chlorine atom from the C₇H₁₁Cl₄ radical, represents a rather unusual liquid-phase reaction. The addition-elimination reactions between atoms or radicals and unsaturated compounds has been postulated in the photochemical and radiation-induced isomerization

of olefins in the liquid phase.⁵ These addition-elimination reactions, however, involve the same species and can be rationalized on the basis of the formation of a complex between the radical and the double bond, the unsaturated compound being re-formed upon the subsequent release of the original atom or radical. In our case the addition of a pentyl radical to the π -bond of tetrachloroethylene would seem to result in the formation of a vibrationally excited $C_7H_{11}Cl_4$ radical which splits off a chlorine atom before being quenched by the solvent molecules.

It would seem that the only alternative to postulating processes (3) and (4) would be to assume the following reaction:⁶



This can be visualised as involving hydrogen atom-abstraction from the solvent by the $C_7H_{11}Cl_4$ radical, followed by the breakdown of the $C_7H_{12}Cl_4$ molecule into $C_7H_{11}Cl_3$ and HCl.

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³ G. R. Freeman, *J. Chem. Phys.*, 1960, **33**, 71.

⁴ P. E. M. Allen, H. W. Melville, and J. C. Robb, *Proc. Roy. Soc.*, 1953, *A*, **218**, 311.

⁵ H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 4141; M. A. Golub, *ibid.*, 1958, **80**, 1794; M. A. Golub, *ibid.*, 1959, **81**, 54.

⁶ The Authors are grateful to a Referee for suggesting this reaction.