Radiation-induced Chain Reaction in Solutions of Tetrachloroethylen 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 ^{60}Co γ-rays at room temperature.

TABLE

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

C_2Cl_4 mmole	Scavenger mmole	$G(C_5H_{11}Cl)$[a]	$G(C_2Cl_3H)$[b]	$G(C_7H_{11}Cl_3)$[a]	$G(HCl)$[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_2O 200			21·4	22	
500	C_6H_6 200			20·7	21	
500	C_5H_{10} 400			2·2	3·5	
500	I_2 200			$<0·2$	≈ 3	

[a] Total dose 7·2 10^{19} eV ml.$^{-1}$
[b] Total dose 4·5 10^{18} 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 ($C_7H_{11}Cl_3$) 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 $C_7H_{11}Cl_3$, 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 $C_7H_{11}Cl_3$. 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 $C_7H_{11}Cl_3$ 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 $G(C_4Cl_6)$ was less than 0·5 at 0·5 M-concentration of C_2Cl_4 and that no C_2Cl_2 could be detected would also preclude the possibility that $C_7H_{11}Cl_3$ 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 $C_7H_{11}Cl_3$ and HCl was tested. The results of these experiments are shown in the Table. N_2O and SF_6, both of which compounds are known to be highly efficient electron scavengers,[2] had no effect on the yields of $C_7H_{11}Cl_3$ 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 $C_7H_{11}Cl_3$ 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:

$$C_5H_{12} \rightarrow C_5H_{11} + H \qquad (1)$$

$$C_5H_{11} + C_2Cl_4 \rightarrow C_7H_{11}Cl_4 \qquad (2)$$

$$C_7H_{11}Cl_4 \rightarrow C_7H_{11}Cl_3 + Cl \qquad (3)$$

$$Cl + C_5H_{12} \rightarrow HCl + C_5H_{11} \qquad (4)$$

$$C_5H_{11} + C_5H_{11} \rightarrow C_{10}H_{22} \qquad (5)$$

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 C_2Cl_4 is known to exhibit very low reactivity toward hydrogen atoms[4] and alkyl radicals[1] 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 $C_7H_{11}Cl_4$ 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]

$$C_7H_{11}Cl_4 + C_5H_{12} \rightarrow C_7H_{11}Cl_3 + HCl + C_5H_{11}Cl \qquad (6)$$

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