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The Radiation Chemistry of Solutions of Chloromethanes in Cyclohexane

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THE radiation chemistry of solutions of chloroform and carbon tetrachloride in cyclohexane has been studied by Stone and Dyne.[1] From the nature of the product yields, a strong case was made for energy transfer from the solvent, which absorbed the primary radiation, to the solute. However, it was not possible to distinguish the exact nature of the transfer mechanism, i.e., whether via thermal electrons or excitation energy. In an attempt to clarify this problem a comparative study of the γ-radiolysis of cyclohexane solutions containing methyl chloride, methylene chloride, chloroform, and carbon tetrachloride is reported here. Methyl chloride would seem to be of special interest since gas-phase studies indicate that it does not attach thermal electrons,[2] whereas chloroform and carbon tetrachloride undergo dissociative electron capture readily.

The sole radiolytic product gaseous at liquid-air temperature in solutions of CH_2Cl_2, $CHCl_3$, and CCl_4 was hydrogen; while in the CH_3Cl–cyclohexane system methane was identified in addition to hydrogen. Of the higher-boiling products only hydrogen chloride was analysed (by amperometric titration of chloride ions), and was found to be a product with all four solutes.

$G(H_2)$ decreased and $G(HCl)$ increased with increasing solute concentration in the solutions of all four solutes (see Table). The three polychloro-methanes fit a similar $G(H_2)$ against [solute] plot, while the plot for CH_3Cl is shallower; for a given [CH_3Cl] the decrease in hydrogen yield compared with that from pure cyclohexane, $\Delta G(H_2)$, is significantly lower than that observed

with the polychloromethanes. Within the limits of the experimental error $\Delta G(H_2) = G(HCl)$ in the CH_3Cl–cyclohexane system at all concentrations. This equality is not observed with the other solutes.

In order to obtain a measure of the importance of electron-scavenging processes, solutions containing both nitrous oxide and a chloromethane were studied. Nitrous oxide has been shown to react with electrons produced in irradiated cyclohexane,[3] and it has been suggested that the yield of nitrogen is a specific measure of the electrons scavenged by nitrous oxide.[4] A second solute, S, which competes with nitrous oxide for electrons would therefore decrease $G(N_2)$, the relative reactivity, k_{N_2O}, being given by expression (A).[4]

$$k_{N_2O} = \frac{\Delta G(N_2) \ [N_2O]}{G(N_2) \ [S]} \qquad (A)$$

In the radiolysis of equimolar solutions of a given chloromethane and nitrous oxide significant decreases in $G(N_2)$ compared with that from a solution containing nitrous oxide alone were observed only with the polychloromethanes. The decrease with CH_3Cl was small, and it was found that the presence of an excess of this solute was required to bring about a sizeable decrease in $G(N_2)$. Calculated k_{N_2O}-values are listed in the last column of the Table.

It has been pointed out elsewhere[5] that the ability of aromatic solutes to diminish the hydrogen yield in the radiolysis of cyclohexane solutions may be correlated with their reactivity towards electrons

TABLE. *γ-Radiolysis of cyclohexane solutions*

Solute, mM		Nitrous Oxide mM	$G(H_2)$[a]	$G(CH_4)$[a]	$G(HCl)$[b]	$G(N_2)$[a]	k_{N_2O}[c]
—	—	—	5·6	—	—	—	—
—	—	5·0	4·9	—	—	1·1	—
—	—	50	4·1	—	—	2·5	—
CH₃Cl	5·0	—	5·1	0·25	0·30	—	—
,,	50	—	4·3	0·83	1·3	—	—
,,	,,	50	4·2	1·2	0·20	0·37	0·2
,,		50	3·7	0·74	0·88	2·1	0·2
,,	100	—	4·0	0·94	1·6	—	—
CH₂Cl₂	5·0	—	4·9	—	0·45	—	—
,,	,,	5·0	4·9	—	0·40	0·55	1·0
,,	50	—	3·4	—	1·8	—	—
,,	,,	50	3·2	—	1·7	1·2	1·1
,,	100	—	3·3	—	2·3	—	—
CHCl₃	5·0	—	4·9	—	0·80	—	—
,,	,,	5·0	4·7	—	0·80	0·48	1·2
,,	50	—	3·4	—	2·3	—	—
,,	,,	50	3·6	—	2·1	1·1	1·2
,,	100	—	3·2	—	2·6	—	—
CCl₄	5·0	—	4·7	—	1·1	—	—
,,	,,	5·0	4·6	—	1·0	0·46	1·3
,,	50	—	3·3	—	3·1	—	—
,,	,,	50	3·1	—	2·7	1·1	1·3
,,	100	—	2·9	—	3·8	—	—

[a] Total dose, $6·0 \times 10^{18}$ ev ml.$^{-1}$; dose rate, $4·0 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$
[b] Total dose, $7·2 \times 10^{19}$ ev ml.$^{-1}$; dose rate, $4·0 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$
[c] Calculated from expression (A).

(as measured in competitive radiolyses with nitrous oxide). The same correlation may be seen for the four chloromethanes.

The increase in $G(CH_4)$ on the addition of 5×10^{-3} M-nitrous oxide to a solution of 5×10^{-2} M-CH₃Cl requires comment. Dyne[1] has pointed out that the presence of an electron acceptor in irradiated alkanes increases the yield of radicals. This could be an explanation for the enhancement of the yield of methane in the presence of 5×10^{-3} M-nitrous oxide. However, on the basis of this argument it is not clear why the presence of 5×10^{-2} M-nitrous oxide does not increase $G(CH_4)$.

It has been pointed out that in a molecule R–X dissociative electron attachment is favourable whenever the electron affinity of X exceeds the bond dissociation energy of R–X.[6] This situation prevails with the chloromethanes.[7] It is therefore tempting to write a dissociative electron-capture mechanism for the formation of hydrogen chloride, e.g.,

$$CCl_4 + e^- \rightarrow CCl_3 \cdot + Cl^-$$
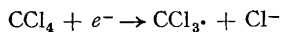
followed possibly by

$$Cl^- + C_6H_{12}^+ \rightarrow C_6H_{11} \cdot + HCl.$$
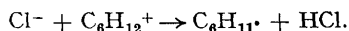
However, the observations that nitrous oxide does not appreciably decrease the yields of hydrogen chloride would appear to be inconsistent with this mechanism being of major importance. Furthermore, it would be difficult to attribute the yields of HCl in the radiolysis of CH₃Cl solutions to an electron-capture process in view of the low electron affinity of CH₃Cl.

It may be concluded that while it is possible to explain at least part of the reduction in hydrogen yields brought about by the presence of the chloromethanes by an electron-capture process, the latter cannot be of major importance in the formation of hydrogen chloride. Some other energy-transfer process must be involved in the formation of this product, and presumably the other chlorine-containing products.

[1] J. A. Stone and P. J. Dyne, *Canad. J. Chem.*, 1964, **42**, 669. See also, P. J. Dyne, *ibid.*, 1965, **43**, 1080.
[2] V. H. Dibeler and R. M. Reese, *J. Res. Nat. Bur. Stand.*, 1965, **54**, 127.
[3] G. Scholes and M. Simic, *Nature*, 1964, **202**, 895; G. Scholes, M. Simic, G. E. Adams, J. W. Boag, and B. D. Michael, *ibid.*, 1964, **204**, 1187.
[4] W. V. Sherman, *J. Chem. Soc. (A)*, 1966, 599.
[5] W. V. Sherman, *Nature*, in the press.
[6] W. H. Hamill, J. P. Guarino, M. R. Ronayne, and A. J. Ward, *Discuss. Faraday Soc.*, 1963, **36**, 169.
[7] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, p. 149; T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954, p. 277.