Electron Attachment to DCl in the γ-Radiolysis of Cyclohexane + DCl Solutions

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γ-RADIOLYSIS of solutions of DCl in cyclohexane results in the formation of HD and D_2: *G*-values for the yields of HD, D_2, and H_2 (Table) were obtained from yield against dose plots, which were linear over the dose range studied (1—3 × 10^{18} ev. ml.$^{-1}$). The results indicate that DCl can, at low concentrations, react with a precursor of hydrogen in irradiated liquid cyclohexane, which, since $k(H + DCl)/k(H + C_6H_{12}) \not> 10$, cannot be a thermal H atom. These observations are compatible with our original proposal[1] that electron attachment to suitable scavengers (*e.g.*, N_2O) can occur in these irradiated non-polar systems. On this basis, the formation of HD and of D_2 in cyclohexane + DCl solutions will result mainly from the reactions:

$$e^- + DCl \xrightarrow{(DCl)} D + Cl^-_{DCl} \quad (1)$$

$$D + C_6H_{12} \rightarrow HD + C_6H_{11}\cdot \quad (2)$$

$$D + DCl \rightarrow D_2 + Cl \quad (3)$$

Reaction (3) should be of significance only at higher DCl concentrations, and the observed D_2 yields (see Table) are consistent with this premise. A contribution to the HD yield can also arise from the reaction of any radiolytically produced H atom with DCl, *viz.*,

$$H + DCl \rightarrow HD + Cl \quad (4)$$
$$\rightarrow HCl + D$$

but here also, the contribution will only be significant at higher scavenger concentrations.

TABLE

γ-Radiolysis of cyclohexane + DCl *solutions*

[DCl]	*G*-values H_2	HD	D_2	HD + D_2
0	5·40	—	—	—
3·2	5·15	0·76	0·006	0·77
9·8	4·67	1·33	0·013	1·34
82·6	3·81	2·07	0·084	2·15
100	3·12	2·65	0·17	2·82
208	2·64	3·01	0·40	3·41
356	2·35	3·26	0·62	3·88

The values of $G(HD) + G(D_2)$ at the various DCl concentrations will therefore represent an *upper* limit for the extent of reaction (1). These values are lower, by about 25%, than those of $G(N_2)$ from irradiated cyclohexane + N_2O solutions of equivalent N_2O concentration, even though $k(e^- + N_2O)/k_1 \sim 1$; hence, in this latter system it is possible that some nitrogen is formed from a process other than $N_2O \xrightarrow{e^-} N_2 + O^-$.

Since the formation of D atoms from DCl by dissociative capture of a thermal electron is endothermic to the extent of 0·7 ev, the electron attachment process, reaction (1), may involve more than one DCl molecule; such association has already been suggested for electron capture by HCl both in the solid[2] and gaseous[3] phase.

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