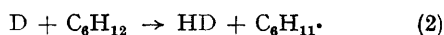
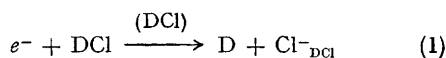


Electron Attachment to DCl in the γ -Radiolysis of Cyclohexane + DCl Solutions

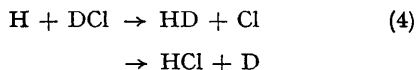
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γ -RADIOLYSIS of solutions of DCl in cyclohexane results in the formation of HD and D₂: G-values for the yields of HD, D₂, and H₂ (Table) were obtained from yield against dose plots, which were linear over the dose range studied ($1-3 \times 10^{18}$ ev. ml.⁻¹). The results indicate that DCl can, at low concentrations, react with a precursor of hydrogen in irradiated liquid cyclohexane, which, since $k(\text{H} + \text{DCl})/k(\text{H} + \text{C}_6\text{H}_{12}) \gg 10$, cannot be a thermal H atom. These observations are compatible with our original proposal¹ that electron attachment to suitable scavengers (*e.g.*, N₂O) can occur in these irradiated non-polar systems. On this basis, the formation of HD and of D₂ in cyclohexane + DCl solutions will result mainly from the reactions:



Reaction (3) should be of significance only at higher DCl concentrations, and the observed D₂ 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.*,



* G. Scholes and M. Simic, *Nature*, 1964, **202**, 895.

² D. A. Armstrong, *Canad. J. Chem.*, 1962, **40**, 1385.

³ R. A. Lee, *Nature*, 1967, **216**, 57.

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

TABLE
 γ -Radiolysis of cyclohexane + DCl solutions

[DCl]	H ₂	G-values		
		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 $G(\text{HD}) + G(\text{D}_2)$ 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 $G(\text{N}_2)$ from irradiated cyclohexane + N₂O solutions of equivalent N₂O concentration, even though $k(e^- + \text{N}_2\text{O})/k_1 \sim 1$; hence, in this latter system it is possible that some nitrogen is formed from a process other than $\text{N}_2\text{O} \xrightarrow{e^-} \text{N}_2 + \text{O}^-$.

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 solid² and gaseous³ phase.

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