

Elimination of Halogen Radical Anions from Vic-Dihalides  
on exposure to High Energy Radiation

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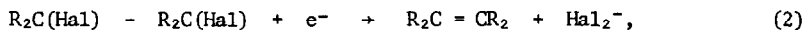
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Abstract : Vic-dihalides such as  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Br}$ ,  $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$  and  $\text{CH}_2\text{I}-\text{CH}_2\text{I}$  in methanol glasses at 77K gave strong e.s.r. signals characteristic of  $\text{Cl}_2^-$ ,  $\text{BrCl}^-$ ,  $\text{Br}_2^-$  and  $\text{I}_2^-$  respectively, after exposure to  $^{60}\text{Co}$   $\gamma$ -rays.

The normal reaction between alkyl halides and electrons is dissociative electron capture (1)



However, vic-dihalides seem to be unique in preferring to undergo the elimination (2)

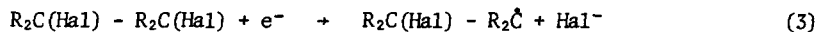


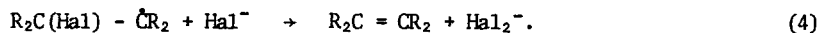
in preference to (1). For the pure solids after irradiation, e.s.r. spectra were complex, and evidence for process (2) was somewhat ambiguous. However, the use of methanol ( $\text{CO}_3\text{OD}$ ) glasses suppressed inter-molecular interactions, and the formation of electron-loss centres by the organic halides, and the e.s.r. spectra gave well-defined features characteristic of  $\text{Hal}_2^-$  radical ions.<sup>1,2</sup>

In order to ensure that clustering was not occurring and facilitating inter-molecular effects, we studied solutions containing either  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Br}$ , or a mixture of  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$  and  $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ . The former gave features characteristic of  $\text{BrCl}^-$  with no sign of  $\text{Cl}_2^-$  or  $\text{Br}_2^-$  features, whereas the latter gave a mixture of features characteristic of both  $\text{Cl}_2^-$  and  $\text{Br}_2^-$ .

Methyl substitution had no effect on the relative yields of these anions, and dihalide anions were not obtained from 1,1- 1,3- or 1,4- dihalides under these circumstances. Thus process (2) seems to be quite characteristic of vic-dihalides, presumably because of the high stability of the olefinic product.

It is, of course, possible that the formation of  $\text{Hal}_2^-$  occurs in two stages, (3) and (4):





However,  $\beta$ -halo radicals,  $R_2C(Hal) - \dot{C}R_2$  are usually stable at 77K <sup>3-5</sup> and it seems to us improbable that process (4) would occur spontaneously at that temperature. Since no spectral features for  $\beta$ -halo radicals were detected, we favour the direct elimination (2).

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