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

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Abstract : Vic-dihalides such as CH_2Cl-CH_2Cl, CH_2Cl-CH_2Br, CH_2Br-CH_2Br and CH_2I-CH_2I in methanol glasses at 77K gave strong e.s.r. signals characteristic of Cl_2^-, $BrCl^-$, Br_2^- and I_2^- respectively, after exposure to ^{60}Co γ-rays.

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

$$\mathrm{RHal} + e^- \rightarrow \mathrm{R}\cdot + \mathrm{Hal.}^- \qquad (1)$$

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

$$\mathrm{R_2C(Hal)} - \mathrm{R_2C(Hal)} + e^- \rightarrow \mathrm{R_2C = CR_2} + \mathrm{Hal_2}^-, \qquad (2)$$

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 (CO_3OD) 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 Hal_2^- radical ions.[1,2]

In order to ensure that clustering was not occurring and facilitating inter-molecular effects, we studied solutions containing either CH_2Cl-CH_2Br, or a mixture of CH_2Cl-CH_2Cl and CH_2Br-CH_2Br. The former gave features characteristic of $BrCl^-$ with no sign of Cl_2^- or Br_2^- features, whereas the latter gave a mixture of features characteristic of both Cl_2^- and 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 Hal_2^- occurs in two stages, (3) and (4):

$$\mathrm{R_2C(Hal)} - \mathrm{R_2C(Hal)} + e^- \rightarrow \mathrm{R_2C(Hal)} - \mathrm{R_2\dot{C}} + \mathrm{Hal}^- \qquad (3)$$

$$R_2C(Hal) - \dot{C}R_2 + Hal^- \rightarrow R_2C = CR_2 + Hal_2^-. \qquad (4)$$

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

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