

Radiolytic Hydrogen Yield from Solutions of Chloro-substituted Ethylenes in Cyclohexane

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THE presence of olefins, even at dilute concentration, is known to reduce considerably the yields of hydrogen formed in the radiolysis of saturated hydrocarbons. To account for this, both chemical reactions involving hydrogen-atom scavenging,¹ and physical interactions such as charge or energy transfer have been invoked.^{2,3} We report here the effect of several chloro-substituted ethylenes on the radiolytic hydrogen yield from cyclohexane, as these results illustrate clearly the importance of physical interactions in the reduction of the radiolytic hydrogen yield.

cyclohexane by ethylene is due to hydrogen-atom scavenging. The substitution of hydrogen atoms in ethylene by bulky chlorine atoms would be expected to reduce the hydrogen affinity of the olefin because of steric hindrance. The inductive effects of the halogens on the π -bond should not affect the ease of addition of a neutral species, such as atomic hydrogen to an olefin. Thus the chloro-substituted ethylenes should be less effective scavengers of hydrogen atoms, and indeed tetrachloroethylene has been reported to be unreactive towards hydrogen-atom addition.⁶

TABLE

Effect of solutes on the radiolytic hydrogen yield in cyclohexane.
(Total radiation dose 8.6×10^{19} ev ml.⁻¹)

Solute concentration	G(H ₂) solutes:			
	C ₂ H ₄ ^a	cis-C ₂ Cl ₂ H ₂	C ₂ Cl ₃ H	C ₂ Cl ₄
mmole				
10	5.3	4.57	4.26	4.10
25	4.9	4.13	3.66	3.53
50	4.8	3.66	3.23	2.90
100	4.8	3.05	2.91	2.75

^a Values were taken from the data of Cramer and Piet (see ref. 5).

Solutions of freshly distilled *cis*-1,2-dichloro-, trichloro-, and tetrachloro-ethylene in cyclohexane were deaerated under vacuum and irradiated with ⁶⁰Co γ -rays at room temperature. Hydrogen, the only product volatile at liquid-air temperature, was measured volumetrically. Comparison of the hydrogen yields at all the concentrations of solutes used (see Table) shows clearly that the decrease in radiolytic hydrogen yield becomes more pronounced with the progressive substitution of the hydrogen atoms of ethylene by chlorine atoms. Ethylene is reported to be unreactive towards low-energy electrons.⁴ The possibility of charge transfer from a molecular solvent cation to ethylene is not plausible since the ionization potential of cyclohexane is lower than that of ethylene. Neglecting the possibility of excitation transfer, it has therefore been suggested⁵ that the reduction in the radiolytic hydrogen yield from

Therefore the radiolytic hydrogen yields in our experiments should be higher than those in the presence of unsubstituted ethylene. However the opposite is found, and we therefore conclude that hydrogen-atom scavenging by solutes is not a major cause of the observed decrease in hydrogen yield.

The ionization potentials of *cis*-1,2-dichloro-, trichloro-, and tetrachloro-ethylene are very close, namely 9.65, 9.47, and 9.5 eV, respectively.⁷ Thus the occurrence of charge-transfer processes would not account for the more pronounced decrease in hydrogen yield in the presence of higher chloro-substituted ethylenes. However the electron affinity of chloro-ethylenes might well rise with increasing chlorine content of the alkene. Electron-scavenging processes by the solute are thus consistent with our experimental findings.

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