Isotope Effects in the Radiolysis of Methanol–Perdeuterobenzene Solutions

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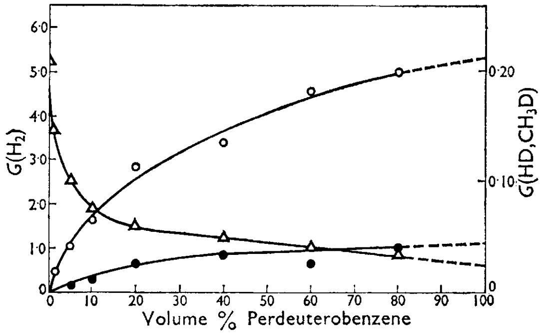
DURING an investigation into the mechanism of the "protection" effect in the radiolysis of binary mixtures[1,2] both positive and inverse secondary isotope effects (Table) have been observed in the yields of predominant products from the radiolysis of methanol–perdeuterobenzene solutions. This result is of considerable importance for reaction mechanism studies in radiation chemistry[3] for the following reasons. (i) Positive isotope effects have been found over the whole range of benzene concentration studied for those products (biphenyl and anisole) which may involve rupture of C–H or C–D bonds at some stage of their formation. (ii) Inverse isotope effects, which become increasingly more negative as the concentration of methanol increases, have been observed for those products (cyclohexa-1,4-diene, phenylcyclohexa-2,5-diene, and cyclohexadienemethanol) which present evidence[1,2] indicates may be formed by addition of radicals to benzene. (iii) Radical scavenging by benzene as distinct from energy transfer, contributes significantly to the "protection" phenomenon. (iv) Both substitution (anisole) and addition reactions would appear to be involved in the mechanism of scavenging product formation. It is also significant that the addition of 5% by volume of methanol to perdeuterobenzene[4] results in a marked decrease in the isotope effects of cyclohexa-1,4-diene and phenylcyclohexa-2,5-diene, indicating that radical reactions may occur even at this high concentration of benzene.



FIGURE

Yield of H_2, HD *and* CH_3D *from methanol–perdeuterobenzene solutions. All yields corrected for the dilution of methanol by perdeuterobenzene.*

● CH_3D ○ HD △ H_2

Examination of the yields of HD and CH_3D from the methanol–perdeuterobenzene solutions (Figure) suggests that a significant fraction of the apparently unscavengable molecular yield of hydrogen from methanol is formed through species derived from both methanol and benzene. The formation of CH_3D with a perdeuterobenzene concentration dependency similar to that of HD is important, particularly since the yield of methane from methanol is not affected by the addition of benzene.[5,6] It would thus appear that the methyl radical, rather than reacting with benzene by addition as has been proposed for other species[1,2] is capable of abstracting a hydrogen or deuterium atom from benzene, even though the latter process is energetically less favoured, at least in conventional thermal reactions.[7] This observation may also contribute to the understanding of the mechanism of formation of those radiolysis products from methanol (*e.g.*, formaldehyde and methane) which are not affected by benzene, while the yields of other products (ethylene glycol and hydrogen) are drastically reduced.[1,2] In this respect it is significant that inorganic radical scavengers such as iodine and ferric ion, which do not possess hydrogen atoms capable of abstraction, do decrease the yield of methane from methanol.[8,9]

TABLE

*Isotope effects observed in the formation of radiolysis products in methanol–benzene solutions**

Mole fraction benzene	Biphenyl	Phenyl-cyclohexadiene	Cyclohexa-1,4-diene	Cyclohexadiene-methanol	Anisole
1·00	2·13	2·25	2·30	—	—
0·90	2·35	1·16	1·10	0·70	1·50
0·81	2·23	1·02	0·95	0·69	1·40
0·65	2·31	0·94	0·90	0·70	1·23
0·41	2·23	0·91	0·90	0·75	1·31
0·23	2·67	0·90	0·95	0·70	1·50
0·10	2·21	0·89	0·90	0·82	1·43
0·05	2·19	0·87	0·85	0·80	1·60

* Isotope effect is the ratio of product *G*-values in $CH_3OH + C_6H_6$ to those in $CH_3OH + C_6D_6$

With respect to the secondary inverse isotope effects observed in the formation of cyclohexadiene, phenylcyclohexadiene and cyclohexadienemethanol, negative isotope effects of the same order of magnitude have previously been reported for conventional free-radical reactions involving radical addition to unsaturated compounds[10,11] and in the radiation-induced addition of tritium and hydrogen atoms to normal benzene.[12] These results therefore indicate that inverse isotope effects of considerable magnitude are observed in the addition of radicals to deuterated materials and by implication of the work of Yang, Scott, and Burr[12] in the addition of hydrogen and deuterium to normal benzene. It is thus essential to consider the significance of the present isotope effects in the interpretation of data from the radiolysis of binary mixtures, particularly the mechanistic aspects associated with the "protection" phenomenon in benzene–methanol.

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