Effect of Polycyclic Aromatic Additives on the Radiolysis Yields from Methanol

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RECENT studies on the radiolysis of polycyclic arenes in aliphatic alcohols[1,2] have emphasised the significance of the scavenging of the solvated electrons by these additives. During a comprehensive investigation into the effects of a number of polycyclic additives on the yields of radiolysis products from methanol, evidence has also been obtained for the extensive participation of free-radical scavenging by these additives. Of importance here is the chemical fate of the polycyclic additives. For example, the addition of each of the polycyclic hydrocarbons (Fig. 1 and 2) decreases the yields of hydrogen and ethylene glycol from methanol and at the same time extensive decomposition of the hydrocarbons occurs. Moreover, whilst evidence of a two-step production in the hydrogen yield from methanol is obtained for the polycyclics reported in Figure 1, in agreement with previously published results,[3] this observation is absent in the effect of the polycyclics on the ethylene glycol yield from methanol. Since the decrease in hydrogen yield at very low additive concentrations has been attributed to the scavenging of the solvated electrons by the additives[3] the present results indicate that the scavenging of the solvated electron results in a decrease in the hydrogen, but not of the ethylene glycol, yield.

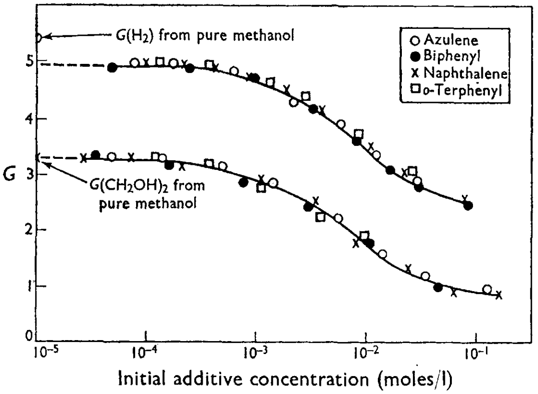

FIGURE 1.

Effect of initial additive concentration on the yields of hydrogen and ethylene glycol from methanol.

From Figure 2 it can be seen that the decrease in the hydrogen and ethylene glycol yields from methanol upon addition of the polycyclic hydrocarbons is also accompanied by the appreciable decomposition of the additives. In the case of naphthalene and naphthalene-d_8 this decomposition is associated with a reverse isotope effect, which is analogous to the reverse isotope effects previously observed for certain scavenging products in the radiolysis of methanol–benzene and methanol–benzene-d_6 solutions.[4,5] Analysis of the decomposition products from some of the hydrocarbon additives indicated that these were predominantly of a higher molecular weight and only little indication of aromatic character was obtained.

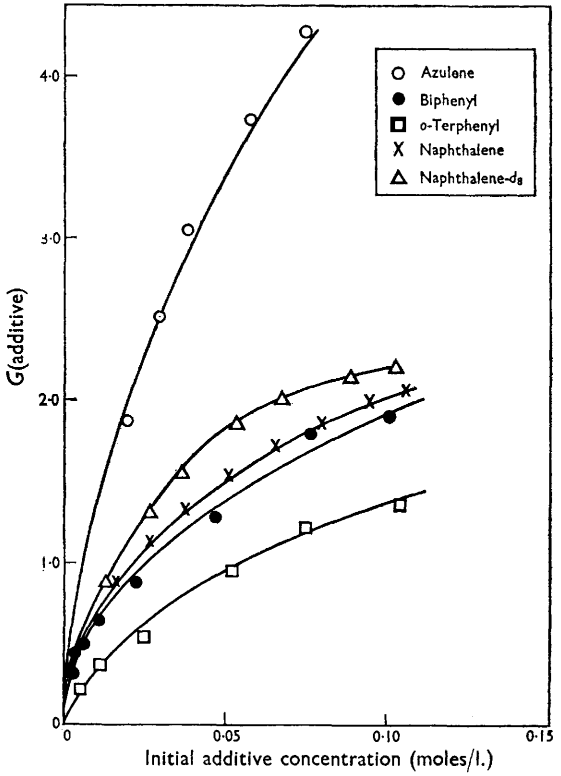

FIGURE 2.

Effect of initial concentration on the decomposition of arenes in methanol solution.

Taken in conjunction with the reverse isotope effects which are characteristic of free-radical addition to unsaturated systems,[6,7] the results suggest that the decomposition of the additives is due predominantly to radical scavenging by the additive and by implication, that free-radical scavenging contributes significantly to the "protection effects" observed in these systems.

(*Received, October 13th,* 1966; *Com.* 772.)

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