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REVIEW

Recent Developments in the Mechanism of the Protection effect of Aromatic Compounds on the Radiolysis of Aliphatics

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ABSTRACT

The proposed mechanisms by which aromatic compounds protect aliphatic materials from enhanced radiolytic decomposition are reviewed. Recent developments in this field using the radiolysis of methanol-benzene as a typical system are discussed. Emphasis has been placed on the identification and isolation of the scavenging products from methanol-benzene also the chemical fate of the added benzene. Isotope effects have been used to elucidate possible mechanisms of formation of the scavenging products. The application of the results of this study to the problem of self-destruction of radioactive compounds is discussed. An interpretation of the mechanism of the protection effect in terms of the storage of labelled molecules is made.

I. INTRODUCTION.

The use of aromatic compounds such as benzene to protect aliphatic material such as cyclohexane from excessive degradation during radiolysis is well known (1). The mechanism by which this protection effect occurs is important, not only in fundamental radiation chemistry but also in analogous fields such as the labelling of compounds with radioactive tracers where storage of the finished product without radiation-induced decomposition prior to use is a problem (2). This self-destruction of radioactive compounds is predominant in aliphatics and also unsaturated hydrocarbons because of extensive cross-linking and polymerisation whereas aromatic hydrocarbons are relatively stable. Conventional methods used for storing radioactively labelled compounds thus involve (i) solution in a protecting solvent which is usually benzene or some other aromatic compound, (ii) standing in a deep freezer since destructive coefficients usually decrease with decreasing temperature and (iii) storage in vacuo since oxygen almost always increases the magnitude of the destruction.

It is the purpose of the present paper to review mechanistic work published on the protection effect of aromatic compounds on the radiolytic decomposition of aliphatic materials and to use the radiolysis of benzene in methanol to discuss recent developments in this field. In particular, emphasis will be placed on the detection and yield estimation of the scavenging products, also the chemical fate of the added benzene.

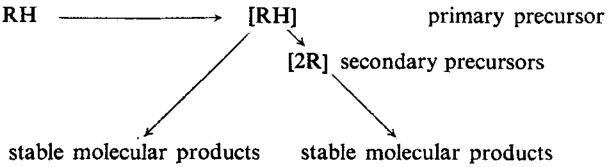
II. THE PROTECTION EFFECT — THE ADDITIVITY RULE.

It is commonly suggested that in the radiolysis of liquid mixtures, the fraction of the total absorbed energy absorbed by each component of the mixture is proportional to the number of electrons the component contributes to the total number of electrons present in the mixture. This postulate is the basis of the additivity rule (1, 3) which for a binary mixture, may be expressed as follows :

$$G(P)_{\text{observed}} = e_A G_A(P) + e_B G_B(P)$$

where $G(P)_{\text{observed}}$ is the observed yield formed from a mixture whose components give yields $G_A(P)$ and $G_B(P)$ and e_A, e_B are the electron fractions of components A and B in the mixture.

This rule applies essentially to the Compton energy range, and furthermore refers only to the yield of primary products. Since the primary products ensuant from the radiolysis of a liquid are usually not amenable to direct observation (due to their high reactivity), it must be assumed that the yields of the observable (stable) products are in direct proportion to their primary and secondary precursors. As a typical example, the radiolysis of an organic liquid may result in the formation of a primary precursor (either an ion or excited molecule) which in turn may decompose or react to form either stable products or a secondary precursor which may be a free radical (Eq. 1) :



(1)

Hence in the radiolysis of a binary mixture of organic compounds, the yields of the observable molecular products (e.g. H_2) can only be expected to follow the additivity rule if the following conditions are satisfied :

(1) The energy absorbed by each component in the mixture is proportional to the electron fraction of the component in the mixture;

(2) The individual components of the mixture do not interact with the primary precursors to the radiolysis products of the other components;

(3) The individual components of the mixture do not interact with the secondary precursors to the radiolysis products of the other components.

The additivity rule has been found to be observed in a number of systems, particularly if the components of the mixture are chemically similar compounds (1, 4, 5).

However in a number of systems, and in particular, in the well-known cyclohexane-benzene system (1), large deviations from the additivity rule are observed (Fig. 1). Since these deviations are usually negative, i.e. the yields are lower than predicted, it has been customary to refer to these deviations as the protection phenomenon (1).

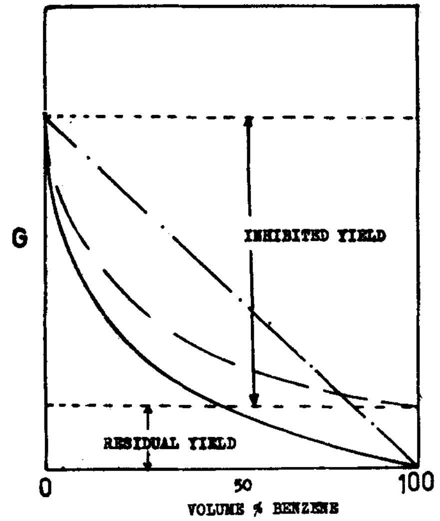


FIG. 1. Schematic representation of a typical inhibition curve.

———— Experimental curve.

—.—.— Curve expected from additivity rule.

— — — Yields corrected for the dilution of the solvent by benzene.

Only a small change in the shapes of the curves is observed if the yields are plotted as a function of electron fraction rather than volume percent.

III. INTERPRETATION OF THE PROTECTION PHENOMENON.

It is thus clear that three conditions require to be fulfilled before the yields of radiolysis products from a given binary mixture can be expected to follow the additivity rule. Conversely the elucidation of the mechanism of protection operating in a given system resolves itself into determining which of the three conditions (or combination of conditions) are not fulfilled by the system. Hence the following interpretations may be considered :

(*a*) The additive absorbs a greater fraction of the total absorbed energy than expected from its electron fraction in the mixture;

(*b*) The additives interact with the primary precursors of the solvent radiolysis products by some form of charge or energy transfer;

(*c*) The additive interferes with the reactions of the secondary precursors of the solvent radiolysis products in such a way as to yield products differing from those which would have been obtained in the absence of the additive.

The above interpretations correspond approximately to interactions in the physical, physico-chemical and chemical stages of the radiolysis (6), and each has been postulated as a possible mechanism. These mechanisms will be examined in some detail below.

(a) *The preferential absorption of energy by the additive.*

Implicit in the derivation of the additivity rule is the assumption that the secondary electrons transfer their energy to each of the components of the mixture in the same proportion as the primary radiation. This assumption is of considerable importance since the secondary electrons are considered to be responsible for an appreciable part of the total radiation-induced chemical change (7).

Recently Inokuti (8) has concluded that the cross-section of excitation by fast electrons of the π electrons of benzene and other aromatic compounds is much greater than the total inelastic cross-section of the σ electrons. Lamborn and Swallow (9) and Swallow (7) have used this data and suggested that the protection phenomenon is in fact a reflection on the selective absorption of energy by the (usually) aromatic additive. This interpretation has been questioned by Merklin and Lipsky (10) and Matheson (11). It is also difficult to see why, for example in the methanol-benzene system (12-14) the yields of hydrogen and ethylene glycol do *not* follow the additivity rule, while the yields of methane and formaldehyde do obey the rule over the whole range of benzene concentration.

(b) *Interaction between the additive and the primary precursors.*

(i) *Excitation energy transfer.*

The role of excitation energy transfer as an interpretation of the protection phenomenon was first discussed by Manion and Burton (1), and has since been extensively used to interpret the yields of radiolysis products from a variety of binary mixtures (15-18). The mechanism considers that the excited molecules (A*) formed upon irradiation of solvent A can efficiently transfer their energy to the additive B if the excitation potential of A is greater than the excitation potential of B (Eq. 2) :

$$A^* + B \rightarrow B^* + A \tag{2}$$

This transfer thus prevents the decomposition of solvent A into stable products or free radicals, thus profoundly affecting the subsequent radiation chemistry. Recently the theory has been extended (19, 20) to include delocalised energy absorption in the solvent followed by localisation of the energy on the additive molecule.

Although there can be little question of the physical reality of energy transfer mechanisms particularly with respect to scintillation and sensitised fluorescence phenomena (21, 22), the precise nature of the energy transfer mechanism *as applied to the protection phenomenon* is largely unknown, and several authors (10, 23) have indicated the difficulties associated with the extrapolation of conclusions and research from scintillation and fluorescence experiments to the protection phenomenon of radiation chemistry. It is however interesting to note that a direct observation of excitation energy transfer has recently been made (24), but it is not clear if this observation can be related to the protection phenomenon.

(c) *Charge transfer and electron capture* *.

The possibility of charge transfer and electron capture reactions as interpretations of the protection phenomenon was first proposed by Manion and Burton (1) and was subsequently discussed in detail by Burton and Lipsky (25) and more recently by Dyne (26). The discovery of the participation of the solvated electron (and by implication, its parent ion) in the physico-chemical and chemical stages of the radiolysis (27) and the experiments of Hamill and co-workers illustrating the importance of both associative and dissociative electron capture (28-30), have clearly shown the importance of ionic interactions in systems where the solutes have high electron affinities.

(d) *Interactions between the additive and the secondary precursors.*

The secondary precursors to the ultimate radiolysis products are probably to a large extent free radicals, so that the mechanism of protection at present under consideration is one of free radical scavenging by the additive. Although it is well known that free radicals react readily by addition with unsaturated centres in molecules and would hence be expected to react with benzene, the interpretation of the protection phenomenon exclusively in terms of free radical scavenging presents considerable difficulties and has not generally been accepted (1, 17, 26, 31). This conclusion has been reached primarily because the reaction products (scavenging products) which must result from the scavenging action of the additive have, with very few exceptions, not been observed or, if observed, their yields have been far too low to account for the protection observed. Typically, even in the most thoroughly investigated cyclohexane-benzene system (32), no scavenging product has to date been identified which could be attributed to the addition to benzene of hydrogen atoms derived from cyclohexane.

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* For a detailed discussion the reader should consult reference 26.

However the high decomposition of benzene in cyclohexane during radiolysis (17, 26, 33) suggests that a chemical interaction occurs, and in the radiolysis of *n*-hexane cyclohexene solutions, cyclohexane is formed. Similarly a study (34) of the radiolysis of ^{14}C-cyclohexene solutions in cyclohexane provided evidence for the scavenging of hydrogen atoms by the ^{14}C-cyclohexene, this conclusion contrasting with that reached by Dyne (17) from a study of the same system.

It may finally be pointed out that although it is often found that additives of greatly differing chemical and physical properties have almost identical effects on the yields of radiolysis products from a common solvent, it cannot be taken as established that all additives decrease the yield by the same mechanism. It is felt that the precise mechanism of protection afforded by any particular additive can only be elucidated by examining the effect of the additive on all of the radiolysis products and by a detailed examination of the chemical fate of the additive.

The principles outlined above are illustrated in the data reported in the remainder of the manuscript for the radiolysis of the benzene-methanol system. Particular emphasis is given to the separation and identification of the scavenging products in order to elucidate the possible mechanisms of formation of these compounds. Isotope effects in the radiolysis system have also been examined from a mechanistic viewpoint. Methanol was chosen as a representative compound in the present studies, since methanol is more polar than cyclohexane and thus a more varied range of scavenging products should be obtained than with benzene-cyclohexane.

IV. METHODS AND RESULTS.

Details of the experimental procedures have been previously described (13, 14, 35). Methanol was purified by the method described by Baxendale and Mellows (12), benzene by triple crystallisation followed by distillation from sodium. The gaseous products were analysed by mass spectrometry, the ethylene glycol by the periodate method (36), and the scavenging products by gas chromatography. Benzene-d_6 was prepared by the catalytic exchange method (37), and contained 98 atom percent deuterium.

Figure 2 shows the effect of benzene concentration on the yields of hydrogen and ethylene glycol from methanol-benzene solutions. The curves obtained are typical inhibition curves observed on a number of occasions (1, 10, 15, 17, 26), and are in good agreement with the results previously described for the methanol-benzene system (12, 38).

Figure 3 shows the effect of benzene concentration on the yields of anisole and cyclohexadiene-methanol. The yields of both products are sharply increased by the addition of small concentrations of benzene to methanol, a maximum yield being reached at 20% by volume benzene, the yields then decreasing linearly with further addition of benzene. This behaviour is

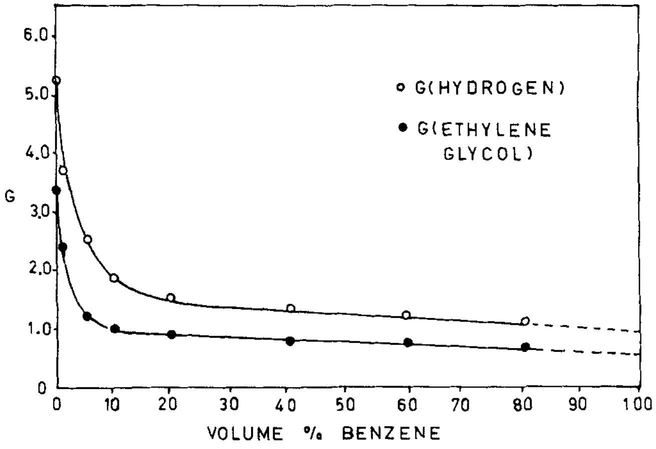


Fig. 2.

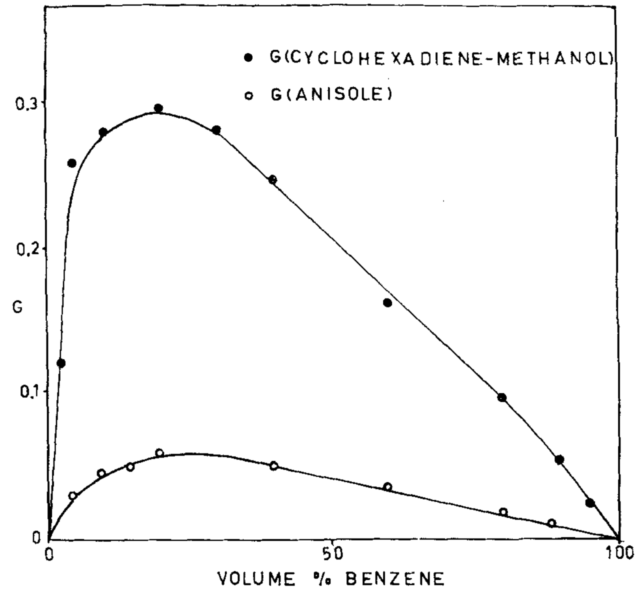


Fig. 3.

analogous to that previously observed for the yield of phenyl-cyclohexadiene from cyclohexane-benzene solutions (32). Correction of the yields for the dilution of methanol by benzene (Fig. 4) suggests that this decrease in yield is probably due to the dilution of the solvent by the additive. Plotted in this fashion, the results also emphasise the relationship between the formation of the scavenging products and the decrease in the radiolysis yields from methanol.

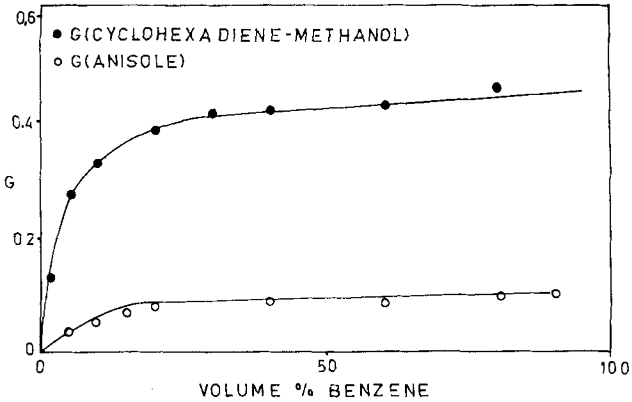


FIG. 4.

Figure 5 shows the effect of benzene concentration on the yields of biphenyl and phenyl-cyclohexadiene, both products being formed with a small yield in the radiolysis of pure benzene. The results show that while the addition of methanol to benzene decreases the yield of biphenyl, it sharply increases the yield of phenyl-cyclohexadiene, a maximum value being reached at approximately 70% by volume benzene.

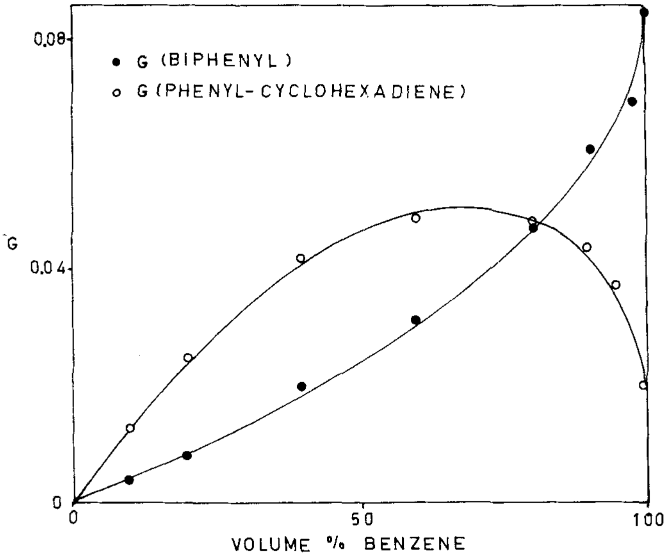


FIG. 5.

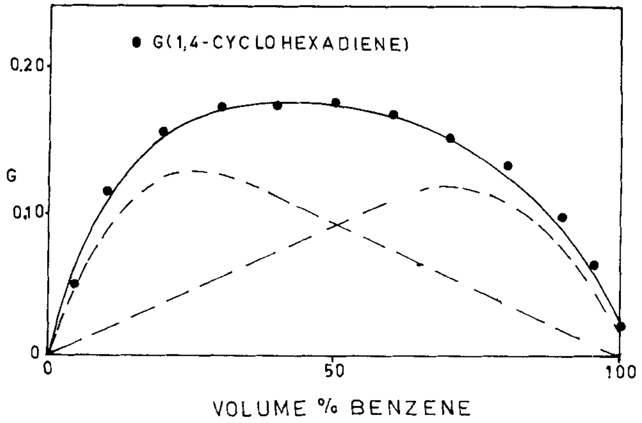


FIG. 6.

Figure 6 shows the effect of benzene concentration on the yield of 1,4-cyclohexadiene from methanol-benzene solutions. An almost symmetrical curve reaching a maximum value at 40% by volume of benzene is obtained for this scavenging product. 1,4-Cyclohexadiene is formed with a small yield in pure benzene but the yield is sharply increased by the addition of methanol. The benzene concentration dependency of this scavenging product is perhaps best understood in terms of two mechanisms operating simultaneously, one resulting in a benzene concentration dependency similar to cyclohexadiene-methanol, the other resulting in a benzene concentration dependency similar to phenyl-cyclohexadiene. These are indicated by the broken lines of Figure 6,

TABLE 1. Effect of low concentrations of benzene on the yield of methanol radiolysis products.

Initial benzene concentration M × 10^2	G(glycol)	G(H_2)	G(-benzene)	$\frac{\Delta G(H_2) + \Delta G(\text{glycol})}{G(\text{-benzene})}$
11.2	2.02	3.8	1.0	2.72
10.1	2.08	4.1	0.90	2.62
9.0	2.25	4.2	0.78	2.68
7.9	2.42	4.3	0.70	2.60
6.8	2.52	4.2	0.59	3.08
5.6	2.66	4.3	0.49	3.20
4.5	2.84	4.4	0.40	3.20
3.4	2.90	4.6	0.30	3.12
2.3	2.96	4.8	0.20	3.90
1.1	3.20	5.1	0.10	2.20
0.0	3.24	5.3	0.00	0.00

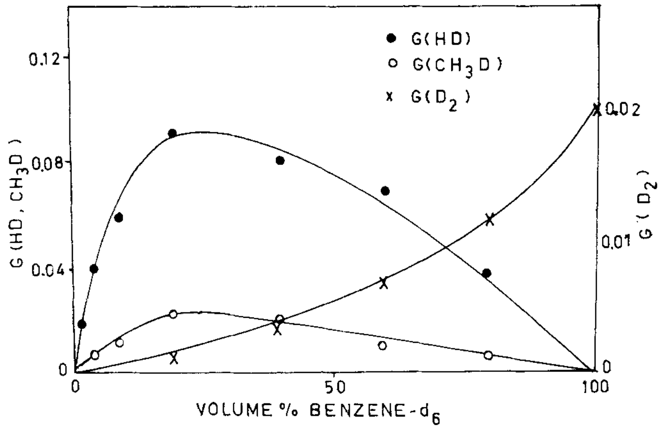


Fig. 7.

and it is apparent that when these two curves are added together, the experimental curve will be obtained.

Table 1 summarizes the effect of small concentrations of benzene on the yield of hydrogen and ethylene glycol from methanol and on the value of G(-benzene). Over the benzene concentration range examined, the ratio [ΔG(ethylene glycol) + ΔG(hydrogen)]/G(-benzene) is approximately constant, the average value being 2.9. This result implies that for each molecule of benzene decomposed the combined yield of hydrogen and ethylene glycol is reduced by nearly three molecules.

Figure 7 shows the effect of benzene-d_6 concentration on the yields of HD, CH_3D and D_2 from methanol-benzene-d_6 solutions, the results obtained

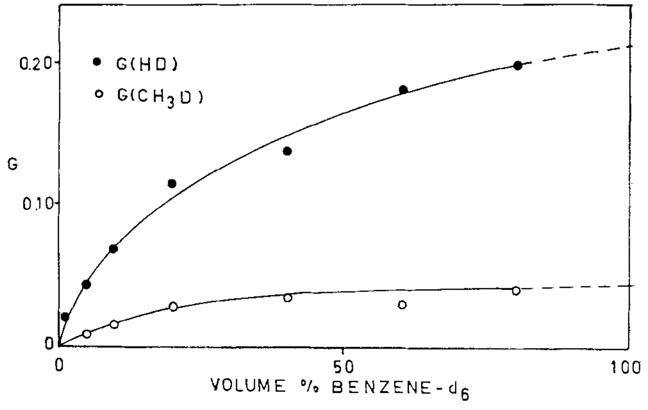


Fig. 8.

being similar to those reported for the cyclohexane-benzene-d_6 system (31). The benzene-d_6 concentration dependency of the D_2 yield from benzene-d_6 resembles that already observed for the biphenyl yield from benzene (Fig. 5), and the HD and CH_3D yields are similar to those observed for anisole and cyclohexadiene-methanol. The decrease in HD and CH_3D yields observed when the benzene-d_6 concentration exceeds approximately 20% by volume may again be attributed to the dilution of methanol by benzene-d_6, since a smooth curve is obtained when allowance is made for this dilution (Fig. 8).

Table 2 summarizes the isotope effects associated with the formation of the various scavenging products in methanol-benzene solutions. The results show that constant positive isotope effects are associated with the formation of biphenyl and anisole and constant reverse isotope effects with the formation of cyclohexadiene-methanol. However both 1,4-cyclohexadiene and phenyl-cyclohexadiene show a variable isotope effect which is positive in solutions containing high concentrations of benzene and reverse in solutions containing low concentrations of benzene. In this respect it may be recalled that the yields of both of these products are small in pure benzene and are sharply increased by the addition of methanol to benzene.

TABLE 2. Isotope effects in the formation of radiolysis products in methanol-benzene solutions [a].

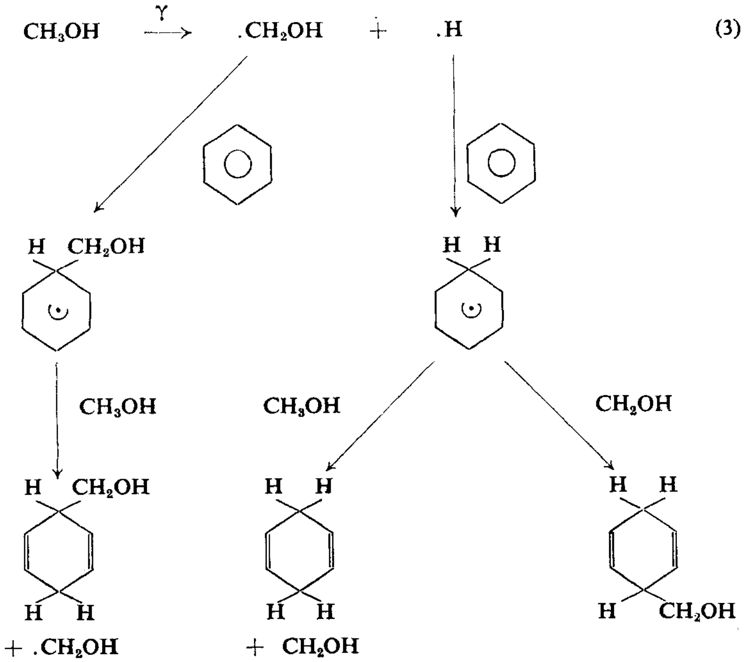
Mole fraction benzene	Biphenyl	Phenyl-cyclohexadiene	1,4-cyclohexadiene	Cyclohexadiene-methanol	Anisole
1.00	2.13	2.25	2.30	—	—
0.90	2.35	1.16	1.10	0.70	1.50
0.81	2.23	1.02	0.95	0.69	1.45
0.65	2.31	0.94	0.90	0.70	(1.23)
0.41	2.23	0.91	0.90	0.75	1.41
0.23	2.67	0.90	0.95	0.70	1.50
0.10	2.21	0.89	0.90	0.82	1.53
0.05	2.19	0.87	0.85	0.80	1.50

[a] $$\text{Isotope Effect} = \frac{\text{Yield of Product from Methanol-Benzene Solutions}}{\text{Yield of Product from Methanol-Benzene-d}_6\text{Solutions}}$$

V. DISCUSSION.

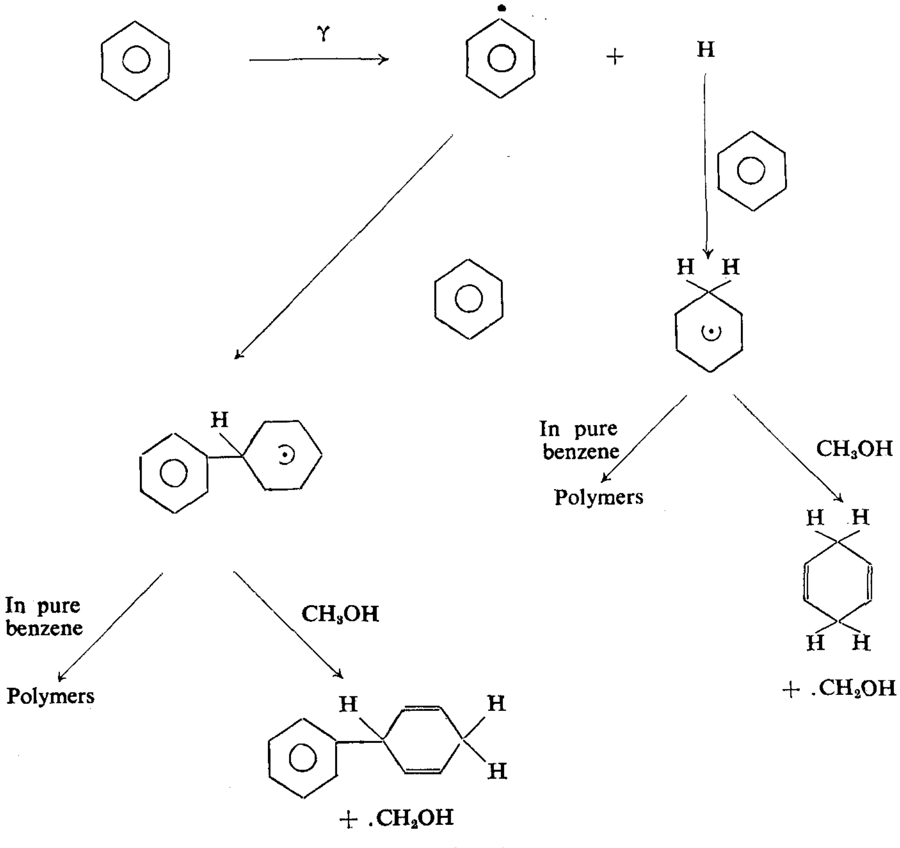
The benzene concentration dependency of the scavenging product yields suggest that two groups of scavenging mechanisms are operating in the present system. Group I achieves a maximum yield at 15% by volume of benzene and includes anisole, cyclohexadiene-methanol and part of the 1,4-cyclohexadiene yield, while group II reaches a maximum value at 80% by volume of benzene and includes phenyl-cyclohexadiene and again part of the 1,4-cyclohexadiene yield.

It would appear valid to suggest that the group I scavenging products, i.e., those reaching a maximum value at relatively low initial benzene concentrations are formed by the reaction of reactive species derived from methanol with benzene molecules (Eq. 3). At 15 % by volume of benzene, sufficient benzene molecules are present to scavenge all of the available reactive species from methanol and no further increase in the yields of the products are observed.



From the above reaction scheme the observable products are formed via the intermediate cyclohexadienyl radical, the formation of which has been directly observed in a number of cases involving the radiolysis of benzene solutions (39-41). Although only the possible reactions leading to the formation of the identified scavenging products are summarised in Equation 3, it is apparent that the cyclohexadienyl radicals may also react by further addition to benzene and by dimerisation with each other, in both cases resulting in the formation of high molecular weight polymers, which are difficult to identify by conventional techniques. In this respect it is interesting to note that a high resolution mass spectrum of the residue from irradiated methanol-benzene solutions indicated the presence of products of molecular weight as high as 500 which were not formed in either pure benzene or pure methanol.

The second group of scavenging products reaching a maximum value at 80 % by volume of benzene are also formed with a small yield in pure benzene, but this yield is sharply increased by the addition of methanol. The radiolysis of benzene containing small concentrations of methanol will result in a preponderance of reactive species derived from benzene rather than methanol. While in pure benzene these reactive species will react largely with benzene itself, they may, in the presence of methanol also react by hydrogen atom abstraction with methanol. These reactions are summarised in Equation 4, and again the formation of both the cyclohexadienyl (42) and phenyl-cyclohexadienyl (43) radicals in the radiolysis of pure benzene has been established. From Equation 4 it is seen that the increase in the yield of both cyclohexadiene and phenyl-cyclohexadiene from benzene upon addition of small concentrations of methanol is interpreted in terms of the ability of methanol to terminate the quasi-chain reactions of the cyclohexadienyl and phenyl-cyclohexadienyl radicals, reactions which in the absence of methanol result in the formation of high unimolecular weight products.



Equation 4

The isotope effects associated with the formation of the identified scavenging products are, as will be shown, consistent with the various mechanisms postulated above. It has been shown (44) that a reverse secondary isotope effect should accompany a reaction in which the hybridisation of the carbon atom under attack is altered from planar sp^2 to tetrahedral sp^3. Such a change accompanies the addition of free radicals to carbon-carbon double bonds, and reverse secondary isotope effects have previously been observed to accompany a number of such free radical addition reactions (45-47).

In the present study a constant reverse isotope effect accompanies the formation of cyclohexadiene-methanol, consistent with the free radical addition mechanism postulated for the formation of this scavenging product. With respect to the isotope effects associated with the formation of 1,4-cyclohexadiene and phenyl-cyclohexadiene, it is apparent that in pure benzene both products must be formed by the addition of hydrogen atoms derived from benzene to benzene molecules, and hence a positive isotope will be observed. However as suggested above, in benzene-methanol solutions both products may also be formed by the addition of hydrogen atoms *from methanol* to benzene, and a reverse isotope effect should accompany these reactions. It is therefore apparent that the decrease in the isotope effects observed for 1,4-cyclohexadiene and phenyl-cyclohexadiene upon addition of methanol to benzene is due to the increasing occurrence of the addition of hydrogen atoms from methanol to benzene and is thus consistent with the reactions outlined in Equation 4.

The results obtained at low initial benzene concentrations are of interest. As shown in Table 1, the ratio $[\Delta G(H_2) + \Delta G(CH_2OH)_2]/G(\text{-benzene})$ is approximately constant at a value of 3. Thus for each molecule of benzene decomposed the combined yield of hydrogen and ethylene glycol is reduced by three molecules. Assuming that the preponderance of the hydrogen and ethylene glycol yield scavengeable by benzene is formed according to Equation 5, the scavenging of two H atoms by a benzene

$$CH_3OH + H \rightarrow + H_2 + .CH_2OH \qquad (5)$$

$$2\,.CH_2OH \longrightarrow (CH_2OH)_2$$

molecule which is decomposed will decrease the combined yield by two hydrogen molecules and one molecule of $(CH_2OH)_2$. Alternatively, the scavenging of one H atom and one CH_2OH radical will reduce the total yield by one molecule of hydrogen and one molecule of ethylene glycol. The results thus suggest a multiple scavenging role for benzene in the present system, and it is interesting to note that Yang, Scott and Burr (48) have recently shown that in the cyclohexane-benzene system, two to three hydrogen atoms from cyclohexane are added to each molecule of benzene or its polymer.

The results of Figure 2 show that part of the hydrogen and ethylene glycol yields are not scavengeable by benzene. Previous studies (12, 38) have also shown that all of the methane and formaldehyde yields from methanol are not scavengeable by benzene. The results obtained in the present system for the HD and CH_3D yields from methanol-benzene-d_6 solutions (Figs. 7 and 8) show that the benzene-d_6 concentration dependency of these yields is complementary to the curves obtained for the effect of benzene concentration on the hydrogen yield (compare Figs. 2 and 8). Clearly part of the unscavengeable hydrogen yield from methanol-benzene solutions consists of hydrogen which is constituted by one hydrogen atom from methanol and one from benzene (d_6). Assuming the extrapolation of Figure 8 is valid, the hydrogen yield so constituted is 0.2 or approximately 20% of the total unscavengeable hydrogen yield.

Both the HD and CH_3D yields are probably formed by the deuterium atom abstractions outlined in Equation 6.

$$H. + C_6D_6 \rightarrow HD + C_6D_5. \qquad (6)$$

$$.CH_3 + C_6D_6 \rightarrow CH_3D + C_6D_5.$$

These reactions must compete with the corresponding free radical addition reactions which are greatly favoured energetically. Reactions such as those outlined in Equation 6 may therefore be ascribed to "hot" reactions or to reactions occurring in "thermal spurs" (49, 50, 51), in order to explain their occurrence in the present system, despite the unfavourable energetics of their formation.

VI. CONCLUSIONS.

The present data from the radiolysis of the methanol-benzene system show that radical scavenging processes, in addition to energy transfer discussed in the Review section, play an important role in explaining the manner by which aromatic compounds "protect" aliphatic alcohols (and aliphatics in general) from radiation-induced decomposition. The results indicate the type of scavenging products observed and should thus be of assistance in determining methods for radiochemical purification of labelled aliphatics after storage for appreciable periods of time in aromatic solvents.

Future mechanistic developments in this field include a thorough study of the radiolysis of binary aromatic-aliphatic mixtures at different temperatures. The yields of the scavenging products at low temperatures will be exceedingly useful since it is recommended that radioactive labelled molecules should be stored in solution at reduced temperature to minimise decomposition (2). Not only will the temperature dependence of the scavenging products be important, but also problems of phase separation during freezing should be considered. Preliminary work (52) with the radiolysis of methanol-benzene at -196° C indicates that no scavenging products are formed if the solutions are quickly frozen and also that all evidence of "protection" is lost at this temperature.

Data also are accumulating to show that this loss of protection can be attributed to phase separation (53) at -196° C and thus for all binary solutions containing labelled compounds care should be exercised in storing at low temperature in order to minimise self-radiolysis.

ACKNOWLEDGMENTS.

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