1004. *Solute Effects in the Radiolysis of Cyclohexane Solutions. Effect of Substituted Aromatic Compounds*[1]

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The effect of a number of monosubstituted aromatic compounds on the yields of hydrogen, cyclohexene, and bicyclohexyl formed in the γ-radiolysis of liquid cyclohexane solutions has been studied. The observed decrease in yields of all three products is discussed in terms of various processes which have been proposed for radiation-induced reactions.

In the radiolysis of cyclohexane–benzene mixtures the yield of cyclohexane-derived product is below that obtained in the radiolysis of pure cyclohexane.[2-4] Since this reduction is greater than the equivalent chemical change in the benzene, a process other than scavenging of chemical intermediates (atoms, radicals, ions) must operate, and the term "protection" has been used.[3] The mechanism of this protection has been discussed [5-8] in terms of the transfer of energy (in the form of electronic excitation and/or charge) to the solute from the primary excited molecule formed by the absorption of the radiation by cyclohexane. For this transfer of energy a route must be available which competes favourably with the chemical breakdown of the excited cyclohexane. Furthermore, the energy must be transferred to the solute without the latter undergoing appreciable chemical reaction. Based on this mechanism for the observed effect of benzene, it may be predicted that substituted benzenes might have a greater protective effect since they have both a larger cross-section for charge-transfer and a greater multiplicity of subionisation electronic energy levels available for excitation-transfer than benzene itself. This Paper reports experiments on the effect of several monosubstituted benzenes, *o*- and *m*-terphenyl on the yields of the major products (hydrogen, cyclohexene, and bicyclohexyl) of the radiolysis of cyclohexane solutions, and the results are compared with those obtained in the cyclohexane–benzene system.

EXPERIMENTAL

Materials.—All the solutes (Eastman or Fisher reagent grade) were used without purification, their purity having been checked by vapour-phase chromatography. Cyclohexane (Fisher spectroscopic grade) was also used without purification.

Prepartion and Irradiation of Solutions.—0·1M-Solutions in cyclohexane of the monosubstituted benzenes and *o*- and *m*-terphenyl were prepared. Aliquots (2 ml.) were placed in 13 × 110 mm. Pyrex tubes fitted with break-seals, which were degassed by the freeze–thaw method (three cycles) on a vacuum line, and sealed. (Blank runs in which the reaction mixtures were not irradiated were carried out to determine any loss of solute during the degassing procedure.) The ampoules were placed in an aluminium container which was lowered into the centre of the underwater source consisting of eight 23 × 270 mm. cobalt-60 rods (each with a nominal activity of 3 Kc) equally spaced at 116 mm. from the centre of the container. The temperature of the water circulating around the source was in the range 15—20°. The radiation doses received by the solutions were determined with a ferrous–copper dosimeter [9] [a solution of 10^{-3}N-ferrous sulphate and 10^{-2}N-copper sulphate in 10^{-2}N-sulphuric acid, taking $G_{\mathrm{Fe}^{2+}(\mathrm{Cu}^{2+})} = 0{\cdot}66$]. (The author is grateful to Mr. John W. Halliday for carrying out these measurements.) The dose rate at the commencement of the experiments was 1·11 Mrad. hr.$^{-1}$,

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[1] A preliminary communication of some of the data reported here appears in *Chem. and Ind.*, 1964, 1266.

[2] C. S. Schoepfle and C. H. Fellows, *J. Ind. Eng. Chem.*, 1931, **23**, 1396.

[3] J. P. Manion and M. Burton, *J. Phys. Chem.*, 1952, **56**, 560.

[4] H. A. Dewhurst, *J. Phys. Chem.*, 1959, **63**, 813.

[5] M. Burton and S. Lipsky, *J. Phys. Chem.*, 1957, **61**, 1461.

[6] G. R. Freeman, *J. Chem. Phys.*, 1960, **33**, 71.

[7] J. S. Stone and P. J. Dyne, *Radiation Res.*, 1962, **17**, 353.

[8] J. G. Burr and F. C. Goodspeed, *J. Chem. Phys.*, 1964, **40**, 1433.

[9] E. J. Hart and P. D. Walsh, *Radiation Res.*, 1954, **1**, 342.

dropping to 0·95 Mrad. hr.$^{-1}$ at the end. The electron densities of the dosimeter and cyclohexane are 0·554 and 0·445 electron mole ml.$^{-1}$, respectively. In the calculations of the dose received by the reaction solutions, the dose received by the same volume of the ferrous–copper dosimeter were multiplied by a factor of 0·445/0·554 = 0·803. Each sample was irradiated with a dose of 9·8 × 10^{20} ev ml.$^{-1}$.

Analysis of the Irradiated Solutions.—Cyclohexene, bicyclohexyl, and the aromatic solutes were determined by gas chromatography on an Aerograph model A 700, with a thermal conductivity detector, and helium as carrier gas. For cyclohexene and benzene, a six-foot column of silver nitrate (8%) and benzyl cyanide (11%) on 80—100 mesh Chromosorb W (Johns Manville) at 30° was used. The amounts of cyclohexene and benzene present were determined by comparing the peak areas with that of cyclohexane. The mole ratios of cyclohexene and benzene to cyclohexane were 0·70 and 0·95 times the peak-area ratios, respectively. In the radiolysis of pure cyclohexane the yield of cyclohexene was also determined by its infrared absorption band [4] at 720 cm.$^{-1}$. The results were in good agreement with the gas-chromatographic measurements. For the analysis of bicyclohexyl, the mono-substituted benzenes, *o*-terphenyl, and *m*-terphenyl, a six-foot column of 10% fluorosilicone resin (Dow QFI) on 80—100 Chromosorb W was used at 130°. Naphthalene was used as an internal standard; a weighed amount was dissolved in 1 ml. of the reaction mixture after radiolysis.

In the determination of the gaseous products the break-seal was opened under a vacuum while cooled in an acetone–solid carbon dioxide bath. The gas was then transferred to an evacuated flask of known volume by means of a Toepler pump and the pressure measured. While no positive identification of the gaseous product was made, on the basis of previous work [2,3] it is assumed to be almost solely hydrogen in the later discussion. The results of each experiment were confirmed by at least one duplicate run. Deviations of not more than ±5% were noted in the determinations of product yields and solute concentrations.

RESULTS AND DISCUSSION

The yields of hydrogen, cyclohexene, and bicyclohexyl, and the loss of solute, in the v-radiolysis of cyclohexane solutions which initially contained 0·10M solute are summarised in the Table. The yields in the radiolysis of pure cyclohexane are also included for comparison.

The γ-radiolysis of 0·1M-solutions in cyclohexane (total dose 9·8 × 10^{20} ev ml.$^{-1}$)

Solute	*G* (hydrogen) *	*G* (cyclohexene) *	*G* (bicyclohexyl) *	*G* (solute) *
None	4·6	2·3	1·3	—
Benzene	3·7	1·6	0·94	0·81
Toluene	3·3	1·6	0·81	1·3
Biphenyl	2·8	1·1	0·41	0·30
Chlorobenzene	2·6	0·50	1·2	4·2
Bromobenzene	2·3	0·56	0·36	2·4
Nitrobenzene	2·9	1·3	0·21	2·3
Phenol	3·4	1·8	0·38	1·9
Aniline	2·6	1·6	0·56	1·1
Thiophenol	3·5	1·6	0·21	4·2 †
Benzonitrile	2·2	1·3	0·44	1·9
Benzophenone	2·2	1·0	0·36	0·75
o-Terphenyl	2·0	0·79	0·32	0·16
m-Terphenyl	2·0	0·79	0·32	0·13

* Yield in molecules per 100 ev. † Diphenyl disulphide formed with *G* = 1·6.

The yields of the three major products resulting from the radiolysis of pure cyclohexane are all lower than previously reported primary yields,[10,11] owing to the larger doses used in the present work and the consequent appreciable yield of cyclohexene which itself can effectively decrease the yield of radiolysis products from cyclohexane.[3] This proportional decrease in yields with increasing dose was noted by Freeman,[6] and the present yields of major products are in good agreement with values obtained by extrapolating his results.

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[10] P. J. Dyne and J. A. Stone, *Canad. J. Chem.*, 1961, **39**, 2381.

[11] S. K. Ho and G. R. Freeman, *J. Phys. Chem.*, 1964, **68**, 2189.

All the monosubstitued benzenes and the terphenyls have a greater influence on the yields of the three major products than benzene itself, and, with the exception of benzophenone, biphenyl, and the terphenyls, show a greater decrease in concentration. The behaviour of chlorobenzene is exceptional in that it has a marked effect on the yields of hydrogen and cyclohexene but little effect on that of bicyclohexyl.

With the low solute concentrations used in this work it is reasonable to assume that all the ν-radiation is absorbed initially by the cyclohexane solvent. Therefore, the influence of the solute upon the radiolysis products derived from cyclohexane is due solely to the interaction of the solute with either secondary radiation, in the form of fast electrons ejected from the solvent, or reactive species derived from the solvent. Owing to the limitations of the thermal conductivity detector used in the gas-chromatographic estimation of the non-gaseous products, it was necessary to irradiate the solutions with a dose of not less than $\sim 10^{21}$ ev ml.$^{-1}$ in order to obtain sufficient product concentration for accurate analysis. At this dose the final concentration of cyclohexene ranges from $0{\cdot}8 \times 10^{-2}$M for the chlorobenzene–cyclohexane system to $2{\cdot}9 \times 10^{-2}$M for the phenol–cyclohexane system. While the protective effect of cyclohexene is smaller than that of benzene,[3] the significant final concentrations of cyclohexene must be considered to contribute measurably to the observed protection by the aromatic solutes in the Table. Therefore, the subsequent discussion of the protective effect of these solutes must be qualitative rather than quantitative.

With the exception of chlorobenzene and bromobenzene the gas chromatograms of the irradiated reaction mixtures gave no evidence of any appreciable fragmentation of the solute molecule to give compounds which would be eluted under the chromatographic conditions used (column temperatures up to 180°). In the case of chlorobenzene and bromobenzene, appreciable yields of benzene and phenylcyclohexane were identified by their retention times. For the chlorobenzene reaction the *G*-values were 2·4 and 0·2, respectively, while for bromobenzene they were 2·3 and 0·2. Phenylcyclohexane was also formed in the radiolysis of the benzene–cyclohexane system, with $G = 0{\cdot}1$. The identification of benzene and phenylcyclohexane in the products of these reactions is consistent with the reaction of hydrogen atoms with the solute to give phenyl radicals.

$$H\bullet + C_6H_5X \longrightarrow C_6H_5\bullet + HX \qquad (1)$$

$$C_6H_5\bullet + C_6H_{12} \longrightarrow C_6H_6 + C_6H_{11}\bullet \qquad (2)$$

$$C_6H_5\bullet + C_6H_{11}\bullet \longrightarrow C_6H_5C_6H_{11} \qquad (3)$$

Chlorocyclohexane was identified (by retention time and infrared spectrum of a sample collected at the exit port of the gas chromatograph) among the liquid products of the radiolysis of the chlorobenzene–cyclohexane system. Its formation is consistent with the addition of hydrogen chloride (formed in reaction 1) to cyclohexene, and perhaps explains the exceptionally low yield of cyclohexene in this system. However, no biphenyl could be detected among any of the reaction products. While this does not conflict with the radical processes outlined above (the phenyl radical may be expected to have a very short life in cyclohexane, making the probability of dimerisation of two phenyl radicals to give biphenyl small), it is somewhat surprising that no bibenzyl could be detected in the toluene–cyclohexane system even though this is an important product of the reaction of cyclohexyl radicals in toluene solution.[12]

While, compared with benzene, the solutes listed in the Table show a greater ability to reduce the yields of hydrogen, cyclohexene, and bicyclohexyl, they show also an increased tendency to be destroyed themselves, with the exception of benzophenone, biphenyl, and terphenyls. It is probable that, as in the case of the benzene–cyclohexane system,[8,13] this solute loss may be accounted for by a polymeric product in which it is

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[12] G. H. Williams and W. V. Sherman, unpublished results.

[13] J. A. Stone, P. J. Dyne, and M. G. Bailey, *Canad. J. Chem.*, 1964, **42**, 963.

combined with material derived from cyclohexane. While it may be argued that the observed decrease in yields of cyclohexene and bicyclohexyl were due to incorporation of cyclohexyl groups into the polymeric product, in all cases the possible yield of the process solute ⟶ polymer was less than the combined decrease in yields of hydrogen, cyclohexene, and bicyclohexyl. This lack of chemical equivalence between loss of solute and decrease in radiolysis products provides a strong argument against radical-scavenging being the sole process in the protecting action of benzene in the benzene–cyclohexane system,[7] and appears to apply equally well to systems containing substituted benzenes. Also, there is a lack of correlation between the relative effects of the substituted benzenes on the yields of cyclohexene and bicyclohexyl and the known reactivites of these compounds toward alkyl radicals as measured by their methyl affinities.[14] Such a correlation would be expected if the cyclohexyl radicals were the sole precursor of these two products and if the scavenging of this radical by the solute were solely responsible for the observed decrease in yield.

The identification of solute anions formed with appreciable yields in the radiolysis of aromatic compounds in alkane glasses [15] indicates that the scavenging of sub-excitation electrons may be relevant to the present discussion, especially since the existence of scavengeable electrons in the radiolysis of cyclohexane has been established.[16] If an electron-scavenging process were of major importance, a correlation between the degree of protection and the electron affinity of the solute might be expected. However, no simple correlation is observed between the present results and the electron affinities, as measured by the polarographic half-wave potential, of the aromatic solutes listed in the Table. On the other hand, benzophenone, which is among the most effective in reducing the yields of all three radiolysis products, has been shown to be an efficient scavenger of thermal electrons,[17] and, furthermore, the spectrum of $(C_6H_5)_2CO^-$ has been identified in the pulse radiolysis of benzophenone in cyclohexane.[18]

Finally, the suggestion [3] that energy transfer from excited cyclohexane to benzene plays an important role in the protection of cyclohexane by benzene should be considered in relation to the present data. It has been proposed [19] that an electron in an upper excited state degrades (by internal conversion) very rapidly (10^{-13} sec.) to the lowest excited state of the same multiplicity. Hence, in this theory of protection by energy transfer [20] it is these low-lying excited states of cyclohexane which are quenched by the aromatic solute (both the lowest excited singlet and triplet levels of benzene are of considerably lower energy than those of cyclohexane). Since it has been demonstrated [21] that excitation-energy transfer is a diffusion-controlled process when the energy of the acceptor triplet is considerably lower than that of the donor (this rule presumably holds for singlet–singlet interactions), there should not be the substituent effect in the observed protection by monosubstitued benzenes since they all have acceptor levels well below cyclohexane. (No differences have been detected [22] in the phosphorescence quenching efficiency of naphthalene and a number of monosubstituted naphthalenes.) The lack of importance of the role of low-lying excited states in radiation-induced reactions was recently demonstrated [23] in the γ-radiation-induced reduction of benzophenone in

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[16] G. Scholes and M. Simic, *Nature*, 1964, **202**, 895.

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[22] A. N. Terenin and V. L. Ermolaev, *J. Chim. phys.*, 1958, **55**, 698.

[23] W. V. Sherman and S. G. Cohen, *J. Amer. Chem. Soc.*, 1964, **86**, 2390.

propan-2-ol where it was shown that the reaction does not proceed *via* the excited triplet responsible for the photochemical reaction. Examples have been given [24] where upper-level triplet states do not efficiently degrade to the lowest level by internal conversion. Evidently, if excitation-energy transfer is important in radiation protection, quenching of upper-level excited states, possibly with energy in excess of the ionisation energy (" super-excited " [25]) plays an important role.

To summarise, while this study is essentially qualitative it does indicate that the mechanism of protection of cyclohexane by aromatic compounds cannot be solely scavenging of hydrogen atoms or cyclohexyl radicals, scavenging of thermal electrons, or excitation-energy transfer involving only the lower excited states. This conclusion falls in line with the currently accepted theories that no single process can adequately account for the observed solute effects in the radiolysis of cyclohexane solutions.

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