

# Radiolysis of Triphenyl Arsine in a Mixture of Benzene and Cyclohexane

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A number of degassed samples of triphenylarsine ( $\text{As}\Phi_3$ ) were irradiated by gamma radiation in a mixture of benzene and cyclohexane. The condensable products formed were pentane, hexane, benzene and cyclohexane in cyclohexane solution containing  $\text{As}\Phi_3$  and cyclohexane in benzene in presence of  $\text{As}\Phi_3$ . When the composition of the solvent was varied by stepwise addition of benzene from 5 to 50%, the main condensable radiolytic products observed by vapour phase chromatography were hexane, benzene and cyclohexane. No pentane was observed when benzene was present in the mixture upto 15%. However, it was detected in the presence of 20-30% benzene mixture. When the amount of benzene was 35-50% in the mixture, two isomers of hexane and hexane were also detected. A mechanism has been worked out for the formation of these compounds and protection and sensitization mechanisms have been invoked to explain the yields per 100 e.v. From the kinetic analysis, it has been found out that the rate of formation of cyclohexene is much faster than other rates of different products formed during gamma radiolysis and from the analysis of experimental data, sponge type protection has been postulated in this radiolytic system.

THE radiolysis of a mixture of benzene and cyclohexane has been done by a number of workers<sup>1-4</sup>.

Burton has explained the formation of compounds on the basis of protection mechanism<sup>5</sup>. Since phenyls are more resistant to radiation, it was thought worthwhile to use dilute solutions of some metal phenyls in the mixture to observe the changes involved in the protection phenomenon, which might be useful in nuclear technology.

## Experimental

### Materials :

**Benzene :** B. D. H. AnalaR grade benzene was successively crystallized three times and one fourth of benzene was rejected after each freezing. Sodium metal was added to the rest, which was subsequently distilled.

**Cyclohexane :** AnalaR grade B. D. H. cyclohexane was mixed with concentrated sulphuric acid and the organic layer was separated and washed several times with distilled water, dried with  $\text{CaCl}_2$ , refluxed and finally distilled over sodium and the middle fraction was collected and stored, and the purity of cyclohexane and benzene were tested by vapour phase chromatography.

**Preparation of samples :** Pyrex glass cells of approximately 15 ml capacity constructed from 25 mm (outer diameter) pyrex tubing cells were cleaned with chromic acid and washed several times with distilled water before drying them in an oven. Ten ml of solutions, containing triphenylarsine ( $4 \times 10^{-3} M$ ) in the mixture of benzene and cyclohexane, ranging the concentration of benzene from 5% to 50% was pipetted out into a number of sample cells, which were attached to a vacuum line. Conventional freeze and thaw technique was used to degas samples. The liquid in the cell was frozen by liquid air and the oxygen was

removed by repeated evacuations. When the pressure was of the order of  $10^{-4}$  mm of Hg, the samples were cut off while still under vacuum. However, it has been found out that traces of oxygen come out from the glasses when the samples are degassed even to  $10^{-5}$  mm of Hg. The result has been confirmed by mass-spectrometry.

**Gamma Irradiation :** Gamma cell 200 of 2 kilocuries of the Indian Agricultural Research Institute, New Delhi was used for irradiation. For measuring the dose rate, Fricke Dosimeter was used using  $G(\text{F}_2^{\cdot+})$  as 15.6. The dose rate was  $8.498 \times 10^{16}$  e. v./ml/min. The amount of energy absorbed per ml/min in benzene and cyclohexane was determined by multiplying the energy absorbed per ml/min in the Fricke dosimeter by the ratio of the electron densities of the two systems. In the case of mixture these values were multiplied by electron fraction. The electron densities in electron moles/ml, at 25° are : Fricke dosimeter, 0.566, cyclohexane, 0.4441, benzene<sup>6</sup>, 0.470. The solutions were irradiated for 30 min.

**Product Analysis :** The product analysis was carried out with F-11 Perkin Elmer Gas chromatographs.

For the present work, a stainless steel dual column, two metres in length and 1/2" outer diameter, packed with di-2-ethylexylsebacate on chromosorb-P (20 : 80), was used. Approximately one microlitre samples were introduced into the column by a syringe of 1  $\mu\text{l}$  capacity.

Nitrogen gas was used as carrier gas at a flow-rate of 40 ml/min, which was determined by soap bubbleflow meter. Flame-ionization detector was used as the detecting device which had high sensitivity and very stable base line. Recorder speed of Perkin-Elmer Gas chromatograph was 1/2 inch/min. Column tempera-

ture was 70°. The condensable products were tentatively identified as pentane, hexane, hexene, cyclohexane, benzene and cyclohexene from its relative retention times.

**Results and Discussion**

Results are summarized in the Table I.

The radiolysis of benzene in presence of  $As\phi_3$  formed only cyclohexane. Cyclohexane in presence of  $As\phi_3$  formed pentane, hexane, cyclohexene and benzene. A mixture of pure benzene and cyclohexane gave three additional products, one isomer of hexane, and hexene and methylcyclopentane. In the presence of 5% benzene the mixture of cyclohexane and  $As\phi_3$  formed one isomer of hexane and hexene and cyclohexene. The yield of these products is very negligible. With increasing concentration of benzene, pentane is not formed upto 15% benzene. When concentration of benzene in the mixture is 20%, pentane is formed but its concentration begins to decrease as the concentration of benzene increases. Out of two isomers of hexane, one is not formed upto 30% benzene. Yield of other isomers also decreased with increasing percen-

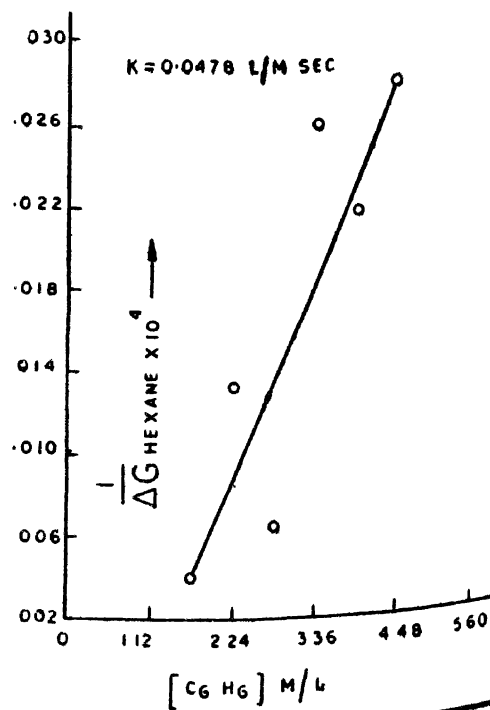


Fig. 1

TABLE I—YIELD (G-VALUES) OF THE CONDENSABLE PRODUCTS IN THE CO<sup>60</sup>-GAMMA RADIOLYSIS OF TRIPHENYL ARSINE ( $4 \times 10^{-3}M$ ) IN A MIXTURE OF CYCLOHEXANE AND BENZENE

Percentage of solvents	20% C <sub>6</sub> H <sub>6</sub> (Pure)	100 C <sub>6</sub> H <sub>6</sub>	100 C <sub>6</sub> H <sub>12</sub>	5 C <sub>6</sub> H <sub>6</sub>	10 C <sub>6</sub> H <sub>6</sub>	15 C <sub>6</sub> H <sub>6</sub>	20 C <sub>6</sub> H <sub>6</sub>	25 C <sub>6</sub> H <sub>6</sub>	30 C <sub>6</sub> H <sub>6</sub>	35 C <sub>6</sub> H <sub>6</sub>	40 C <sub>6</sub> H <sub>6</sub>	45 C <sub>6</sub> H <sub>6</sub>
<i>Products</i>												
Pentane	.00336	.01192	—	—	—	—	.00509	.00343	.00145	—	.01437	—
Hexane*	.00347	.00262	—	.00311	.00216	.0026	.00965	.00353	.0001	.00125	.00166	.00075
Hexane**	.02083	—	—	—	—	—	—	—	—	.00093	.00133	.00033
Hexene*	4.04669	—	—	.01497	.0148	.00182	.02489	.0174	.00188	.00589	.00593	.02237
Hexene**	—	—	—	—	—	—	—	—	—	.00458	.00627	.00237
Methyl-cyclopentane	.7359	—	—	—	—	—	—	—	—	—	—	—
Cyclohexene	—	.54208	—	.00882	.03413	.04856	.00684	.01171	.00353	.0101	.00258	.00325
Benzene	—	.212551	—	—	—	—	—	—	—	—	—	—
Cyclohexane	—	—	.05183	—	—	—	—	—	—	—	—	—

tage of benzene. Hexene is also not formed upto 30% benzene and its formation is observed beyond that concentration of benzene. In the presence of 35 to 40% benzene, more products are observed. The least number of products say, three are formed in presence of 5 to 15% benzene. But the lowest amount of radiolytic products are observed with 5% benzene.

Since the mixture of benzene and cyclohexane formed five products and cyclohexane in presence of  $As\phi_3$  formed four products, it is quite obvious that 5% benzene protects cyclohexane against the radiolytic decomposition. The formation of numerous products is reported in the radiolysis of cyclohexane in presence of  $As\phi_3$ ; quite a few of these products are eliminated, leaving four in the liquid. Their number is reduced to three by addition of 5% benzene. Benzene reduces the G values by a factor of 1/30. The total yield in presence of 10 and 15% benzene is double to that of 5% benzene. These data show that 5 to 15% benzene reduces the radiolytic products to 3 to 6%.

The plot of benzene concentration in moles/litre versus  $1/\Delta G_{Hexene}$  is linear and the value of rate constant is  $4.78 \times 10^{-2}$  litre/mole. sec. as shown in

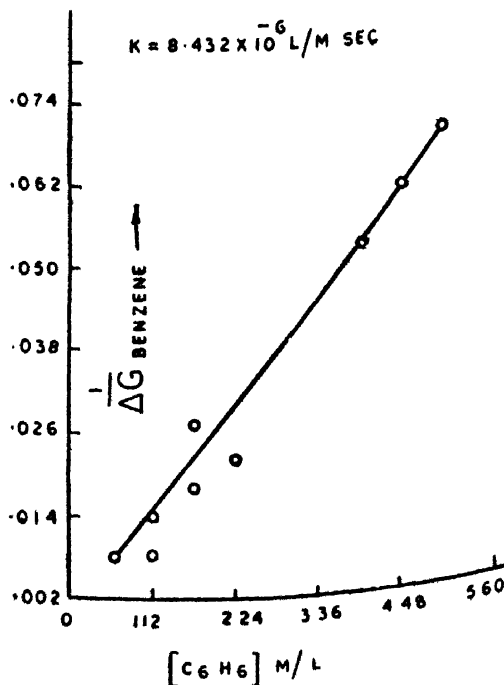


Fig. 2

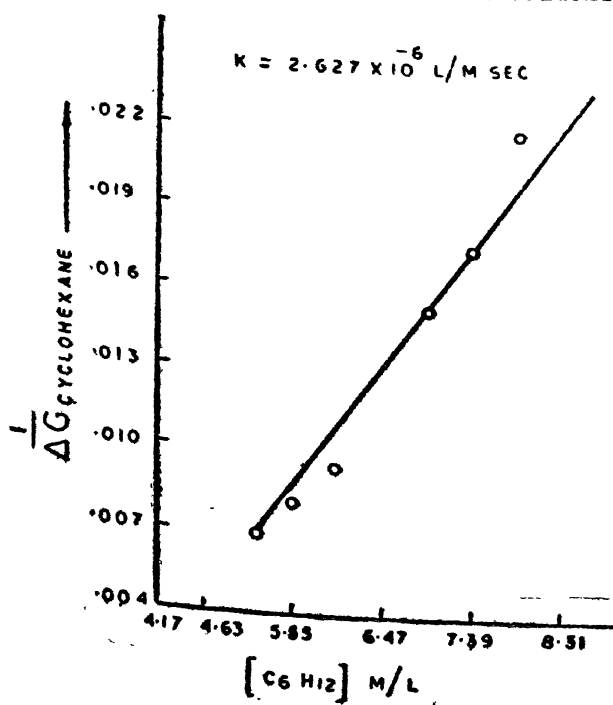
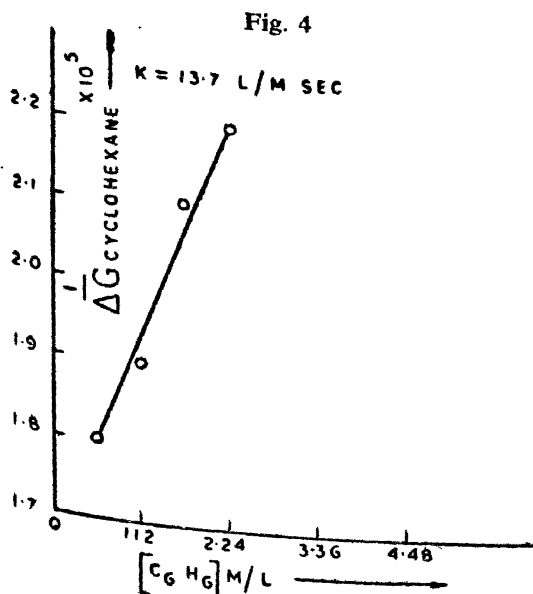
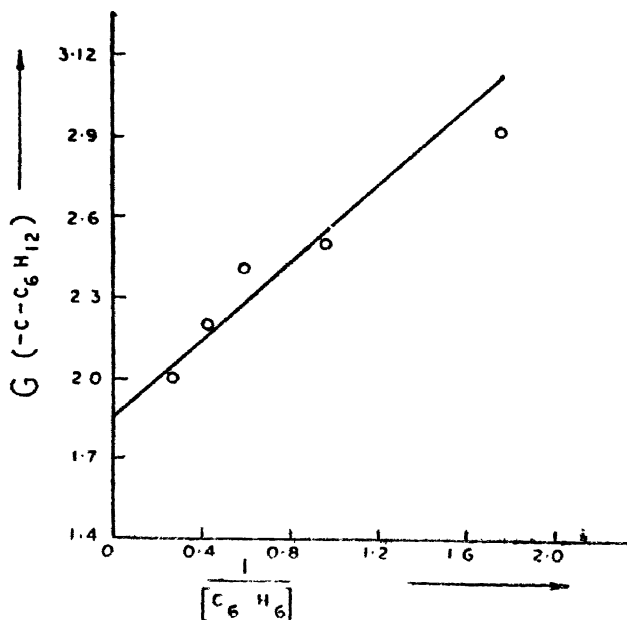
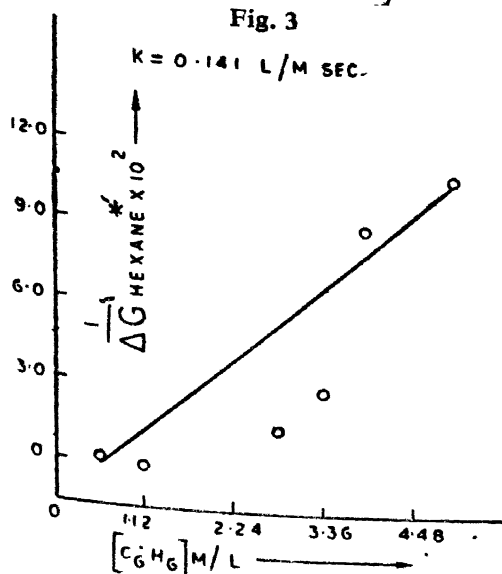


Fig. 1. The plots of benzene concentration in moles/litre versus  $1/\Delta G^{\text{Benzene}}$  and  $1/\Delta G^{\text{Cyclohexane}}$  versus cyclohexane concentration in moles/litre are linear as shown in Figs. 2 and 3 respectively. The rate of benzene is three times greater than cyclohexane. Similar plots are obtained with hexane and cyclohexane. The rate constants are 0.141 and 13.7 litre/mole. sec. respectively as shown in Figs. 4 and 5. A comparison of the rate constants shows that cyclohexane > hexane > hexene > benzene > cyclohexane.

A plot of  $1/[C_6H_6]$  versus  $G(-c-C_6H_{12})$  is linear and it shows sponge type protection as shown in Fig. 6. Sponge type protection can be explained in the following manner :



In this case, benzene has excited or ionized states lying energetically lower than those of cyclohexane and energy transfer from cyclohexane to benzene may occur either via emission of virtual photon or by charge transfer. An additive of higher radiation stability i. e. benzene would then sponge the electronic excitation energy from excited cyclohexane species and promote distribution of initially localized energy among vibrational-rotational degrees of freedom of neighbouring solvent molecules.

In the radiolysis of a multicomponent system containing benzene, cyclohexane and some metal phenyl, benzene is more stable than cyclohexane. The system also contains a number of excited species. The pi electrons of benzene transfer their excitation energy to the sigma electrons of cyclohexane and to the metal phenyl. The sigma electrons are tightly bound in the molecule and the excited cyclohexane molecules lose their energy by collisional deactivation with other unexcited molecules in the system, because all molecules are not excited. The energy in the initial state is dissipated in the wave packets leading to the domain formation. The domains spread and the cyclohexane and metal phenyl is protected against gamma radiation.

Thus pi electrons of benzene behave like a sponge type agent and protect other components. This is called the sponge type protection.

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