447. The Effect of Quinones on the γ-Irradiation of Cyclohexane.

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The γ-irradiation of solutions of *p*-benzoquinone in cyclohexane results in the formation of quinol, 2,5-dicyclohexylquinol, and 2,5-dicyclohexylbenzoquinone. It has been shown that the presence of quinone causes decreases in the *G* values (number of molecules per 100 ev) for hydrogen and bicyclohexyl production, but hardly affects the yield of cyclohexene. Irradiation of cyclohexane solutions of *p*-toluquinone has also been studied.

Yields of cyclohexene and bicyclohexyl from irradiated cyclohexane in the absence of added solutes have been confirmed by an isotopic dilution method.

THE exposure of cyclohexane to ionizing radiation gives as the main products hydrogen, cyclohexene, and bicyclohexyl.[1] Detailed analyses of the gaseous and the liquid products have been reported,[2,3] and the mechanism of hydrogen formation and the effects of iodine and other radical-scavengers have been studied extensively.[4,5,6] The effect of added quinone has received but little attention.[7] We have determined the nature of the products derived from benzoquinone and toluquinone and made a detailed study of the effect of benzoquinone on the yields of the main reaction products when solutions in cyclohexane are exposed to γ-radiation.

EXPERIMENTAL

Analyses were by Miss J. Cuckney and the staff of the Organic Chemistry Microanalytical Laboratory, Imperial College, London. Ultraviolet and infrared spectroscopic measurements were by Mrs. A. I. Boston and Mr. R. L. Erskine, B.Sc., A.R.C.S.

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[1] Dewhurst, *J. Chem. Phys.*, 1956, **24**, 1254; *J. Phys. Chem.*, 1959, **63**, 813.
[2] Hamashima, Reddy, and Burton, *J. Phys. Chem.*, 1958, **62**, 246.
[3] Nixon and Thorpe, *J. Chem. Phys.*, 1958, **28**, 1004.
[4] Burton and Patrick, *J. Phys. Chem.*, 1954, **58**, 421.
[5] Hentz, *J. Phys. Chem.*, 1955, **59**, 380.
[6] Schubert and Schuler, *J. Chem. Phys.*, 1952, **20**, 518.
[7] Adams, Baxendale, and Sedgwick, *J. Phys. Chem.*, 1959, **63**, 854.

Materials.—" Spectrosol " grade cyclohexane (Hopkin and Williams Ltd.) was fractionally crystallised to remove saturated hydrocarbon impurities. The quinones were resublimed.

Reaction Products.—(*a*) A solution of benzoquinone (3·0 g.) in cyclohexane (625 ml.) under nitrogen was exposed to the radiation of a (nominally) 100-curie ^{60}Co source for 118 hr. (energy input = $3·1 \times 10^{23}$ ev). The dark green solid (1·27 g.) which separated was recrystallised from ethanol and then had m. p. 169—172°, undepressed by authentic quinhydrone. The deep yellow filtrate was passed through a column of alumina (acid-washed). Elution of the column with benzene and evaporation of the eluate gave 2,5-*dicyclohexylbenzoquinone* as an orange oil (0·240 g.) which solidified and on crystallisation from ethanol gave pale yellow plates, m. p. 138—139° (Found: C, 79·45; H, 9·0; O, 11·75. $C_{18}H_{24}O_2$ requires C, 79·35; H, 8·9; O, 11·75%), $\lambda_{max.}$ (in EtOH) 261, 312 mμ (ε 13,700, 560); $\nu_{max.}$ (in KBr) 2924s, 2849ms, 1649s, and 1447ms cm.$^{-1}$. The quinone was reduced with zinc and boiling acetic acid to the *quinol*, which crystallised from benzene in colourless needles, m. p. 225° (Found: C, 78·85; H, 9·85; O, 11·5. $C_{18}H_{26}O_2$ requires C, 78·8; H, 9·95; O, 11·65%), $\lambda_{max.}$ (in cyclohexane) 291 mμ (ε 4250); $\nu_{max.}$ (in KBr) 3311s, 2924s, 2857ms, 1445m, 1422m, 1176s, and 871m cm.$^{-1}$. The quinone on reduction with zinc dust and sodium acetate in boiling acetic anhydride gave the *quinol diacetate*, m. p. 202—203° (from chloroform–light petroleum) (Found: C, 73·7; H, 8·3. $C_{22}H_{30}O_4$ requires C, 73·7; H, 8·45%).

The orientation of the groups in the disubstituted quinone follows from a comparison of the infrared spectra of its quinol and the derived diacetate with the spectra of the 2,3-, 2,5-, and 2,6-dimethylquinol.[8] The nuclear magnetic resonance spectrum of the quinone confirms that the cyclohexyl groups cannot be in the 2,3-relation, since a band in the olefinic C–H region is split as a doublet with a separation of about 1 c./sec., indicative of coupling between the olefinic proton and one allylic proton.[9] 2,5-Dicyclohexylbenzoquinone proved to be identical with the quinone obtained by oxidising the product, isolated in 1·5% yield, of the reaction of cyclohexyl toluene-*p*-sulphonate and quinol at 120°.[10] 2,5-Dicyclohexylquinol and its diacetate have the same m. p.s as those reported by Fieser *et al.*[11] for a dicyclohexylquinol, formed by the reaction of cyclohexene and quinol in the presence of hydrogen fluoride, and its diacetate.

(*b*) *p*-Toluquinone (5 g.) in cyclohexane (625 ml.) under nitrogen was irradiated for 160 hr. The green-black solid which separated was removed and the filtrate treated as in (*a*). A yellow oil was obtained which on distillation at 10^{-4} mm. gave a fraction (bath-temp. 160—180°) which solidified below room temperature. The oil (0·30 g.), on reduction with zinc dust and boiling acetic acid, gave 2-*cyclohexyl*-5-*methylquinol* (0·20 g.), m. p. 149—150° (from benzene) (Found: C, 75·6; H, 8·9; O, 15·7. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8; O, 15·5%), $\lambda_{max.}$ (in cyclohexane) 292 mμ (ε 5000), $\nu_{max.}$ (in KBr) 3300s, 2925s, 2857m, 1422s, 1181vs, 870s cm.$^{-1}$. In one irradiation an orange oil was obtained, having n_D^{21} 1·5412, which was a mixture of isomeric dicyclohexylmethylbenzoquinones (Found: C, 79·7; H, 9·4. Calc. for $C_{19}H_{26}O_2$: C, 79·7; H, 9·15%), $\lambda_{max.}$ (in EtOH) 264 mμ (ε 22,600), $\nu_{max.}$ (liquid) 2923s, 2866s, 1651s, 1605m cm.$^{-1}$.

Quantitative Studies.—(*a*) Solutions contained in break-seal ampoules were degassed, sealed, irradiated in reproducible positions with respect to the source, and then broken into a vacuum-line. The gas, non-condensable at −196° and assumed to be hydrogen,[1] was passed by means of a Töpler pump into a gas-burette. The remainder of each sample was run through a short column of alumina to remove quinone and its derivatives. The yield of cyclohexene was obtained by measuring the light-absorption intensity of the eluate at 183 mμ, ε for pure cyclohexene being 7800 (in cyclohexane). The yield of bicyclohexyl in the eluate was obtained by adding a known amount of phenylcyclohexane, evaporating off most of the cyclohexane, and subjecting the residue to gas–liquid chromatography. The relative areas of the peaks due to bicyclohexyl and phenylcyclohexane when compared with those of standard mixtures gave yields of bicyclohexyl considerably lower than those reported by Dewhurst,[1] and somewhat lower than the value derived by the isotopic-dilution method described below. In the absence of the standard, two other peaks could be discerned at slightly longer retention times than that of bicyclohexyl and these are assumed to be due to cyclohexenylcyclohexane[3] and (very

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[8] Cf. Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 64.

[9] Cf. Roberts, " Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 54.

[10] Cf. Hickinbottom and Rogers, *J.*, 1957, 4124.

[11] Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3186.

tentatively) bicyclohexenyl. The yields of the last two entities, relative to bicyclohexyl, were obtained from the areas under the three peaks.

(*b*) The yields of products derived from benzoquinone were obtained by diluting the irradiated solution with ethanol and determining the light-absorption intensities at 241 (benzoquinone), 260 (dicyclohexylbenzoquinone), and 291 mμ (quinols). The solutions were, as far as possible, kept in the dark since bands appeared at 260 and 291 mμ when solutions of quinone in cyclohexane were exposed to the light. When only small amounts of 2,5-dicyclohexylquinol were present, quinol could be determined by evaporating the irradiated solution to dryness, dissolving the residue in dilute sulphuric acid, and titrating it with standard ceric sulphate, diphenylamine sulphate being used as indicator.

Dosimetry.—The radiation doses received by samples in standard positions with respect to the source were determined by ferrous ammonium sulphate dosimetry, 15·6 ferrous ions being assumed to be oxidised by 100 ev.[12] The dose rate was *ca.* 5×10^{16} ev ml.$^{-1}$ min.$^{-1}$. In quantitative studies we used for most samples (volume 10 ml.) a standard energy input of 6×10^{20} ev, and the dependence of G values on dose given was not studied.

Isotopic-dilution Method for Cyclohexene and Bicyclohexyl.—[^{14}C]Cyclohexane (1 mc., supplied by the Radiochemical Centre, Amersham) was distilled under a vacuum into an ampoule containing " Spectrosol " cyclohexane (5 ml.), and the sealed ampoule irradiated for 288 hr. Inactive cyclohexene (0·1 ml., freshly distilled from sodium) and bicyclohexyl (0·1 ml.) were added and the solution was distilled at atmospheric pressure. The residue was fractionally distilled under reduced pressure and the radioactivity of a portion of the high-boiling distillate (bath-temp. 160°/24 mm., mainly bicyclohexyl) was counted in " diethylcarbitol," a methane-flow proportional counter being used. The remainder of the high-boiling distillate was subjected to gas–liquid chromatography on an 11 ft. silicone–Celite column. The activity of the fraction consisting of bicyclohexyl and its olefinic analogues was significantly lower than before chromatography but was not altered on rechromatography. Part of the atmospheric-pressure distillate was combusted in a microanalytical apparatus. The carbon dioxide produced was collected and absorbed in a *ca.* 2% solution of phenyl-lithium in " diethylcarbitol," and the radioactivity of the reaction mixture counted,[13] thus enabling the activity of the cyclohexane used to be calculated. The remainder of the atmospheric-pressure distillate was treated *in the dark* with a solution (2 ml.) of bromine (1·118 g.) in cyclohexane (10 ml.) at 0° with stirring. The mixture was distilled, and the residue of dibromocyclohexane fractionated under reduced pressure, two fractions being collected and a small residue rejected. The activity of the higher-boiling fraction was measured in " diethylcarbitol." Redistillation of this fraction gave a middle cut having a substantially unchanged specific activity. Further purification was not attempted. Typical values for the activities of cyclohexane, bicyclohexyl, and dibromocyclohexane were 4867, 956, and 206 counts min.$^{-1}$ mg.$^{-1}$, respectively. Since the energy input was $3{\cdot}66 \times 10^{21}$ ev, the derived G values for bicyclohexyl and cyclohexene are 2·15 and 2·26 respectively.

RESULTS AND DISCUSSION

γ-Irradiation of a solution of benzoquinone in cyclohexane gives a mixture of quinol, which separates as quinhydrone, and 2,5-dicyclohexylbenzoquinone and its quinol. There is no evidence of the formation of any monocyclohexylated product, or of any ethers derived from quinol.

The formation of 2,5-dicyclohexylbenzoquinone may be represented as shown in the chart. The oxidation of 2,5-dicyclohexylquinol to the corresponding quinone by benzoquinone has been confirmed separately. Nuclear substitution of benzoquinone has previously been observed with very reactive free radicals. For instance, Kharasch and his co-workers [14] obtained 2,5-disubstituted quinones when the reaction of t-butyl peroxide and benzoquinone was carried out in the presence of butadiene and a ferrous salt. Less reactive radicals, such as triphenylmethyl and 2-cyano-2-propyl, react with quinone to give ethers of quinol.[15] The postulate that very reactive cyclohexyl radicals and hydrogen

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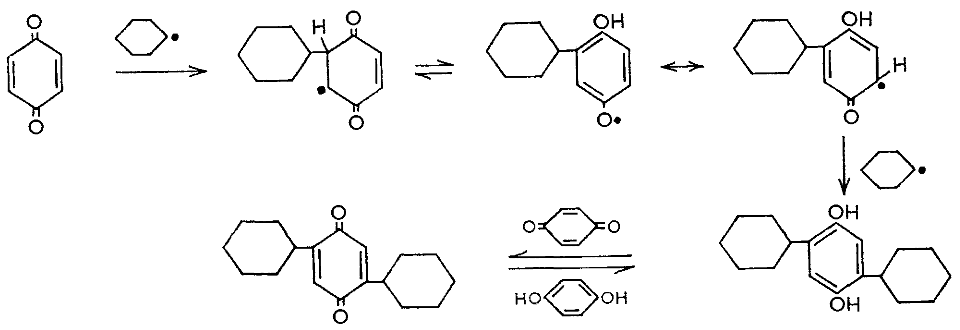
[12] Hochanadel, *J. Chem. Phys.*, 1953, **21**, 880.

[13] Hardy, Ph.D. Thesis, London, 1958.

[14] Kharasch, Kawahara, and Nudenberg, *J. Org. Chem.*, 1954, **19**, 1977.

[15] Bickel and Waters, *J.*, 1950, 1764.

atoms are formed on irradiation of cyclohexane thus accounts rationally for the production of 2,5-dicyclohexyl-benzoquinone and -quinol, when benzoquinone is present.



Irradiation of cyclohexane solutions of toluquinone results in the formation of a mono-cyclohexylated product, 2-cyclohexyl-5-methylbenzoquinone, as shown by the infrared spectrum of its quinol. In at least one case, however, a mixture of dicyclohexylated quinones was produced.

Quantitative Studies.—The effect of benzoquinone concentration on the yields of the main reaction products is shown in Fig. 1. The hydrogen yield decreases smoothly with increasing quinone concentration. Pure cyclohexane was found to give hydrogen with $G = 5{\cdot}3 \pm 0{\cdot}2$, in good agreement with values previously reported.[1,7] $G(H_2)$ for unpurified " Spectrosol " cyclohexane was found to be 4·9 ± 0·2. It must be borne in mind that appreciable amounts of reaction products are formed by the rather large radiation dose given, about 20 joules/g., and that these " impurities " will decrease the hydrogen yield below the true value for cyclohexane.[16] The variation of $G(H_2)$ with quinone concentration reported here is in excellent agreement with the results recently published by Adams, Baxendale, and Sedgwick,[7] and may be compared with the effect of iodine, which causes a much more rapid decrease.[17] The decrease in hydrogen yield is paralleled by the decrease in the yield of bicyclohexyl. In the absence of solutes, bicyclohexyl and its unsaturated analogues are produced with $G = 2{\cdot}2 \pm 0{\cdot}2$, which is in good agreement with the value of 2·4 for the yield of non-volatile residue obtained by allowing irradiated cyclohexane to evaporate. Clearly, very little polymeric material of high molecular weight is formed. Dewhurst [1] has reported that electron bombardment of cyclohexane produces bicyclohexyl with $G = 2{\cdot}0$. From the gas–liquid chromatograms we conclude that bicyclohexyl is produced with $G = 1{\cdot}6$, and that the presumed cyclohexenylcyclohexane and bicyclohexenyl are formed with G values of 0·5 and *ca.* 0·1 respectively. These values, together with the value of 2·4 ± 0·2 for G (cyclohexene), give an acceptable hydrogen balance:

Product	G (product), obs.	G (H_2), calc.
Bicyclohexyl	1·6	1·6
Cyclohexenylcyclohexane	0·5	1·0
Bicyclohexenyl (?)	~0·1	~0·3 (?)
Cyclohexene	2·4	2·4
Hydrogen	5·3, 4·9	5·3

The cyclohexene yield, measured by vacuum-ultraviolet spectroscopy, agrees well with the result by isotopic dilution ($G = 2{\cdot}3 \pm 0{\cdot}2$). Dewhurst [1] obtained $G = 2{\cdot}5$ by using infrared and gas–liquid chromatographic methods, which we regard as less satisfactory than our analytical methods.* The presence of quinone scarcely affects the yield of

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* Nixon and Thorpe [3] report a much lower yield, possibly due to the larger dose (4·8 × 10^{21} ev/g.) and dose rate employed.

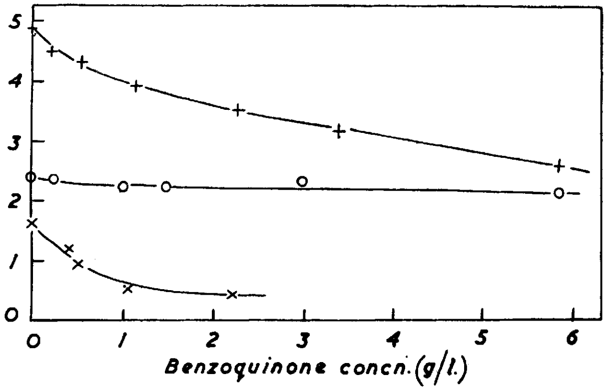
[16] Guenther, Hardwick, and Nejak, *J. Chem. Phys.*, 1959, **30**, 601.

[17] Burton, Chang, Lipsky, and Reddy, *Radiation Res.*, 1958, **8**, 203.

cyclohexene. Evidently quinone, unlike oxygen which reduces $G(C_6H_{10})$ to 1·1, is unable to interfere with this dehydrogenation which has been regarded as an elimination of molecular hydrogen.[1]

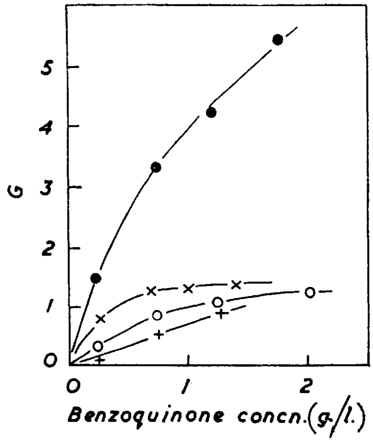
The yields of quinol, dicyclohexylquinol, and dicyclohexylbenzoquinone at various concentrations of benzoquinone are shown in Fig. 2. If the scheme given above for the formation of cyclohexylated products is correct, every molecule of dicyclohexylbenzoquinone produced must be accompanied by one molecule of quinol. *G* values for quinol are always rather larger than the values for dicyclohexylquinone, so some of the former must be produced by another route. Up to quinone concentrations of about 5×10^{-3}M the yield of the " excess " quinol is almost identical with the decrease in hydrogen yield compared with $G(H_2)$ in the absence of quinone. This suggests that benzoquinone is capable of scavenging, though not very efficiently, hydrogen atoms produced in the radiolysis. At quinone concentrations above 5×10^{-3}M the amount of quinol produced is too small to account for the observed decrease in hydrogen yield, and apart from this, more benzoquinone disappears than can be accounted for on the basis of the yields of the other products. Possibly a truly radiation-induced reaction of benzoquinone, or perhaps quinhydrone, occurs to give unidentified products of higher molecular weight. A study of this reaction is made difficult by the low solubility of benzoquinone in cyclohexane.

Fig. 1.



+ *Hydrogen.* ○ *Cyclohexene.* × *Bicyclohexyl.*

Fig. 2.



● *Benzoquinone (disappearance).* × *Quinol.* ○ *Dicyclohexylbenzoquinone.* + *Dicyclohexylquinol.*

The sum of the *G* values for bicyclohexyl and its unsaturated analogues, dicyclohexylbenzoquinone, and dicyclohexylquinol, at a particular benzoquinone concentration, approximates fairly reasonably to the *G* value for bicyclohexyl and its analogues in the absence of quinone. This suggests that the radical yield is not affected by the presence of quinone, as the formation of these compounds presumably involves cyclohexyl radicals.

The effect of benzoquinone in the radiolysis of cyclohexane shows some similarities to the effect of iodine. Thus the decrease in $G(H_2)$ as the iodine concentration is raised from 0 to 10^{-2}M is about 2. A similar decrease has been observed by Burton *et al.*,[17] who have also shown that the addition of larger concentrations of iodine up to 3×10^{-2}M has little further effect. The radical yield, as measured by *G* for the formation of alkyl iodides, is scarcely affected.[18] A significant difference, compared with benzoquinone, is that very little, if any, hydrogen iodide can be detected.[17,18] Burton and his co-workers have attempted to account for the effect of iodine by suggesting that it inhibits the formation of hydrogen by the molecular process. Clearly, benzoquinone does not act in this way.

[18] Fessenden and Schuler, *J. Amer. Chem. Soc.*, 1957, **79**, 273.

Our attempts to measure $G(C_6H_{10})$ in the presence of iodine have been unsuccessful; evidently the alkyl iodides formed have high light-absorption intensities in the far ultraviolet, and their presence vitiates our analytical method for cyclohexene.

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