

## The Effect of Galvinoxyl on the Radiolysis of Benzene-Butene-2 Mixtures

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By the use of galvinoxyl it has been found that the scavengable radical yield ( $G_R$ ) in  $\gamma$ -irradiated benzene is 0.74, but no reaction with excited states is detectable. The effect on the geometrical isomerization of *cis*-butene-2 shows that the stable free radical is able to quench the excited triplet state of benzene with high efficiency. An estimate of about 4 for the triplet  $G$  value in irradiated benzene is quoted. The lifetime of this state is short, *ca.*  $10^{-8}$  sec., under the conditions of the experiments.

Previous work<sup>1</sup> has indicated that the *cis-trans* isomerization of butene-2 in irradiated benzene solutions proceeds *via* an excited-state mechanism with electronic energy transfer from the triplet state of benzene. Although tests for a free-radical mechanism for the reaction were made, it was desirable to examine the effect of a free-radical scavenger more effective than any used in the earlier investigation. Galvinoxyl (2,6,3',5'-tetra-*t*-butyl-4'-phenoxy-4-methylene-2,5-cyclohexadiene-1-one) was selected for this purpose.

Relatively high concentrations, much in excess of those required to scavenge the bulk of the free radicals formed in the solution, caused a considerable decrease in the isomerization yield comparable to that observed with oxygen. Galvinoxyl is known to react efficiently with free radicals,<sup>2</sup> but the question arises whether galvinoxyl can quench excited states by a purely physical process or a chemical process in which there is a reaction between the galvinoxyl and excited benzene as reported by Griffith<sup>3</sup> for DPPH (diphenylpicrylhydrazyl) and triplet benzene. The work described here provides some information on this problem.

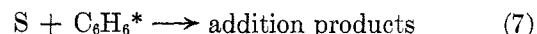
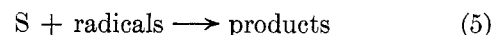
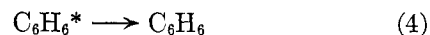
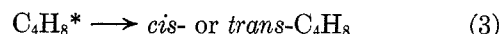
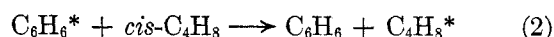
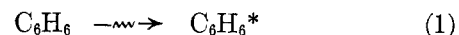
### Experimental

Benzene was purified by the method previously described.<sup>1</sup> *cis*-Butene-2 (Phillips research grade) was used without further purification other than vacuum distillation. Galvinoxyl was prepared by the oxidation of 3,3',5,5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane with lead dioxide.<sup>4</sup> Solutions of galvinoxyl were very readily oxidized in air and were deaerated by the addition of fragments of sublimed solid carbon dioxide. Two-milliliter portions of solutions were thoroughly degassed in tubes fitted with break-seals. A known amount of *cis*-butene-2 was condensed into

the tubes and irradiated with  $\text{Co}^{60}$   $\gamma$ -rays (at  $22 \pm 1^\circ$ ). After irradiation, the tubes were opened under vacuum and the butene-2 was extracted for analysis by gas chromatography. Galvinoxyl was estimated by measuring the absorbance at  $474 \text{ m}\mu$  ( $\epsilon$  145,000) and also iodometrically.<sup>2</sup> The former method appeared preferable because of the difficulty in obtaining a satisfactory end point with the latter. In the determination of galvinoxyl consumed, the tubes were opened under an atmosphere of carbon dioxide.

### Results and Discussion

The experiments were carried out at a constant *cis*-butene-2 concentration (0.21 *M*) and dose rate ( $3 \times 10^{14}$  e.v. g.<sup>-1</sup> sec.<sup>-1</sup>). For convenience, ( $G_{\text{isom}}$ )<sup>-1</sup> values are plotted against the concentration of galvinoxyl (moles l.<sup>-1</sup>) (see Figure 1). The linearity of the plot is consistent with the scheme



(1) R. B. Cundall and P. A. Griffiths, *J. Am. Chem. Soc.*, **85**, 1211 (1963); *Discussions Faraday Soc.*, **36**, 111 (1963).

(2) F. D. Green, W. Adam, and J. E. Cantrill, *J. Am. Chem. Soc.*, **83**, 3461 (1961).

(3) L. R. Griffith, U. S. Atomic Energy Commission, U.C.R.L. 3422 (1956).

(4) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957); M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

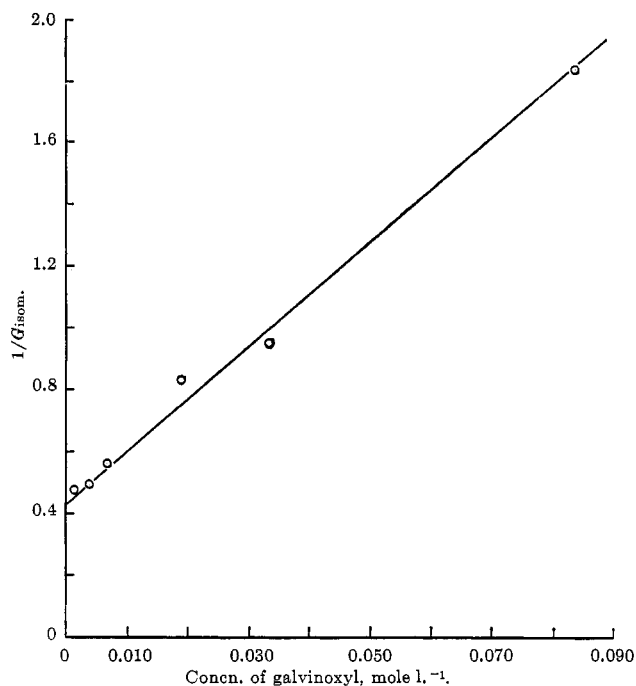


Figure 1. Plot of  $1/G_{\text{isom}}$  vs. concentration of galvinoxyl (mole  $\text{l.}^{-1}$ ) in benzene solution.

$\text{C}_6\text{H}_6^*$  and  $\text{C}_4\text{H}_8^*$  are the triplet states of benzene and butene-2. Evidence for stages (1) to (4) has been presented elsewhere.<sup>1</sup> In the presence of galvinoxyl (S), the process (5) to (6) are also possible and a steady-state treatment yields

$$1/G_{\text{isom}} = 1/k' + k_4/k'k_2[\text{C}_4\text{H}_8] + (k_6 + k_7)[\text{S}]/k'k_2[\text{C}_4\text{H}_8]$$

where  $k'$  is a constant at fixed dose rate involving the efficiency of benzene excitation. From the plotted data  $(k_6 + k_7)/k_2$  is found to be 9.6 ( $k' = 0.38100$  e.v. molecule $^{-1}$ ).<sup>1,5</sup> A value of  $2 \times 10^{-2}$  for the  $k_4/k_2$  ratio can also be derived in good agreement with the value of  $1.8 \times 10^{-2}$  derived from data better suited for this purpose.<sup>5</sup> The ratio of  $(k_6 + k_7)/k_2$  is comparable with 9.0 for oxygen and 3.2 for both naphthalene and anthracene.<sup>5</sup> Apart from oxygen, nitric oxide, and other triplets, paramagnetic molecules are less effective quenchers of the triplet state than those in which an exothermic triplet-triplet energy interchange is possible.<sup>6</sup>

Information on the relative importance of reactions 6 and 7 can be obtained from the results in Table I. At the lower galvinoxyl concentrations, the  $G$  value agrees well with other estimates for free-radical yields in irradiated benzene. Cherniak, Collinson, and Dainton<sup>7</sup> have measured and listed values for  $G(\text{radicals})$  obtained with a variety of scavengers, the most re-

Table I

Concn. of galvinoxyl, mole $\text{l.}^{-1}$	Total dose, e.v. $\times 10^{-20}$ (in 2 ml.)	$G(-\text{galvinoxyl})$	Observed decrease in $G_{\text{isom}}$
$2.5 \times 10^{-3}$	0.138	0.74	0.22
$1.42 \times 10^{-2}$	1.66	0.63	0.83

liable of which lie between 0.70 and 0.75. If the isomerization method is valid for the estimation of the triplet yield in benzene

$$G(\text{triplet } \text{C}_6\text{H}_6) = G_{\text{cis} \rightarrow \text{trans}} + G_{\text{trans} \rightarrow \text{cis}} \approx 4$$

where the  $G_{\text{isom}}$  values are limiting ones in the presence of 0.2  $M$  olefin. The only comparable data are those of Cherniak, Collinson, and Dainton,<sup>7</sup> who have obtained a value of about half this using ferric chloride as scavenger. If excited states were chemically scavenged, than  $G(-\text{galvinoxyl})$  should increase with galvinoxyl concentration up to about 5. This is not found, *i.e.*,  $k_7 \ll k_6$ , and it is possible that the slight decrease observed may be due to some deactivation of a radical-forming excited state. Although galvinoxyl quenches excited triplet states in irradiated systems, it only disappears through free-radical, as distinct from excited-state, attack; *i.e.*, reaction 5 alone is responsible for galvinoxyl disappearance.

The value of  $k_6/k_4$  is  $4.8 \times 10^2$  and, if  $k_6$  is about  $10^{10}$   $\text{l. mole}^{-1} \text{ sec.}^{-1}$  as expected for a diffusion-controlled reaction,  $k_4$  must be  $2.1 \times 10^7 \text{ sec.}^{-1}$ . This implies that the lifetime of the benzene triplet is surprisingly short, ( $5 \times 10^{-8} \text{ sec.}$ ). If a longer lifetime for the benzene triplet is assumed, the value of  $k_6$  becomes less than that for a diffusion-controlled reaction, which is anticipated from the close similarity in behavior between oxygen and galvinoxyl.

The identity of the absorption spectra of galvinoxyl in benzene and chloroform suggests that a solvent-solute complex is not responsible for the benzene triplet state quenching by galvinoxyl as could be the case with DPPH in benzene.

**Acknowledgments.** The authors are indebted to Dr. G. B. Gill for his invaluable assistance and comments. Thanks are due to the Petroleum Research Fund of the American Chemical Society for support.

(5) R. B. Cundall and P. A. Griffiths, to be published; the data quoted differ somewhat from those given in ref. 1.

(6) G. Porter and M. R. Wright, *Discussions Faraday Soc.*, **27**, 18 (1959).

(7) E. A. Cherniak, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, **60**, 1408 (1964).