

**Table VII.** Resonance Energies of Linear Polyenes<sup>a</sup>

<i>n</i>	<i>E<sub>R</sub></i> , e.v.	
	PPP	SPO
1	-0.031	-0.019
2	-0.046	-0.023
3	-0.060	-0.028
4	-0.076	-0.035
5	-0.094	-0.043
6	-0.112	-0.051
7	-0.132	-0.061
8	-0.151	-0.071
9	-0.172	-0.083
10	-0.194	-0.094
11	-0.216	-0.107
12	-0.239	-0.119

<sup>a</sup> From eq. 12.

rather than the equation of part II which was derived on the assumption that all bonds have a common length (1.40 Å.). Table VIII shows resonance energies calculated on this basis for the compounds that were predicted in part II to show strong bond alternation; the values are all close to zero, indicating that these "classical" hydrocarbons are also well represented in terms of "localized" single and double bonds.

### Summary and Conclusions

The results and arguments presented in this paper seem to provide strong support for the idea<sup>5</sup> that classical conjugated hydrocarbons can be well repre-

**Table VIII.** Resonance Energies of Some Nonbenzenoid Hydrocarbons<sup>a</sup>

Molecule	<i>E<sub>R</sub></i> , <sup>b</sup> e.v.	
	PPP	SPO
Fulvene	+0.003	+0.020
Heptafulvene	-0.044	-0.011
Fulvalene	+0.053	+0.083
Sesquifulvalene	-0.013	-0.020
Heptafulvalene	-0.028	0.000

<sup>a</sup> From eq. 12. <sup>b</sup> Allowing for bond alternation.

sented in terms of "localized" single and double bonds. It should perhaps be emphasized again that this applies only to collective properties, and only in the sense that bond localization is regarded in the empirical way indicated earlier. If we are concerned with one-electron<sup>4</sup> properties of molecules, or with purely theoretical discussions of the nature of binding in conjugated molecules, then the localized bond picture fails; but in these cases the picture is inapplicable to *any* molecules, saturated or unsaturated, conjugated or nonconjugated.

An immediate corollary follows. If "resonance" in the chemical sense is unimportant in classical conjugated polyenes, then it must certainly be unimportant in "hyperconjugated" molecules, for there can be little doubt that the interaction between the localized bonds of an idealized model must be less important in the latter case.

## The Radiolysis of 1,4-Cyclohexadiene and 1,4-Cyclohexadiene-<sup>14</sup>CH<sub>3</sub>I Mixtures<sup>1</sup>

Manfred K. Eberhardt, George W. Klein, and Thomas G. Krivak

Contribution from the Radiation Research Laboratories, Mellon Institute, Pittsburgh, Pennsylvania. Received October 17, 1964

The radiolysis of 1,4-cyclohexadiene was studied in order to provide information about the reactions of cyclohexadienyl radicals. The disproportionation of cyclohexadienyl radical, produced by radiolysis of 1,4-cyclohexadiene, yields 1,4-cyclohexadiene, 1,3-cyclohexadiene, and benzene in a ratio of 2.74:1.0:3.74. In scavenging experiments with small amounts of <sup>14</sup>CH<sub>3</sub>I (0.11 mole %) the two methylcyclohexadienes (I and II) are formed in a ratio of 1.6 ± 0.3. The mechanism of a chain isomerization to 1,3-cyclohexadiene, which is observed in the radiolysis of 1,4-cyclohexadiene-<sup>14</sup>CH<sub>3</sub>I mixtures, is discussed.

In a previous publication<sup>2</sup> we have reported the formation of 1,3- and 1,4-cyclohexadiene in the radiolysis of liquid benzene in a ratio of 1:2.7. This ratio appears to be quite surprising in view of the relative electron spin densities for the *ortho* and *para* positions of the cyclohexadienyl radical of 2 × 0.35:0.5.<sup>3</sup> The

reason for the unexpected behavior of the cyclohexadienyl radical could be that 1,3-cyclohexadiene is consumed by secondary reactions or that the disproportionation of the cyclohexadienyl radical is controlled by factors other than the electron spin density. In order to provide further insight into this problem we have studied the radiolysis of 1,4-cyclohexadiene, pure and in presence of small amounts (0.11 mole %) of <sup>14</sup>CH<sub>3</sub>I.

### Experimental

The 1,4-cyclohexadiene (Columbia Chemical Co.) was purified just before use by the same technique of vapor phase chromatography as employed in the analysis. The sample (about 0.1 ml.) was then degassed by vacuum line techniques and sealed in a glass bulb. For the mixture experiments, the required amount of <sup>14</sup>C-methyl iodide<sup>4</sup> was added to the sample before it was sealed. The sealed sample was then

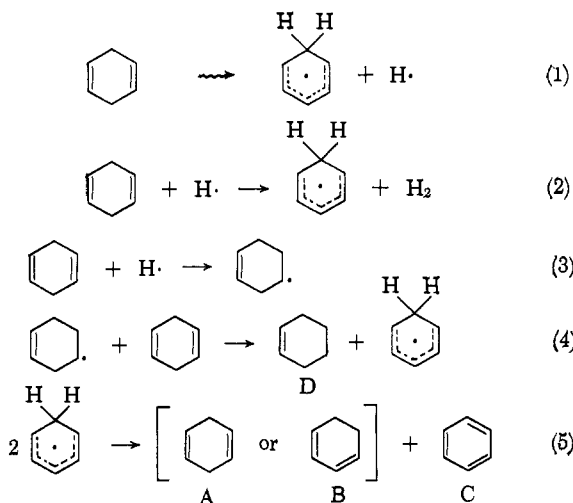
(1) Supported, in part, by the U. S. Atomic Energy Commission.  
 (2) M. K. Eberhardt, *J. Phys. Chem.*, **67**, 2856 (1963).

(3) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).  
 (4) R. H. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).

irradiated in a  $^{60}\text{Co}$  source at room temperature at a dose rate of about  $10^{19}$  e.v./g. hr. In one run indicated in Table II as  $-50$  to  $-15^\circ$ , the sample was placed in a dewar of a mixture of alcohol and water initially cooled to  $-50^\circ$  and irradiated. The temperature rose to  $-15^\circ$  during irradiation. The sample (size determined by difference weighing) was analyzed by vapor phase radiochromatography.<sup>4</sup> The material was separated on a 2.5-m. column of silicone grease on firebrick which was temperature programmed and was followed by a 7.5-m. column of diethylene glycol succinate on firebrick held constant at about  $50^\circ$ . The material is eluted from these columns in the order cyclohexene, methyl iodide, an unknown with a mass spectrometric parent peak of 80, 4-methylcyclohexene, 1,3-cyclohexadiene, methyl-2,4-cyclohexadiene, 1,4-cyclohexadiene, methyl-2,5-cyclohexadiene, and benzene. To facilitate the analysis of benzene which is on the tail of the 1,4-cyclohexadiene elution, an additional 2.5-m. silicone column was inserted in front of the detector after the methyl-2,4-cyclohexadiene and part of the parent 1,4-cyclohexadiene were eluted. This column arrangement was temperature programmed, and the compounds were eluted in the order benzene, 1,4-cyclohexadiene, and methyl-2,5-cyclohexadiene. Except for the two methylcyclohexadienes and the mass 80 product, compounds were identified by retention time comparison with authentic samples.

## Results and Discussion

The products of the radiolysis of 1,4-cyclohexadiene (Table I) can be explained on the basis of the mechanistic scheme shown in eq. 1-5. The  $\text{C}_6\text{H}_9\cdot$  radicals do not



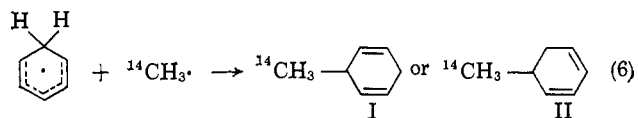
disproportionate with themselves nor with  $\text{C}_6\text{H}_7\cdot$  radicals. Because of the labile carbon-hydrogen bond in the 1,4-cyclohexadiene, the  $\text{C}_6\text{H}_9\cdot$  radicals react rapidly with  $\text{C}_6\text{H}_8$  by hydrogen abstraction (eq. 4). E.s.r. studies confirm this high reactivity of the  $\text{C}_6\text{H}_9\cdot$  radicals. The spectrum shows only the presence of cyclohexadienyl radicals. From the stoichiometry of the disproportionation reaction (eq. 5), we obtain the relationship

$$G(\text{A}) + G(\text{B}) = G(\text{C})$$

or

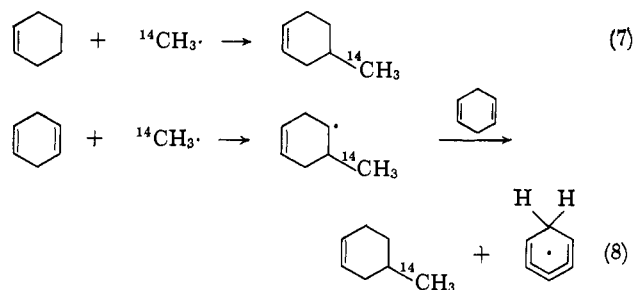
$$\frac{G(\text{A})}{G(\text{B})} = \frac{G(\text{C})}{G(\text{B})} - 1$$

From the experimental determination of the ratio C:B one can therefore calculate the ratio A:B, which is given in the last column of Table I. The above relationship does not take into account the formation of benzene by a unimolecular  $\text{H}_2$  elimination. However, the average value of  $2.74 \pm 0.14$  for the ratio of A:B is in excellent agreement with the ratio of  $2.70 \pm 0.15$  obtained in the radiolysis of benzene.<sup>2</sup> Benzene formation by a unimolecular process therefore appears to be unlikely. The preferred formation of nonconjugated diene products is also evident from results shown in Table II. In these experiments the cyclohexadienyl radicals are scavenged by radioactive methyl radicals, which are produced in the radiolysis of 1,4-cyclohexadiene- $^{14}\text{CH}_3\text{I}$  mixtures.<sup>4</sup> The activity of the methyl

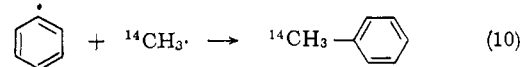
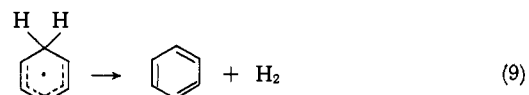


radicals makes it possible to detect very small amounts of methylcyclohexadienes. Despite the large degree of scattering in the ratios of the two isomeric methylcyclohexadienes (Table II), it is obvious that the ratio is in favor of 1-methylcyclohexadiene-2,5, a fact that cannot be explained on the basis of electron spin densities in the cyclohexadienyl radical. In a number of additional experiments at  $-50^\circ$  using a  $10^{-6}$ -amp. beam of 2.8-Mev. electrons, the ratio of I:II was  $1.48 \pm 0.12$ . From the above two pieces of evidence, it is clear that electron spin density values cannot be used in predicting relative positional reactivity in conjugated radicals.

In the above described studies on methyl iodide mixtures, 4-methylcyclohexene was formed in addition to the methylcyclohexadienes. This product can arise from reactions 7 and 8. The relative amount of



4-methylcyclohexene is dependent on dose rate and therefore cannot be used for the calculation of the cyclohexenyl radical yield. Toluene- $^{14}\text{C}$ , which could possibly be formed according to eq. 9 and 10, was



found to be absent. The molecular hydrogen elimination from a  $\text{C}_6\text{H}_7\cdot$  radical has been previously suggested as a mode of  $\text{H}_2$  formation in the radiolysis of benzene.<sup>5</sup>

(5) W. M. Patrick and M. Burton, *J. Am. Chem. Soc.*, **76**, 2626 (1954).

**Table I.** Radiolysis of 1,4-Cyclohexadiene

Dose rate × 10 <sup>-19</sup> , e.v./ g. hr.	Irradi- ation period, hr.	G(D)	G(B)	G(C)	G(80) <sup>a</sup>	C:B	A:B
5.3	2	1.12	0.64	2.54	0.45	4.0	3.0
5.3	5	1.23	0.61	2.33	0.35	3.83	2.83
5.3	10	1.22	0.56	2.06	0.46	3.7	2.7
1.1	22	1.34	0.61	2.16	0.43	3.55	2.55
1.1	48	1.15	0.53	1.91	0.42	3.6	2.6
Av. = 2.74 ± 0.14							

<sup>a</sup> Unidentified product with mass spectrometric parent mass of 80.

The results with 0.11 mole % CH<sub>3</sub>I (Table II) also show a very high yield of isomerization of 1,4-cyclohexadiene to 1,3-cyclohexadiene which is presumably the result of a chain process. As expected from a radical chain reaction, a significant amount of isomerization takes place only at low dose rates in the <sup>60</sup>Co source, but not with 2.8-Mev. electrons at 10<sup>-6</sup> amp. At low temperature (-50 to -15°) the G(B) is considerably decreased. This temperature effect shows that the isomerization requires some activation energy. We propose a mechanism involving the production of iodine atoms by the (indirect) dissociation of the methyl iodide followed by an iodine atom catalyzed isomerization of the cyclohexadiene similar to that indicated in studies with molecular iodine.<sup>6</sup> With increasing dose rates, the chain-terminating steps be-

(6) M. K. Eberhardt, to be published:

**Table II.** Radiolysis of 1,4-Cyclohexadiene-<sup>14</sup>CH<sub>3</sub>I<sup>a</sup>

Irradi- ation period, <sup>b</sup> hr.	G(D)	G(B)	G(C)	G(80) <sup>c</sup>	I:II
2	1.76	58.7	4.84	0.44	1.73
2	1.77	54.7	3.73	0.43	1.15
2 <sup>d</sup>	1.76	4.45	2.54	0.37	1.28
5	1.61	41.8	4.65	0.43	1.85
10	1.51	26.4	2.96	0.41	2.04
Av. = 1.61 ± 0.3					

<sup>a</sup> Amount of <sup>14</sup>CH<sub>3</sub>I, 0.11 mole % ± 10%. <sup>b</sup> At a dose rate of 5.3 × 10<sup>19</sup> e.v./g. hr. <sup>c</sup> Unidentified product with mass spectrometric parent mass of 80. <sup>d</sup> Temperature -50 to -15°.

come more important and thus decrease the amount of isomerization. In the studies with iodine,<sup>6</sup> the disproportionation of 1,4-cyclohexadiene in the presence of small amounts of iodine (0.5 M) gives in quantitative yield cyclohexene, benzene, and some 1,3-cyclohexadiene and 4-iodocyclohexene. The yield of 1,3-cyclohexadiene was found to increase with decreasing iodine concentration. The results observed in the present study can be explained as a continuation of the effect of decreasing iodine concentration, which favors chain propagation over the chain-terminating steps. We have also observed<sup>6</sup> that the photolysis of CH<sub>3</sub>I in 1,4-cyclohexadiene leads to a large amount of isomerization.

The yields of the unknown compound of mass 80 are listed in Tables I and II as G(80). The yield of this compound is not affected by added CH<sub>3</sub>I and must therefore be formed by a nonradical process.

## Acid-Base Equilibria in Benzene. I. A Colligative Property and Infrared Study of the Reactions of Some Carboxylic Acids and Nitrogen Bases

Stanley Bruckenstein and Atsushi Saito

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received August 14, 1964

The reaction of primary, secondary, and tertiary amines (B) with carboxylic acids (HX) in benzene as solvent was studied at a base concentration of 0.01 M. A dynamic differential vapor pressure technique and infrared spectroscopy were used to establish the stoichiometry of the acid-base reactions. The principal species identified were ion pairs and other uncharged ionic aggregates. Three types of ion pairs are postulated: (1) BH<sup>+</sup>X<sup>-</sup>, (2) BH<sup>+</sup>HX<sub>2</sub><sup>-</sup>, and (3) BH<sup>+</sup>X(HX)<sub>2</sub><sup>-</sup>. These ion pairs tend to form oligomers; the stronger the acid or base, the greater the oligomer formation. Reaction of mixtures of two bases with an acid indicates that specific, strong interactions can occur between ion pairs containing different cations.

### Introduction

Relatively few quantitative equilibrium studies have been made in benzene. Early indicator studies by LaMer and Downes,<sup>1</sup> involving both indicator acids and bases with colorless acids and bases, demonstrated that aqueous equilibrium concepts could not adequately account for their experimental results. They interpreted their data semiquantitatively by assuming equilibrium constants of the form

$$K_I' = \frac{K_{HA}^n}{K_{H,I}} = \frac{(H_n I)(A)^n}{(I)(HA)^n}$$

(1) V. K. LaMer and H. C. Downes, *J. Am. Chem. Soc.*, **55**, 1840 (1933).