Study of Thermal Aromatization of 1,3-Butadiene

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THE HAGUE and Wheeler aromatization scheme (*13, 38*), which is based on Diels-Alder reactions between butadiene and the lower olefins, followed by dehydrogenation, has gained wide acceptance (*9*), although a close examination of the steps involved reveals considerable difficulties (*7, 16, 25*).

An obvious approach in the investigation of this scheme would have been to study the thermal decomposition of mixtures containing butadiene and olefins. But because butadiene readily undergoes cyclic dimerization and aromatization (*11*), this compound in its pure form was studied first.

Literature Background

Subject	Ref.
Evidence for the Hague and Wheeler scheme from aromatization of naphtha	(*34-36*)
Kinetics of Diels-Alder reactions of butadiene, leading to cyclohexene and 4-vinylcyclohexene	(*25*)
Butadiene at 150 to 700° C., in thermal conditions, yields mainly 4-vinylcyclohexene and other cyclic dimers	(*14, 15, 17-19, 23, 25, 40*)
Butadiene at 300-400° C., over floridine, yields aromatics	(*29-31*)
Direct dehydrogenation of cyclohexenes to aromatics, in thermal conditions, has not been established	(*16, 24, 39*)

EXPERIMENTAL

Butadiene was subjected to both mild and severe temperatures, and the reaction mixtures formed at various contact times were analyzed quantitatively. The reaction steps in formation of the aromatics were reconstructed on the basis of intermediate compounds and variations in both the intermediate and final products with contact time. The results were plotted as change in product concentration *vs.* time. Thus, secondary and primary reactions could be distinguished more easily, because quantities of products formed by secondary reactions tend in many cases towards zero for contact times at which primary products are already present in considerable concentrations (*10*).

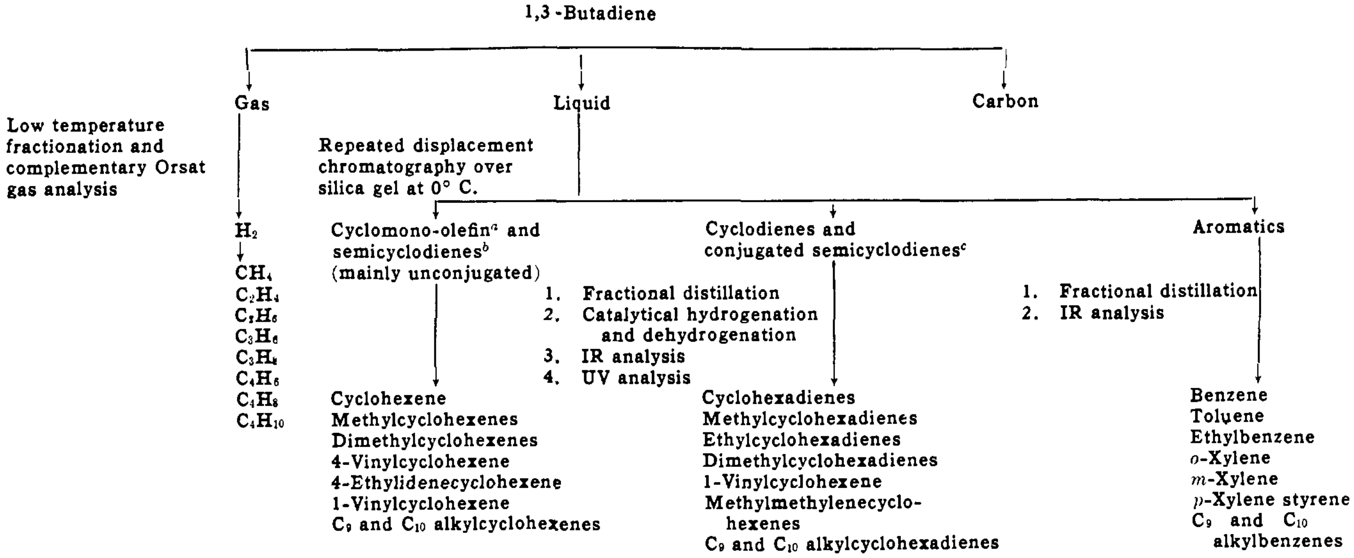
Apparatus and Procedure. A stainless steel reactor, a system for drying and measuring the starting material, and a combination of coolers, traps, a stripping column, and a 250 liter gas holder for the collection and preliminary separation of the products comprised the equipment.

The reactor was a cylindrical tube, 80 cm. long and 3.5 cm. in internal diameter, filled with 20-mesh x 27 British standard wire gage 18/8 stainless steel wire cloth, cut into pieces of 4 x 1 cm. and rolled into a kind of Raschig ring. The reactor was heated by a furnace, provided with one main heating element and an additional resistance coil at each end to compensate for heat losses. An isothermal (±5° C.) zone of 40 to 45 cm. minimum length could thus be obtained. The temperature was measured with 12 thermocouples, equally distributed along the entire length of the reactor.

The system was purged with pure nitrogen at the beginning of each experiment. When the desired temperature was approached, pure butadiene (Phillips, c. p.) was introduced and the heating adjusted until a stable temperature distribution was obtained. Collection of products was started after 1 to 2 hours observation had shown that the gas and liquid formation rate was approximately constant. After each run, the C_3 and C_4 gases, which condensed mainly in the liquid products train, were stripped of C_5 components in an ice-cooled column, packed with Dixon fillings, and led into the gas holder. The C_5 components were then fractionally distilled.

Stainless steel packing was used to ensure good heat transfer, particularly at short contact times. Weizmann and coworkers (*37*) had found that 18/8 stainless steel permitted the cracking of hydrocarbon oils for prolonged periods, without serious formation of carbon and without influencing the nature of the products. The effect on butadiene was checked by an experiment in an empty copper tube. Comparison of the amounts of aromatics (Table I) shows that stainless steel packing does not influence the main course of reaction. Styrene, however, is an exception.

Analytical. The reaction products from 1,3-butadiene at 550° C. were worked up according to the scheme shown below.



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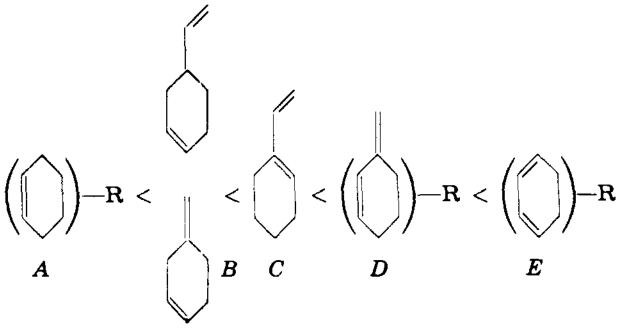
[a] Contains also small quantities of hexenes and octenes. [b] Includes both alkylidene- and alkenylcyclohexenes. [c] Contains some quantities of C_5 and C_6 open-chain dienes.

Gas Composition. Samples of 4 to 6 liters of the gasous products were distilled on a low temperature semi-robot Podbielniak column and the fractions analyzed in an Orsat apparatus. The unreacted butadiene was determined with molten maleic anhydride.

Liquid Composition. CHROMATOGRAPHY. The liquid products obtained at 550° C. were separated by repeated displacement chromatography over silica gel (Figure 1) in columns 300 cm. long and 1.5 cm. in diameter and using less than 20 grams of liquid product per 100 grams of silica gel (28 to 200 mesh). Pressures ranged from 50 to 200 mm. of mercury, and the percolation rate was 20 to 40 cm. per hour. Losses resulting from polymerization were reduced to an average of 10% by cooling the columns with ice water.

The olefinic components showed the following order of affinity towards silica gel:



These classes of compounds could not all be completely separated. However, after repeated chromatography of the different fractions, the liquid product was separated into these cuts: (1) all alkyl-substituted cyclohexenes, *A*, (Table II, components 3 to 5), plus most of the unconjugated diolefins, *B*; (2) practically only conjugated diolefins *C*, *D*, and *E*), (Table II); and (3) aromatics and only a few per cent of diolefins, as shown by ultraviolet analysis. 1-Vinylcyclohexene, *C*, appeared in approximately equal quantities in the first and in the second cut. The low affinity of this component, when compared with methylmethylenecyclohexenes, *D*, is similar to that of 3,8(9)-*p*-menthadiene and 2,4(8)-*p*-menthadiene (*20*).

The subsequent identification and quantitative analysis of the different components were made possible to a very large extent by the preliminary separation by chromatography.

DISTILLATION. Fractional distillation of the chromatographic cuts at atmospheric pressure was done using a Podbielniak Hypercal column, or a Todd column when less than 30 ml. were available (Figure 2). Distillation losses due to polymerization were reduced by adding hydroquinone to the charge and amounted to 5 to 7% for the first chromatographic fraction but reached 10 to 15% for the second fraction (conjugated diolefins). In the aromatic portion, however, most of the styrene polymerized. Therefore, the amount of this component was obtained by separate fractional distillation of a portion of the total aromatics at reduced pressure, followed by quantitative catalytic hydrogenation of the fraction boiling at 75° to 85° C. at 100 mm. of mercury. The accuracy of this method, checked with synthetic blends, was better than 5%.

Table I. Aromatic Products Formed from Butadiene[c]

	Moles/100 Moles Reacted Butadiene	
Component	A[a]	B[b]
Benzene	2.5	2.7
Toluene	3.3	3.4
o-Xylene	1.7	1.6
m-Xylene	0.5	0.5
p-Xylene	1.1	1.0
Ethylbenzene	1.6	1.2
Styrene	2.5	0.2
C_9 alkylbenzenes	0.4	0.4
C_{10} alkylbenzenes	0.7	0.7

[a] In a stainless steel tube filled with stainless steel packing.
[b] In an empty copper tube.
[c] Temp., 550° C., contact, 5 sec.

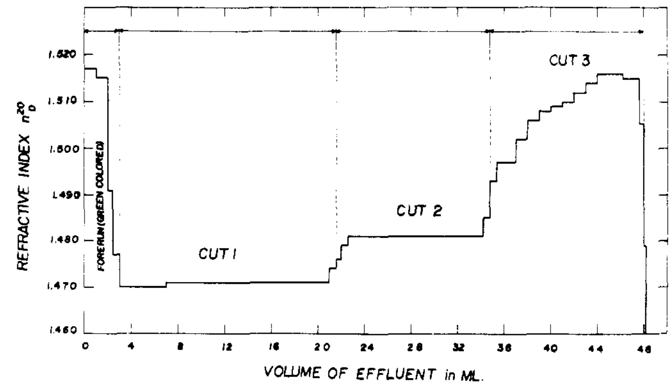


Figure 1. Chromatography leads to separation of liquid product according to structure type

Cut 1, mono-olefins plus unconjugated diolefins; cut 2, conjugated diolefins; cut 3, aromatics

The fractional distillations resulted in the separation of the chromatographic cuts into individual components or groups of isomers which were further examined by chemical and spectroscopic methods.

Catalytic Hydrogenation and Dehydrogenation. The number of double bonds per molecule, and the carbon skeleton of some open chain and cyclic compounds were determined by the identification of the products resulting from catalytic hydrogenations in a semimicroapparatus, in alcoholic solution, using Adams' platinum catalyst. Samples of 0.2 to 1.0 gram were used, and the method, tested with pure 4-vinylcyclohexene, was accurate within ±2%. When the hydrogenation products were needed for further analysis, they were separated from the solvent by chromatography on silica gel in columns 120 cm. long and 3 mm. in internal diameter, or by dilution with water.

Catalytic dehydrogentation with infrared analysis of the aromatics formed was used for determination of the carbon skeleton of individual cyclo-olefins or mixtures of double bond isomers and of the distribution of skeleton isomers in composite cuts. Dehydrogenations were carried out in a

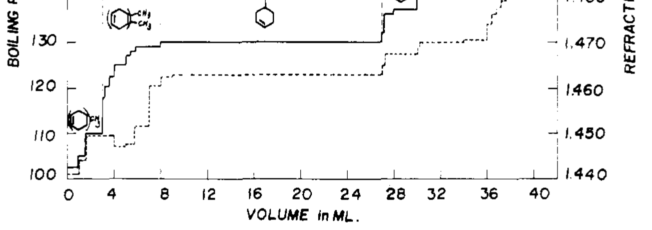


Figure 2. Fractional distillation of first chromatographic cut results in good separation of components

Table II. Analysis of Products of Butadiene,

(Formed at 550° C. and 2.9 sec. contact time)

No.	Component	Quantity, G.	B.P., ° C. at 760 Mm.[a]	n_D^{20} [a]	Hydrogen[b] No.	Analysis
	First Chromatographic Cut					
1	*n*-Pentenes	0.4	30–37	1.3755	. . .	c, d
2	*n*-Hexenes	0.4	63–69	1.3920	1.04	c, d
3	Cyclohexene	0.2	82–83	1.4462	0.92	c, e
4	1-Methycyclohexene	4.8	109–110	1.4495	0.95	c, f, g (22)
	3-Methycyclohexene	1.4	102–104	1.4418–1.4425	0.91	
	4-Methycyclohexene	3.6				
5	*o*-Dimethylcyclohexenes	6.5	118–128.5	1.4465–1.4520	1.12	h, i
	m-Dimethylcyclohexenes	2.2			1.12	
	o-Dimethylcyclohexenes	3.1				
6	4-Vinylcyclohexene	111.9	129–130	1.4635	2.01	c, d, f See text
7	4-Ethylidenecyclohexene	9.8	136–137	1.4673	1.93	d, f, j
8	C_9 alkylcyclohexenes[k]	3.3	149–160	1.4736	1.23	f
9	C_{10} alkycyclohexenes[k]	3.4	161–190	1.4805	1.17	f
	Second Chromatographic Cut					
10	Pentadienes	1.4	40–46	1.4225	1.85	l
11	Hexadienes	3.7	65–80	1.4435	1.93	d, m
12	Cyclohexadienes	2.9	81–88	. . .	2.02	d, f, n
13	Methylcyclohexadienes	2.8	102–111	1.4664	1.97	d, f, o
14	Dimethylcyclohexadienes[t] and methylmethylenecyclohexenes					
	o-Isomers	14.5	121–139[p]	1.4654–1.4790	2.04	h, q
	m-Isomers	5.7				
	p-Isomers	10.3				
15	Ethylcyclohexadienes[t]	18.8	133–139[p]	. . .	2.06	f, q
16	1-Vinylcyclohexene	24.3	144–145	. . .	1.98	d, f, r
17	C_9 alkylcyclohexadienes	1.2	147–170	1.4720	1.95	f, s
18	C_{10} alkylcyclohexadienes	1.7	171–180	1.4790	1.90	f, s
	Third Chromatographic Cut					
19	Benzene	13.3	80–81	1.5006	. . .	c
20	Toluene	22.6	110–111	1.4960	. . .	c
21	Ethylbenzene	10.5	136–136.5	1.4958	. . .	g
22	*o*-Xylene	14.8	144–145	. . .	. . .	g
23	*m*-Xylene	4.7	138–139.5	1.4962–1.4980	. . .	g
24	*p*-Xylene	9.0				g
25	Styrene	44.4	. . .	. . .	. . .	(see text)
26	C_9 alkylbenzenes	5.8	150–170	1.5064	. . .	c
27	C_{10} alkylbenzenes	6.6	171–205	1.5207	. . .	c
	Undetermined	87.7				u
	Total	457.7				

[a] Actual data of corresponding cut, except where indicated. Good agreement found with values for pure components (*1*).

[b] Moles of hydrogen absorbed per mole of substance.

[c] Identified by IR.

[d] Hydrogenated to corresponding saturated compound, which was identified by IR.

[e] Dehydrogentated to benzene in runs yielding larger amount.

[f] Dehydrogenated to corresponding aromatic compound, which was identified by IR.

[g] Mixture analyzed by IR.

[h] Dehydrogenated to mixture of aromatics, which were analyzed by IR.

[i] Contains some open chain olefins; identification procedure, *see* text.

[j] UV. showed absence of conjugated double bonds; IR. showed presence of ethylidence group [absorption bands, 797 cm.$^{-1}$, 3030 cm.$^{-1}$ (*2*), and 1670 cm.$^{-1}$ (*27*)] and absence of vinyl group.

[k] Contains probably also alkenylcyclohexanes; high hydrogen number and lack of absorption in UV indicates presence of some unconjugated dienes.

[l] 1, 3-Pentadiene is main component according to UV; estimation by IR: 35% *cis*-1, 3-pentadiene, 40% *trans*-1, 3-pentadiene, 25% 1, 4-pentadiene.

[m] 2, 4-Hexadiene is main component according to UV.

[n] Contains about 45% of conjugated diene, $\lambda_{max.}$ 2570 A.

[o] Contains about 50% of conjugated diene, $\lambda_{max.}$ 2610 A.

[p] Boiling range of pure compounds.

[q] Contains various types of conjugated dienes, see Table III.

[r] Estimated from corresponding fractions of 1st and 2nd chromatographic cuts and corrected for impurities. United fractions have $\lambda_{max.}$ 2300 A., ϵ = 6700; reported (*3*) $\lambda_{max.}$ 2300 A., ϵ = 8500. 1-5-Cyclo-octadiene was searched for in the impurities but its presence could not be established.

[s] Contains two types of conjugated dienes: alkylidene-cyclohexenes ($\lambda_{max.}$ 2365 A.) and alkylcyclohexadienes ($\lambda_{max.}$ 2670 A.).

[t] Contains a few per cent of diolefins, which were accounted for as "undetermined".

[u] Cyclic unsaturated material, composed of 12.2 grams green colored substance (Figure 1), 27.5 grams distillation residue of first chromatographic cut, 29.9 grams distillation residue of second chromatographic cut and 18.8 grams of distillates unaccounted for by components listed.

semimicroapparatus (*5*) at 275° C., over platinum (5%) on asbestos.

Infrared Analysis. The infrared spectra were determined with a Perkin-Elmer Model 12C spectrophotometer. The absorption curves were compared with published spectrograms (*1*). Compounds, identified by their infrared spectrum (Table II), agreed with published data for the region from 3 to 15 microns, and showed absence of foreign bands. This method was accurate enough to detect 5 to 10% of impurities. Absorptivities, required for quantitative analysis, were determined on pure substances, prepared by fractionation of commercially available products or by synthesis. For the pentadienes, however, quantitative analysis was based on coefficients estimated from published spectra.

Quantitative analysis for mixtures of 1-, 3-, and 4-methylcyclohexene was based on bands at 916, 700, and 990 cm.$^{-1}$, respectively (*22*).

Ultraviolet Analysis. Ultraviolet absorption (2200 to 2700 A.) was measured with a Beckman DU spectrophotometer, using a cell of 1-cm. width and samples dissolved in 95% ethyl alcohol. The results proved the presence of conjugated double bonds and their position in the molecule.

In a number of composite fractions more than one type of conjugated diene were present, and correspondingly, the spectra showed two to three clearly separated maxima (Tables II and III); the amounts of the different conjugated dienic types were estimated, using literature data (*3*).

Analysis of Reaction Mixture Obtained at 550° C. and 2.9 Seconds Contact Time. In these conditions 756 grams of pure butadiene yielded 457.7 grams (60.5%) of liquid, 38.9 grams (5.1%) of gas, 240 grams (31.7%) of unreacted material, and 20.4 grams (2.7%) of carbon (plus losses). The liquid was chromatographed in batches (Figure 1) and separated into (1) 203.5 grams (44.4%) mono-olefins and unconjugated dienes, (2) 120.3 grams (26.3%) conjugated semicyclo- and cyclodienes, and (3) 133.9 grams (29.3%) aromatics. The three cuts were fractionally distilled as follows; (1) Podbielniak Hypercal column, 13 mm. in internal diameter and 108 cm. long; boil-up rate, 300 ml. per hour (100 theoretical plates); take-off rate, 2 ml. per hour, except on the 4-vinylcyclohexene flat, where rate was doubled; charge, 44.5 ml. plus 50 ml. of Tetralin as chaser. (2) Todd column with Monel spiral packing; main portion distilled with boil-up rate of 60 ml. per hour; take-off rate, about 1 ml. per hour; charge, 19.5 grams. (3) Podbielniak column as above; boil-up rate, 250 ml. per hour; take-off rate, 2.2 ml. per hour; charge, 31.5 ml. plus 100 ml. of Tetralin, as chaser.

The liquid was analyzed in terms of 34 individual compounds or groups of isomers (Table II). Where necessary, the purity of the various components is commented upon in the footnotes. The figure for 4-vinylcylcohexene is corrected for the amount of this substance in the preceding component 5 (hydrogen number 1.12, and correspondingly

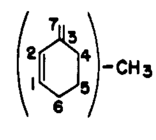
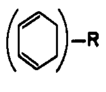
13% of ethylbenzene in the product of dehydrogenation).

The complexity of components 14 and 15 was cleared up to some extent by the ultraviolet spectra (Table III) and the catalytic dehydrogenation results, which show that fractions 1, 2, 3, and 4 are composed chiefly of methylmethylene cyclohexenes and dimethycyclohexadienes (component 14), whereas ethylcyclohexadienes and probably some 3-ethylidenecyclohexene (component 15) predominate in fractions 5 and 6. The presence of some normal C_8 open-chain olefins, with conjugated double bonds in the 1, 3 position, indicated by $\lambda_{max.}$ 2220 A. in fractions 5 and 6, was confirmed as follows: Fraction 6 was first hydrogenated and then dehydrogentated; about 10% of a paraffinic material, identified as *n*-octane by infrared analysis, was isolated from the product by chromatography.

The losses incurred in the different operations were distributed proportionally over the amounts found, so that the sum total adds up to 100%. This procedure slightly affects the distribution of reaction products, particularly the less stable components, such as 1-vinylcyclohexene. With this limitation, the results are estimated to be correct within about 5 to 10%. The high accuracy is mainly due to the efficient resolution by chromatography and the infrared analysis of aromatics, in the final stages Semimiromethods were used throughout, so components present in less than 0.1% presented no difficulty. In future work of this type, however, vapor phase chromatography will be invaluable.

Table III. Ultraviolet Spectra of C_8 Conjugated Diene Fractions[a]

(Formed from butadiene, temp. 550° C., contact time, 2.9 sec.)

		Absorptivity, $G.^{-1}$ L. $Cm.^{-1}$ at $\lambda_{max.}$			
			2300–2320 A.	2370 A.	2600–2650 A.
Diene type		$R \cdot CH = CH \cdot CH = CH_2$ ($R = n - C_4H_9$ or $n - C_4H_7$)			
No.	B. P. ° C. at 760 Mm.		(CH_3 at 4, 5 or 6)	(CH_3 at 1, 2 or 7)	(R = ethyl or dimethyl)
1	121–122	...	22.6	...	13.4
2	125–127	...	32.5	...	12.4
3	128	...	4.5	14.1	8.3
4	131.5–132	...	...	14.6	8.5
5	133–134	9.0	...	10.8	16.7
6	135–139	16.5	...	20.0	18.5

[a] Components 14 and 15, Table II.

All other experiments at 550° C. were worked up in the same way. The mixtures obtained at 700° C., on the other hand, did not require such an elaborate analysis because practically no nonaromatic liquids were formed.

4-Vinylcyclohexene. 4-Vinylcyclohexene (250 grams) was aromatized as above, at 550° C. and 4.0-second contact time to yield 23.7 liters of gas at S. T. P. and 2.18 grams of liquid. Composition of the gas in volume per cent is:

H_2, 23.3 CH_4, 18.1 C_2H_4, 7.4 C_2H_6, 5.5 C_3H_6, 5.5
C_3H_8, 1.2 C_4H_6, 27.0 C_4H_8, 6.5 C_4H_{10}, 5.5.

The analysis of the liquid was limited to chromatography over silica gel (Figure 6).

RESULTS AND DISCUSSION

Experiments at 550° C. At 550° C. aromatization is incomplete and intermediates can be isolated (Table IV and Figures 3 and 4)

At 550° C. the conversion of butadiene proceeds rapidly. The conversion varies from 40% at 1.2 seconds to practically 100% at 15.9 seconds. At short contact times the product is mainly liquid, but as the conversion increases, larger quantities of gases and carbon are formed. However, even at the longest contact times the liquid constitutes about 60% of the reaction products.

The proportion of aromatics in the liquid product rises with increasing contact time from 20% at 1.2 seconds to 61% at 15.9 seconds. Benzene, toluene, the xylenes, and styrene constitute the major part (90 to 100%) of the aromatics, and the C_8 compounds are predominant at all contact times used (Table IV and Figure 4). The nonaromatics consist mainly of a complex mixture of C_8 cyclic

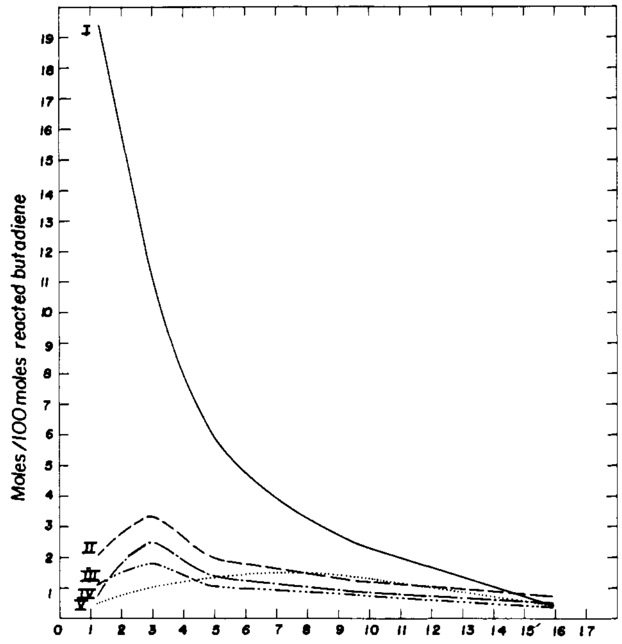


Figure 3. Formation of different cyclic dimers from butadiene at 550° C. as a function of contact time.

I 4-Vinylcyclohexene
II Dimethylcyclohexadienes and methylmethylenecyclohexenes
III Ethylcyclohexadienes
IV 1-Vinylcyclohexene
V Ethylidenecyclohexene

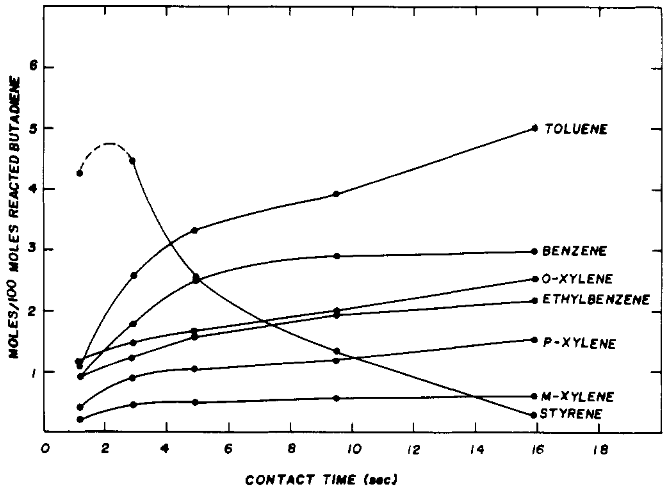


Figure 4. Formation of C_6 to C_8 aromatics from butadiene at 550° C., as function of contact time

Table IV. Products of Butadiene Formed at 550° C.

	Run No. 1	2	3	4	5
Contact time, sec.	1.2	2.9	4.9	9.5	15.9
Butadiene, reacting %	39.3	68.3	79.6	88.6	97.4
Conversion of reacted butadiene, mole %					
Liquid	92.1	88.9	77.2	70.6	57.7
Gas	7.5	9.1	19.1	20.6	25.7
Carbon[a]	0.4	2.0	3.7	8.8	16.6
	Moles per 100 Moles Reacted Butadiene[b]				
Gaseous products[c]					
H_2	4.2	5.3	4.8	5.0	6.4
CH_4	1.0	2.6	3.6	4.9	10.6
C_2H_4	1.7	3.6	4.8	4.9	3.0
C_2H_6	0.8	0.9	1.9	3.3	4.7
C_3H_6	0.9	2.0	3.0	5.9	3.1
C_3H_8	0.0	0.0	0.7	2.5	3.2
C_4H_8	3.7	6.1	9.9	5.8	5.3
C_4H_{10}	0.0	0.0	1.1	3.4	7.0
Liquid products					
Cyclohexene	0.1	<0.1	<0.1	<0.1	<0.1
Methylcyclohexenes	0.48	1.09	1.51	0.76	0.52
o-Dimethylcyclohexenes	0.21	0.37	0.46	0.41	0.36
m-Dimethylcyclohexenes	0.11	0.17	0.16	0.16	0.13
p-Dimethylcyclohexenes	0.02	0.12	0.13	0.13	0.10
C_9 alkylcyclohexenes[d]	0.0	0.29	0.55	0.35	0.30
C_{10} alkylcyclohexenes[d]	0.0	0.26	0.35	0.33	0.48
Cyclohexadienes	0.2	0.3	0.6	0.5	0.3
Methylcyclohexadienes	0.2	0.3	1.1	0.9	0.5
Ethylcyclohexadienes	1.1	1.8	1.1	0.8	0.4
1-Vinylcyclohexene	0.7	2.5	1.4	0.9	0.5
4-Vinylcyclohexene	19.4	11.4	6.0	2.5	0.4
4-Ethylidenecyclohexene	0.5	1.0	1.1	1.3	0.5
Dimethylcyclohexadienes					
o-Isomers	1.1	1.8	1.1	0.8	0.4
m-Isomers	0.26	0.55	0.34	0.12	0.09
p-Isomers	0.7	1.0	0.57	0.32	0.25
C_9 alkylcyclohexadienes[e]	0.0	0.1	0.8	0.6	0.5
C_{10} alkylcyclohexadienes[e]	0.0	0.0	0.4	0.2	0.1
Benzene	0.92	1.79	2.52	2.88	2.96
Toluene	1.10	2.58	3.32	3.91	5.03
Ethylbenzene	0.91	1.24	1.62	1.97	2.18
Styrene	4.28	4.47	2.52	1.36	0.29
o-Xylene	1.15	1.48	1.67	2.01	2.55
m-Xylene	0.21	0.46	0.50	0.57	0.61
p-Xylene	0.42	0.90	1.05	1.20	1.54
C_9 alkylbenzenes	0.1	0.50	0.44	0.58	1.07
C_{10} alkylbenzenes	0.1	0.52	0.73	0.99	0.80
Polycyclics[f]	0.0	<0.1	0.16	0.45	1.98
Pentenes	<0.1	<0.1	0.1	0.6	1.6
Hexenes	< 0.1	<0.1	<0.1	<0.1	0.1
Octenes	0.3	<0.1	<0.1	<0.1	<0.1
Pentadienes	< 0.1	0.28	<0.1	<0.1	<0.1
Hexadienes[g]	0.68	0.75	1.03	0.2	0.06
Undetermined[f, h]	25.5	17.0	9.8	12.6	5.3

[a] Calculated by difference.
[b] < 0.1%, component identified; 0.0%, not detected.
[c] No acetylene detected.
[d] Probably contains some alkenylcyclohexanes also.
[e] Contains alkylidenecyclohexenes also.
[f] Expressed as number of moles of butadiene converted into product.
[g] Presence of heptenes and heptadienes not definitely established.
[h] Cyclic unsaturated material composed of green colored substance, distillation residues, and unidentified distillates.

diolefins isomeric with 4-vinylcyclohexene, the expected normal cyclic dimer of butadiene. A certain amount of other olefins is also present.

Examination of the main reaction products *vs.* time indicates relatively simple principle phases of the evolution of butadiene in spite of the complexity of the experimental material. 4-Vinylcyclohexene is the main product at a very short contact time (Figure 3), as found by others (*25*). As contact time increases, the concentration of this compound decreases, while that of its isomers rises in a manner typical for secondary reactions, and at the same time aromatics begin to appear (Figures 3 and 4). The isomers of 4-vinylcyclohexene are also unstable, and after about 3 seconds of contact time, all cyclic diolefins begin to decrease and slope towards zero, while the concentration of the aromatics continues to increase. That aromatics seem to form through the intermediate of the C_8 cyclic diolefins can be tested quantitatively by drawing a weight balance around a certain section of the reaction period. In the interval between 1.2 and 2.9 seconds where side reaction is small, the amount of C_8 cyclic diolefins disappearing (4.2 moles) corresponds closely to the sum of C_6, C_7, and C_8 aromatics formed (4.2 moles). The nature of the intermediate reaction steps of aromatization was formulated essentially on the basis of the various cyclic diolefins found.

Experiments at 700° C. Conversion of butadiene was further studied at the temperature of commercial aromatization processes, such as that of Weizmann, Bergmann, Steiner, and others. Under these conditions aromatization was practically complete even at a contact time of 2.7

Table V. Products of Butadiene, Formed at 700° C.

	Run no. 1	2	3
Contact time, sec.	2.7	7.5	15.2
Butadiene reacting, %	97.3	100.0	100.0
Conversion of reacted butadiene, mole %			
Liquid	64.9	63.6	59.5
Gas	24.6	25.6	26.3
Carbon[a]	10.5	10.8	14.2
Gaseous products[b]	Moles per 100 Moles Reacted Butadiene		
H_2	14.9	15.5	15.6
CH_4	29.1	33.5	40.5
C_2H_4	12.0	11.7	11.5
C_2H_6	2.6	5.1	5.4
C_3H_6	5.0	7.1	5.2
C_3H_8	2.4	1.1	0.16
C_4H_8	1.6	0.0	0.0
C_4H_{10}	0.26	0.0	0.0
Liquid products[c]			
Benzene	11.71	11.76	12.02
Toluene	7.22	8.26	7.95
Ethylbenzene	1.31	0.89	0.61
Styrene	2.81	2.25	1.91
o-Xylene	0.56	0.54	0.52
m-Xylene	0.50	0.49	0.46
p-Xylene	0.53	0.53	0.50
C_9 alkylbenzenes	0.58	1.03	0.71
C_{10} alkylbenzenes	0.19	0.53	0.45
Polycyclic aromatics[d]	14.85	14.75	14.35
Undetermined[d, e]	7.8	4.8	3.35

[a] Calculated by difference.
[b] No acetylene detected.
[c] Contains only small amounts of cyclo-olefins.
[d] Expressed as number of moles of butadiene converted into product.
[e] Unsaturated material boiling mainly below 80° C.

seconds (Table V). Composition of the aromatics differs from that at low temperature in that the C_8 compounds are no longer predominant (only 15 to 23%). Benzene and toluene are the main components, and about 25% of polycyclic aromatics are also formed. Contact time has relatively little influence on the proportions of the individual aromatics with the notable exception of ethylbenzene and styrene, which decrease in quantity as the duration of contact increases.

Mechanism of Aromatization. Formation of C_8 Aromatics. The presence of 4-ethylidenecyclohexene, 1-vinylcyclohexene, and ethylcyclohexadienes (Table IV) demonstrates mobility of the double bonds. Unsaturation can shift both away from the chain towards the ring and in the opposite direction (1-vinylcyclohexene). This is, however, a matter of secondary importance, because the cyclohexadiene structure, which is most favorable for aromatization, should be produced easily by a further resuffling of the double bonds.

On the other hand, the presence of dimethylcyclohexadienes and methylmethylenecyclohexenes (Table IV) shows carbon skeleton isomerization. The change in the skeleton must occur before aromatization, because xylenes, for instance, did not isomerize in these experiments (Table IV and Figure 4). The proportions of xylene isomers do not change as contact time is increased, though equilibrium is far from being reached (Table V). Other authors (*6*) have reported that up to 700° C. xylenes do not isomerize in thermal conditions, and even between 700° and 770° C. only partial isomerization takes place.

The various isomers of 4-vinylcyclohexene present, and the occurence of double bond and skeleton rearrangements, followed by dehydrogenation, indicate a possible scheme for the formation of the various C_8 aromatics as shown in Figure 5.

An important feature, which distinguishes the proposed scheme from the original Hague and Wheeler hypothesis, is that the cyclohexene derivative, formed in the first step, evolves into cyclohexadienes by migration of an exocyclic double bond, already present in the molecule, and not by dehydrogenation.

Thermal dehydrogenation of cyclohexenes to the corresponding aromatics has not been reported in the literature; instead, a retro-Diels-Alder decomposition predominates (*16*). Even on cracking catalysts, on which hydrogen transfer occurs, cyclohexene yields only 7% of benzene (*33*). The dehydrogenation of cyclohexadienes on the other hand should be easy, because both hydrogens to be removed are allylic, and a retro-Diels-Alder reaction is not possible. Also, the free energies of the stepwise dehydrogenation of cyclohexene (*12*) show that the introduction of the third double bond should be far easier, thermodynamically, than that of the second, because it proceeds with the gain of almost all the resonance energy of the aromatic ring. Studies on the thermal dehydrogenation of pure cyclohexadienes are, however, lacking.

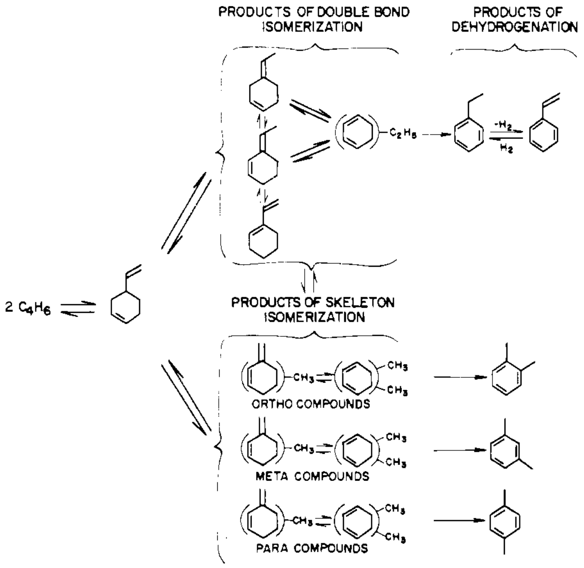


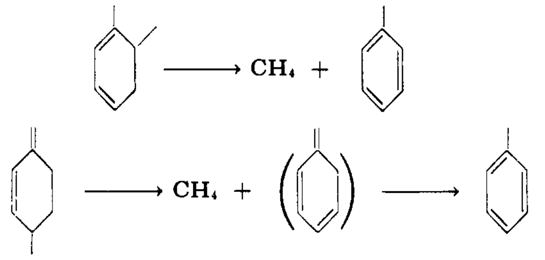
Figure 5. Scheme of formation of C_8 aromatics from butadiene via 4-vinylcyclohexene

Also the skeleton rearrangement explains the formation of the xylenes from butadiene without the need for butenes as reaction partners. At 550° C. *o*- and *p*- predominate over *m*-xylene (about 50 and 30%, respectively, Table IV). Because the meta derivative is the most stable, this result must be due to the mechanism of the skeleton rearrangement of 4-vinylcyclohexene. If, for instance, a biallylic radical mechanism (*21*) is assumed, the rearrangement should produce only ortho and para isomers.

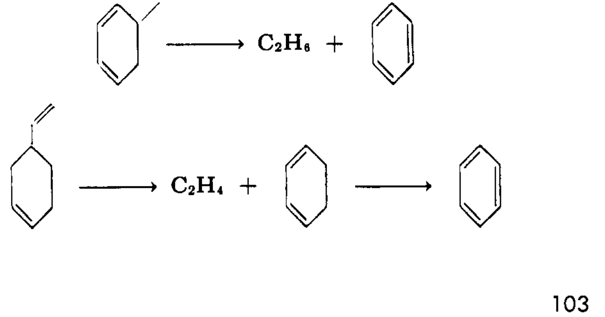
The amount of styrene, the only aromatic affected by the presence of the stainless steel packing, is different from that of a run in an empty tube (Table I). Apparently the packing causes some dehydrogenation of the 4-vinylcyclohexene, possibly by a hydrogen transfer reaction. The decrease of the concentration of styrene above 2.9 seconds contact time (Figure 4) is ascribed to the onset of carbonization of this reactive compound. In fact, the amount of styrene which disappeared between 2.9 and 9.5 seconds (3.2 mole per 100 moles of C_4H_6, equivalent to 25.6 gram atoms of carbon), corresponds closely to the carbon formed in the same interval (27.6 gram atoms).

Formation of C_6 and C_7 Compounds. That C_6 and C_7 compounds should form essentially through the intermediate of C_8 cyclic diolefins implies that reactions occur where either one or two carbon atoms are split off.

When toluene is formed by this route, an equimolecular amount of methane must be formed, as at 550° C. and short contact times. Above 5 seconds, however, the quantity of methane present is larger than expected, because of side reactions. Various proposals can be made about the details of the mechanism—for example, if a methane molecule is split off, the following reaction can be written on the basis of the compounds found:



Similarly, in the formation of benzene, two carbon atoms are split off, and the sum of C_2 hydrocarbons present in the products is always at least equivalent to the amount of benzene (Tables IV and V). The following reactions could occur:



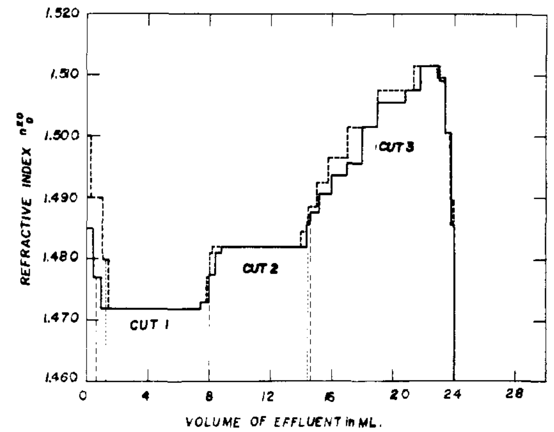


Figure 6. Chromatography shows close similarity of liquid product formed from 4-vinylcyclohexene and from butadiene

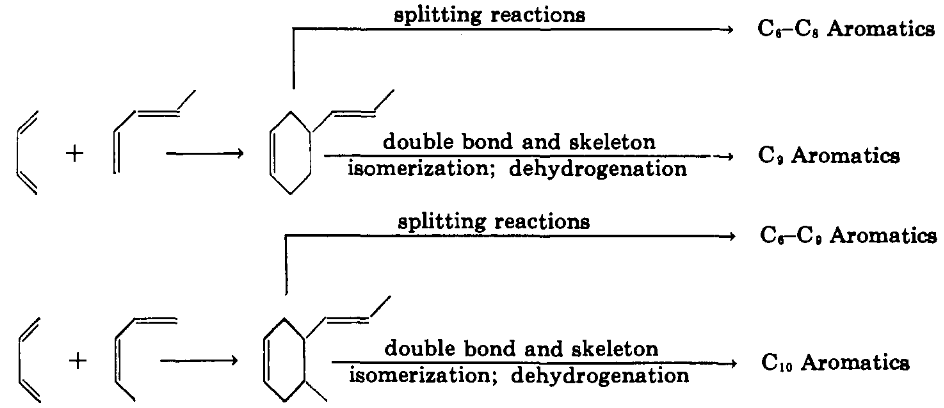
— Product from 4-vinylcyclohexene at 550° C., contact 4 sec.

--- Product from butadiene at 550° C., contact 4.9 sec.

At 700° C., the importance of the splitting reactions increases, and benzene and toluene become the main products.

Pines and Ryer (*21*) also observed carbon-carbon splitting reactions in the thermal decomposition, over copper pellets at 450° C., of limonene, a homolog of 4-vinylcyclohexene, and proposed a mechanism involving rearrangement to *gem*-dialkyl-subsituted cyclohexadienes and subsequent splitting off of one *gem*-alkyl group to form the aromatic ring. By analogy, 4-vinylcyclohexene could rearrange into a *gem*-dimethyl-1,3-cyclohexadiene and then form toluene. The postulated intermediate, however, has not been observed, perhaps because in these experiments, it reacts too rapidly to reach appreciable concentrations.

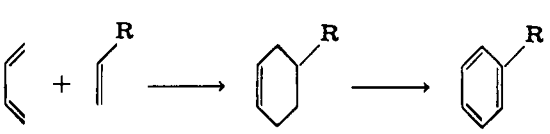
Formation of C_9 and C_{10} Alkylbenzenes. The small amounts of C_9 and C_{10} alkylbenzenes in the product could be derived from higher homologs of 4-vinylcyclohexene. This view is supported by the presence of conjugated pentadienes and hexadienes, and of C_9 and C_{10} cyclodiolefins (Table IV), as well as by the results of aromatization of 1, 3-pentadiene, reported by Shuikin and coworkers (*28*). The excess of butadiene would cause the C_5 and C_6 dienes to interact with butadiene rather than to dimerize:



Aromatization of 4-Vinylcyclohexene. To test the proposed mechanism of aromatization of butadiene, the thermal behavior of 4-vinylcyclohexene was studied (550° C., contact time, 4.0 seconds). Only the distribution of the various classes of compounds in the liquid was determined. For the same content of aromatics in the product, there is full agreement with the results for butadiene (Figure 6). As expected, also, the yield of aromatics (34% on the charge) is higher than for butadiene in comparable conditions.

Because 4-vinylcyclohexene can decompose to butadiene at 550° C., it could be argued that its aromatization occured through butadiene by an alternative mechanism, and therefore, this experiment is inconclusive. However, the rate of depolymerization is not very high, as compared with aromatization, and it has been estimated, on the basis of previous depolymerization data (*4*) and the observed aromatization yields, that only 6% of aromatics could have been formed via butadiene. Further work is required to establish the detailed composition of the products.

Side Reactions. Cyclomono-olefins and Gaseous Olefins Although cyclohexenes are not reported to undergo direct dehydrogenation in thermal conditions, their presence together with gaseous olefins in the product requires that the Hague and Wheeler mechanism be considered:



Accordingly, if quantitative conversion of cyclohexenes to aromatics is assumed, and the rate constants for the reaction of butadiene with ethylene (*25*) and with propene [$k \sim 1000$ mole^{-1} cc. sec.$^{-1}$ (*26*)] is used, it was calculated that at 550° C. and the longest contact time used, a maximum of 7% of the benzene and 4% of the toluene could have originated in this way. The estimated contribution is small, because of the weak dienophilic character of the mono-olefins.

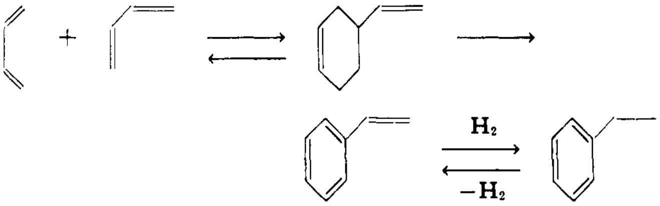
This estimation also shows that the methylcyclohexenes, for instance, should have originated largely by reactions other than Diels-Alder additions, possibly hydrogen transfer reactions. Other components such as butene and butane might also have formed by the latter type of reaction.

A comparison of the products of a butadiene and propene mixture (*26*), and those of pure butadiene shows that in spite of the increased quantity of methylcyclohexenes, the amount of toluene is practically unaffected by the presence of propene. Thus, methycyclohexenes do not undergo appreciable dehydrogenation at the contact time used (3 seconds). However, this might be due to the slowness of the reaction. Further experiments on these lines are in progress.

Green Liquid. On chromatography of the products formed at 550° C., 1 to 5% of a forerun of unknown composition was separated (Figure 1). This fraction had a high refractive index and a green coloration which increased in intensity with contact time. Similar observations had been reported by Moor and coworkers (*19*). The chromatographic behavior and the position of the absorption band (5200 A.) exclude the presence of azulene. The color disappeared on catalytic hydrogenation.

CONCLUSIONS

The scheme outlined for aromatizing butadiene, based on the isolated intermediates, differs from that of Hague and Wheeler, according to whom only ethylbenzene and styrene are expected to form from butadiene:



However, carbon skeleton isomerization and carbon-carbon splitting also occur, which form different C_6 to C_8 aromatics. Therefore, the presence of olefins is not necessary to form these compounds from butadiene, as assumed originally.

On the other hand, the reaction scheme proposed here does not involve dehydrogenation to convert a cyclohexene to a cyclohexadiene to form any of the aromatics considered. Instead, the second double bond required for the progressive evolution of the cyclohexene to the aromatic structure is already present in the molecule of the intermediate compounds and only needs to be shifted into the ring by migration. The problem of the thermal dehydrogenation of the cyclohexenes to aromatics, which is one of the main difficulties of the Hague and Wheeler hypothesis, is thus, not raised.

Preliminary results with 4-vinylcyclohexene subjected to the same conditions as butadiene are in accord with the reaction mechanism proposed. By generalizing these results and using literature data, it is believed that in thermal aromatization of hydrocarbon oils, under conditions similar to those used in these experiments, butadiene and its higher homologs formed in the course of cracking, should yield a whole range of aromatics by the same scheme. The extent of aromatization, based on conjugated dienes, is of course limited to the amounts of these compounds present in the breakdown products. Depending on the starting materials and the conditions, additional mechanisms could also be operative.

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