

## Thermal Isomerization of Butene1 to Butene2

W. Walter McCarthy and John Turkevich

Citation: *The Journal of Chemical Physics* **12**, 461 (1944); doi: 10.1063/1.1723892

View online: <http://dx.doi.org/10.1063/1.1723892>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/12/11?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Photochemistry of Aromatic Olefins. I. Photochemical cis–trans Isomerization of 1Phenyl2butene](#)

*J. Chem. Phys.* **52**, 3277 (1970); 10.1063/1.1673470

[Energy Transfer by Benzene in the CadmiumPhotosensitized Isomerization of Butene2](#)

*J. Chem. Phys.* **50**, 1294 (1969); 10.1063/1.1671190

[Catalytic Isomerization of Butene–1 to Butene–2](#)

*J. Chem. Phys.* **16**, 466 (1948); 10.1063/1.1746919

[The Mercury Photosensitized Reactions of 1Butene and 2Butene](#)

*J. Chem. Phys.* **14**, 581 (1946); 10.1063/1.1724068

[Butene1 and Butene2 Equilibrium](#)

*J. Chem. Phys.* **12**, 405 (1944); 10.1063/1.1723882

---



$\delta$  (C—H) bending frequencies

$$A_g = 1276, 1303, 1437, \\ B_u = 1285, 1385, 1470.$$

$\nu$  (C—H) stretching frequencies

$$A_g = 3000, 3088, 3000, \\ B_u = 3000 (3).$$

$$\text{C—C torsional} = 120.$$

The calculation was modified by assuming the existence of two forms of butadiene—*cis* and *trans*. Taking  $\Delta S = 0$ ,  $\Delta H = \Delta F = 1500$  cal./mole, equilibrium constants for the conversion of *cis* to *trans* and thence correction terms to the molal heat capacities for the fraction converted per degree temperature rise were calculated by standard equations.

The experimental and calculated values are compared in Table V. In this table, column 1 gives the temperature; column 2 gives the value of  $C_p^0$  obtained by plotting the squares of the velocities and calculating  $C_v^0$  by use of these limiting velocity squares, while column 3 gives the value obtained by plotting the values of  $C_v$  (calculated by the use of the equation of state previously discussed) and extrapolating to zero pressure. Column 4 gives the value of  $C_p^0$  obtained by averaging the  $C_v^0$  values listed in

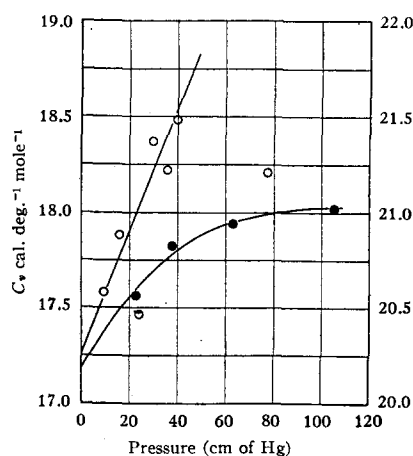


FIG. 2. The heat capacity of butadiene-1,3. ● and left scale— $t = 25.82^\circ\text{C}$ . ○ and right scale— $t = 90.13^\circ\text{C}$ .

Tables III and IV, while column 5 gives  $C_p^0$  calculated from spectroscopic data. Evidently the agreement leaves much to be desired, and indicates that the frequency assignment and/or the molecular model are not entirely correct.

#### ACKNOWLEDGMENT

We wish to thank Professor W. H. Pilemeyer for making available the facilities of his ultrasonics laboratory and for many helpful suggestions in the early part of the work.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 12, NUMBER 11 NOVEMBER, 1944

### Thermal Isomerization of Butene-1 to Butene-2

W. WALTER MCCARTHY AND JOHN TURKEVICH

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

(Received September 7, 1944)

The thermal isomerization of butene-1 was investigated in the temperature range of 450–550°C using infra-red absorption as a method of analysis. The vibrational spectra of butene-1, butene-2, and isobutene are reported.

MOST of the work on the thermal treatment of the butenes was primarily concerned with their decomposition products,<sup>1</sup> polymerization products,<sup>2</sup> or butadiene synthesis.<sup>3</sup> However,

<sup>1</sup> G. Egloff, *Reactions of Pure Hydrocarbons*, Am. Chem. Soc. Monograph Series (Reinhold Publishing Corporation, New York, 1937), pp. 333–4.

<sup>2</sup> Wheeler and Wood, *J. Chem. Soc.* **1930**, p. 1819.

<sup>3</sup> Federov, Smirnova, and Semenov, *J. App. Chem.* (U.S.S.R.) **7**, 1166 (1935).

Runge and Mueller-Conradi<sup>4</sup> passed butene-1 through an empty quartz tube at 550°C to produce 87 percent of butene-2, no isobutylene, and very little liquid polymer. Hurd and Goldsky<sup>5</sup> studied the pyrolysis of butene-1 and butene-2 in the temperature range of 500–700°C and contact times of 9–13 seconds. No shift of

<sup>4</sup> U. S. Patent 1,914,674, June 20, 1933.

<sup>5</sup> *J. Am. Chem. Soc.* **56**, 1812–15 (1934).

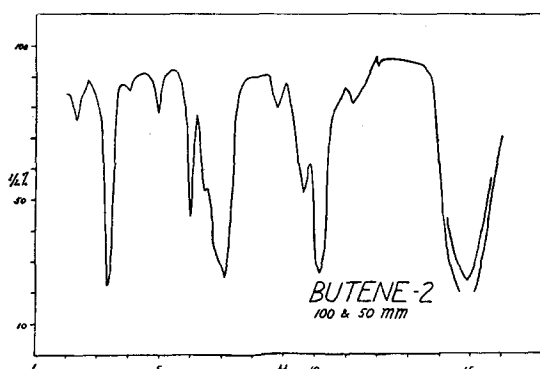
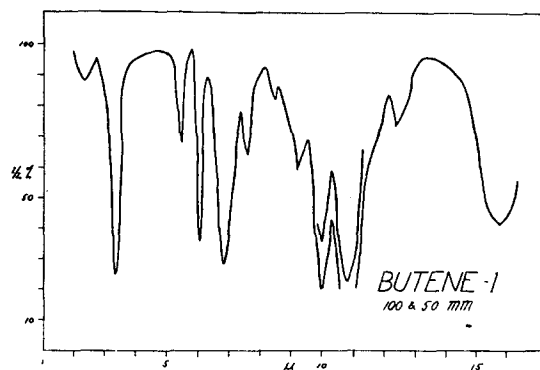


FIG. 1a.

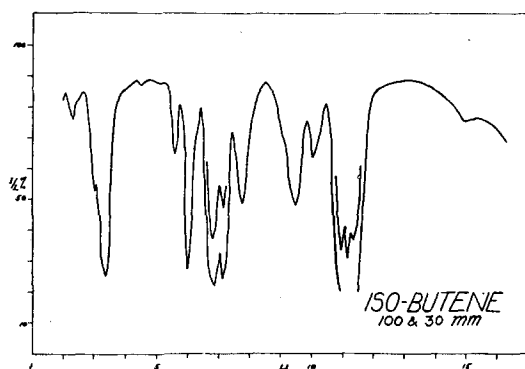


FIG. 1b.

the double bond was observed at the lower temperature. Only at 650°C was there a shift of the double bond and this was accompanied by extensive decomposition. At 700°C the decomposition was so great that the isomerization was reduced to several percent. Finally Krause, Nemtsov, and Soskina<sup>6</sup> reported a small amount of butene-1 in the products of polymerization of butene-2.

<sup>6</sup> Krause, Nemtsov, and Soskina, *J. Gen. Chem. (U.S.S.R.)*, pp. 343-55 (1935).

A primary difficulty in the previous studies of the migration of the double bond is the difficulty of analysis for butene-1 and 2. The use of infrared absorption, however, makes this analysis very simple. It was, therefore, thought worth while to make a study of the thermal isomerization of butene-1 to butene-2.

#### MATERIALS AND APPARATUS

Tank butene-1 was obtained from the Matheson Company, East Rutherford, New Jersey. It was purified by drying over sodium hydroxide asbestos. Vapor pressure measurements by Dr. R. K. Smith indicated that it was pure butene-1.

The static system consisted of a reaction chamber of Pyrex glass of 200-cc capacity, a mercury manometer, a gas burette, and an all-glass sampling system. After evacuation of the system a volume of butene-1 was measured in the gas burette and then transferred to the reaction chamber. Changes in pressure during the course of the run were used to indicate either polymerization or cracking. After a suitable length of time, the sample was drawn off and condensed in a liquid air trap in preparation for analysis.

The flow system consisted of a reactor which was either a Pyrex tube of 8-mm I.D. with a 20-cm heated length, the same tube packed with Fenske glass spirals ( $\frac{3}{16}$ "), or an iron tube of 9-mm I.D. with a 20-cm heated length; flow meters before and after the reactor, a gas drying and a gas sampling system. Temperatures were measured by a Chromel-Alumel thermocouple. The iron pipe was joined to the Pyrex tubing by Picein wax joints. The latter were water-cooled to prevent melting. Contact time was calculated from  $t = DV_1T_2/V_2T_1$ , where  $D$  is the time in which volume  $V_2$  of gas measured at room temperature  $T_2$  flows through the reaction tube of volume  $V_1$  at temperature  $T_1$ .<sup>7</sup>

#### ANALYSIS

The infra-red spectrum of the three butenes is given in Fig. 1 and Table I. The spectrum was studied from 2-16  $\mu$  in a cell 20 cm long and at a pressure of 100 mm. The 5.45- $\mu$  band of butene-1 was used as a measure of the amount of

<sup>7</sup> K. Jellinek, *Lehrbuch der physikalischen Chemie* (Ferdinand Enke, Stuttgart, 1937), Vol. 5, p. 83.

TABLE I.

Butene-1			Butene-2			Isobutene		
	cm <sup>-1</sup>	Intensity of absorption		cm <sup>-1</sup>	Intensity of absorption		cm <sup>-1</sup>	Intensity of absorption
2.31	4329	15	2.30	4348	25	2.31	4329	25
3.35	2985	75	3.33	3030	75	3.01	3322	
5.46	1832	35	4.03	2481	10	3.37	2967	75
6.08	1645	65	4.99	2004	20	4.48	2232	10
6.82	1466	70	6.03	1658	30	5.59	1789	35
7.59	1318	40	6.45	1550		6.01	1664	75
8.53	1172	20	6.88	1453		6.80	1471	85
9.20	1087	40	7.08	1412	75	7.17	1395	85
9.98	1010	90	8.81	1135	20	7.73	1294	50
10.85	922	100	9.64	1037	45	9.48	1055	55
12.43	805	25	10.15	985	75	10.01	999	35
15.80	633	40	11.25	889	20	10.96	912	95
			12.10	826	10	11.15	897	95
			14.93	670	100	11.34	882	95
						14.84	674	10

butene-1 present. Mixtures of known composition of the two butenes were made up and a working curve obtained by plotting butene-1 against the absorption. The infra-red rocksalt spectrometer employed in this investigation was that described by Barnes, Brattain, and Seitz.<sup>8</sup>

### RESULTS

The results obtained are presented in Table II. The run, B-18, at 450°C was carried out in a static system at one atmosphere pressure. During the first half-hour the pressure decreased slightly followed by a subsequent increase of up to 818 mm at the end of the two-hour run. There was substantial decomposition as shown by the brown liquid collecting at the outlet tube. An attempt to obtain runs with the static system at 550°C resulted in such extensive decomposition that an adequate sample could not be obtained for analysis.

In the flow system, isomerization was obtained with the iron tube and with that, only when it was clean. A value of 22.5 percent conversion was

TABLE II.

Run	Tube	Contact time	T°C	Percent conversion to butene-1
B-18	Pyrex	2.0 hours	450	60-70
B-32	Pyrex empty	3.2 sec.	560	none
B-33	Pyrex packed	4.6 sec.	545	none
B-34	Pyrex packed	10.0 sec.	550	none
B-35	iron	8.7	550	22.5
B-36	iron	7.4	550	4.0
B-38	iron	14.0	550	none

obtained with the clean tube. Subsequent runs with the same tube gave increasingly lower conversion values. A small amount of carbonaceous material was scrapped from the interior of the iron tube after these runs. Otherwise, there were no other indications of decomposition.

These results indicate that there is no thermal isomerization of butene-1 up to 550°C unless there be some concomitant decomposition.

We wish to express our thanks to Professor H. D. Smyth and L. G. Smith for the courtesies of the Palmer Physical Laboratory, to the M. W. Kellogg Company for financial sponsorship of this investigation, and to Professor Hugh S. Taylor for his inspiring interest.

<sup>8</sup> Barnes, Brattain, and Seitz, *Phys. Rev.* **48**, 582 (1935).