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Butene-1 and Butene-2 Equilibrium

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The equilibrium between butene-1 and butene-2 was attained on activated alumina at 400 and 450°C. The values obtained were found to agree with calculated results.

ISOMERIZATION of butenes has been studied using a variety of catalysts such as phosphoric acid, perchloric acid, $C_6H_5SO_3H$, and zinc chloride solutions.¹ Others have used floridin, aluminum sulfate, phosphoric acid on charcoal, and various clays² resulting in isobutene production from *n*-butenes.

Some controversy has arisen as to the products of this isomerization and in the related subject of dehydration of *n*-butanol employing activated alumina as the catalyst. Fourneau and Puyal³ using infusorial earths and clays obtained practically 100 percent butene-2 on dehydrating *n*-butanol. Davis⁴ dehydrated the straight chain alcohol over alumina in the temperature range 340–360°C to get 35 percent butene-2 and 65 percent butene-1. His method of analysis involved relative rates of bromination of the two

pressure to minimize the possible thermal isomerization of the brom derivatives. These brom butenes were then reacted with KI to regenerate the butene and iodine. Since the second-order reaction rates of the three normal brom butenes (-1, -2 *cis* and *trans*) differ, a method of analysis was possible, in combination with physical measurements such as refractive indexes and densities. This tedious method was then applied in a study of the dehydration of butanols over various catalysts including alumina.⁶ In a temperature range 335–370°C they obtained from butanol-1, 27 percent butene-2 (*cis* and *trans*) and from butanol-2, 79 percent butene-2. The yields of butene-2 from butanol-1 were much lower than those obtained with acidic catalysts such as sulfuric acid or P_2O_5 . Pines⁷ dehydrated butanol over "Alorco" activated alumina at 375–425°C to form essentially butene-1. Fractional distillation in a Podbielniak precision apparatus was employed in analysis. Pines points out that the fractional distillation of dibrom derivatives can result in isomerization thus rendering such a method questionable. Ipatieff¹ and co-workers and Le Pingle⁸ substantiate these results. Not a single case of production of isobutene in these isomerization and dehydration studies using alumina catalysts was reported.

Matignan, Moreau, and Dode⁹ explained the variance in results as due to trace acidic constituents such as sulfate ion in the catalyst. Alumina prepared from sulfate free aluminum hydroxide gave butene-1 on dehydration of the *n*-alcohol, whereas introduction of a small amount of sulfate or nitrate resulted in high yields of butene-2. Their method of analysis

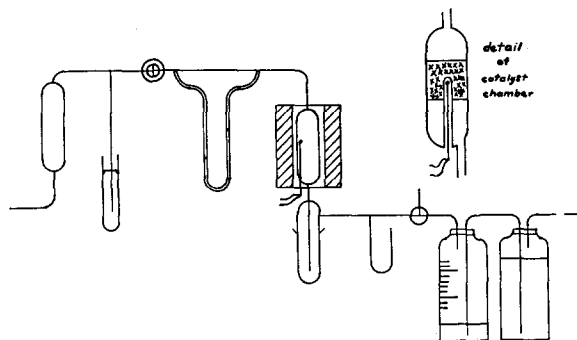


FIG. 1. Gas flow system.

isomers. Lucas, Dillon, and Young⁵ developed a method of analyzing mixtures of the brom butenes by fractional distillation under reduced

¹ Ipatieff, Pines, and Schaad, *J. Am. Chem. Soc.* **56**, 2696 (1934).

² Frost, Rudkovskij, and Serebrajakova, *Comptes rendus (Doklady) Acad. Sci. U.S.S.R.*, [13] **4**, 373 (1936).

³ E. Fourneau and J. Puyal, *Bull. Soc. Chim.* **31**, 424 (1922).

⁴ Davis, *J. Am. Chem. Soc.* **50**, 2769 (1928).

⁵ H. J. Lucas, R. T. Dillon, and W. G. Young, *J. Am. Chem. Soc.* **52**, 1949–52; 1953–64 (1930).

⁶ W. G. Young and H. J. Lucas, *J. Am. Chem. Soc.* **52**, 1964 (1930).

⁷ H. Pines, *J. Am. Chem. Soc.* **55**, 3892 (1933).

⁸ M. Le Pingle, *Bull. Soc. Chim.* **39**, 741 (1926).

⁹ Matignan, Moreau, and Dode, *Bull. Soc. Chim.* [5] **2**, 1169–81; 1181–88 (1935).

involved a study of distillation curves characteristic of mixtures of the dibrom derivatives. For quantitative results preparation of the diacetates and glycol derivatives was necessary with subsequent oxidation to diacetyl, treatment with hydroxylamine to form dimethyl glyoxime, and precipitation as the nickel complex.

In the present work a study of the isomerization of butene-1 to butene-2 and vice versa was conducted at 400 and 450°C over a range of contact times 2–65 seconds. Infra-red absorption spectrum measurements were employed as the method of analysis. Activated alumina was used in this study to remove the complicating factor of possible isomerization to isobutene. In the temperature range 400–450°C equilibrium could be approached from both sides in quite short contact times.

MATERIALS

Tank butene-1 and butene-2 were obtained from the Matheson Company, East Rutherford, New Jersey. They were used without further purification other than drying. Vapor pressure measurements indicated pure butene-1, and a butene-2 consisting of a 70 percent *cis*, 30 percent *trans* mixture. Ten cc of "Alorco" activated alumina (Grade A, 8–14 mesh) was heated slowly in a stream of air to 450°C and was then ready for use.

APPARATUS

All experiments were performed in a simple flow system (see Fig. 1). The gases were fed from the tank and dried by passing through a calcium chloride tube. A Ventille valve served as flow regulator. Rates of flow were read from a calibrated flowmeter. The catalytic chamber was encased in an electrically heated furnace. The chamber's construction permitted preheating of the gases followed by contact with the 10-cc catalyst. A Chromel-Alumel thermocouple embedded in the catalytic mass recorded the temperature by a direct reading pyrometer. Product gases were collected in a calibrated one-liter gas bottle. The entire run product was then transferred to an apparatus which enabled small samples to be cooled to liquid air temperature, residual gases pumped off, and transferred to sample tubes ready for analysis. The catalyst

was flushed with nitrogen and air passed through the mass at 450°C after each run.

ANALYSIS

The intensity of the 5.45- μ band of butene-1 was used as the basis of analysis. The details will be given in a later work.¹⁰ Butene-2 was found to contain no such band. No attempt was made to analyze for *cis*- and *trans*-butene-2. Mixtures of the two olefins of known composition were measured at this wave-length and a calibration curve was obtained, plotting I/I_0 values against percent butene-1. The result of one run was checked by vapor pressure measurements and was found to agree with this method extremely well.

RESULTS

At 450°C the results were as shown in Table I.

The accompanying diagram (Fig. 2) summarizing these results shows graphically the approach to equilibrium from both sides at the two temperatures considered. With long contact

TABLE I.

Run No.	Percent butenes -1 -2		Contact time, sec.	Vol. of run, cc	Butene used
B-39	39.0	61.0	7.1	1000	1
-40	39.0	61.0	7.2	600	1
-41	35.0	65.0	10.9	600	1
-42	50.5	49.5	2.1	800	1
-45	23.5	76.5	7.8	700	2
-46	18.0	82.0	1.9	650	2
-47	23.5	76.5	11.8	725	2
-48	21.0	79.0	43.5	625	2
-49	27.5	72.5	28.8	700	1
-55	22.5	77.5	18.4	875	2
-56	27.5	72.5	18.0	950	1
-58	25.5	74.5	65.0 (d)*	900	1
-60	25.0	75.0	46.3 (d)	975	2
-62	24.0	76.0	2.2	800	2
The results at 400°C:					
B-43	90.0	10.0	2.1	800	1
-44	34.5	65.5	12.3	700	1
-50	48.5	51.5	7.6	700	1
-51	20.5	79.5	14.8	725	2
-52	13.0	87.0	5.6	725	2
-53	—	—	53.5 (d)	700	2
-54	20.5	79.5	18.0	725	2
-57	30.0	70.0	21.4	900	1
-59	26.0	74.0	64.6 (d)	1000	1
-61	21.5	78.5	41.5	925	2

* (d) indicates some decomposition.

¹⁰ W. Walter McCarthy and J. Turkevich, J. Chem. Phys. 12 (1944), in press.

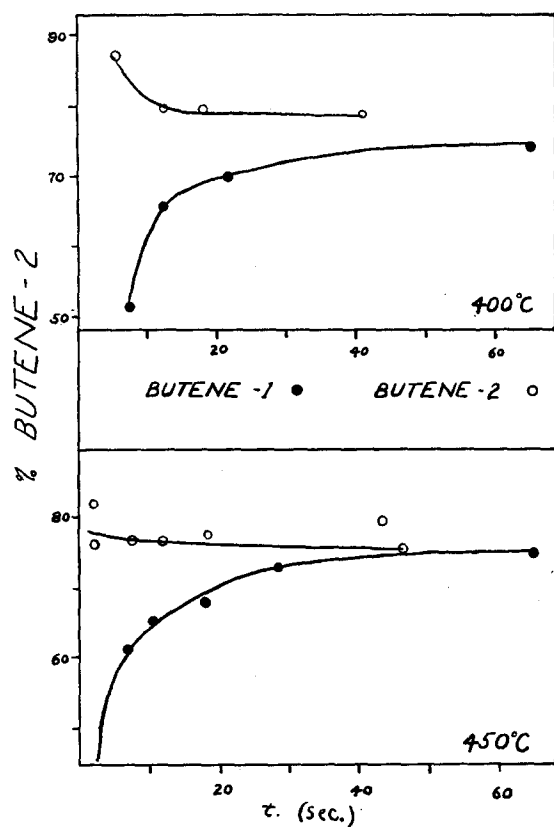


FIG. 2.

times polymerization to a low boiling liquid occurred, qualitatively more so with butene-1 than with butene-2, thus substantiating Hurd's¹¹ results on the relative thermal stabilities of the isomers. Upon flushing the catalyst with nitrogen after these runs the polymerization was made more evident. Smoke and vapors in very noticeable amounts were washed free of the catalyst.

DISCUSSION OF RESULTS

It is obvious that the activated alumina catalyst effected isomerization at 450°C in relatively short contact times. With butene-2 as the starting material equilibrium was attained in a few seconds. Butene-1 having a greater range to cover to reach equilibrium required in the neighborhood of 30 seconds. At such long contact times decomposition set in to a perceptible degree. At 400°C butene-2 attained equilibrium

more slowly while butene-1 failed to reach the correct proportions, since the contact time necessary gave rise to acute decomposition.

The equilibrium results from this study clearly reproduce, within the accuracy of the analytical method, the figures derived from the thermodynamic data of Thacker, Folkins, and Miller.¹²

$$\Delta F_T^0 = \Delta H_0 + aT \ln T + bT^2 + cT^{-1} + I \cdot T$$

	H_0	a	b	c	I
Butene-1	9,988	32.56	-0.0188	-233,800	-153.7
Butene-2 <i>cis</i>	8,217	32.56	-0.0188	-233,800	-151.9
Butene-2 <i>trans</i>	7,267	32.56	-0.0188	-233,800	-151.3

Applying this equation ΔF_T values were calculated over the range 298.1–1200°K. The values of interest in this study are:

$T^\circ\text{K}$	Butene-1	Butene-2 <i>cis</i>	Butene-2 <i>trans</i>
673	40,375	39,814	39,268
723	43,691	43,221	42,706

Since $\Delta F_T = -RT \ln K_{eq} = -RT \ln c_1/c_2$ mole percent of butene-1 and butene-2 at equilibrium may be calculated over the range of temperature (see Fig. 3). The particular values of interest calculated from the above data are:

$T^\circ\text{K}$	Butene-1	Butene-2 <i>cis</i>	Butene-2 <i>trans</i>
673	20.8	31.6	47.6
723	22.9	31.7	45.4

These results compared with those obtained from the equilibrium study of total butene-2 mole

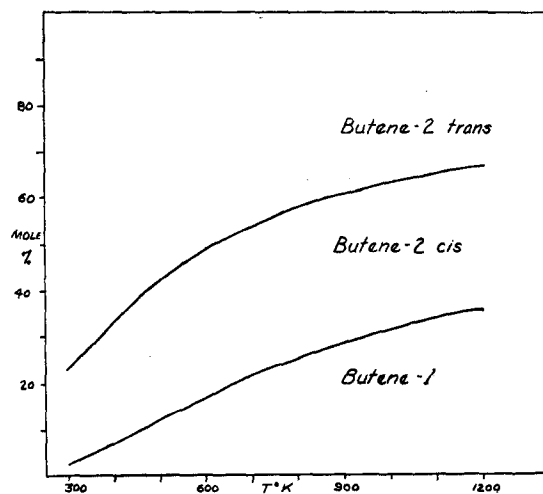


FIG. 3.

¹¹ C. D. Hurd and A. R. Goldsky, J. Am. Chem. Soc. 56, 1812 (1934).

¹² Thacker, Folkins, and Miller, Ind. Eng. Chem. 33, 584 (1941).

percent are:

	Calculated from thermodynamics	Observed
400°C	79.2	78.5±1.5
450	77.1	75.5±1.5.

It is seen that excellent agreement was obtained

well within the experimental error of the analytical method.

The authors wish to express their appreciation to the M. W. Kellogg Company who financially sponsored this work, and to Professor Hugh S. Taylor for his inspiring interest.

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The Thermodynamic Properties of Gaseous Sulfur Trioxide*

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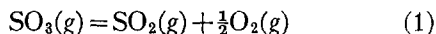
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(Received August 18, 1944)

The thermodynamic properties of sulfur trioxide in the ideal gas state are calculated from molecular data. To obtain satisfactory agreement with the equilibrium data for the reaction $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$, it is necessary to include vibrational anharmonicities, which are somewhat larger than usual because of an accidental degeneracy involving two of the normal frequencies. The standard entropy of $\text{SO}_3(\text{g})$ at 25°C is 61.2 ± 0.2 E.U., and its standard heat and free energy of formation from the elements are $\Delta H_{298.16}^\circ = -94.43 \pm 0.15$ and $\Delta F_{298.16}^\circ = -88.48 \pm 0.20$ kcal./mole.

INTRODUCTION

THE only accurate thermodynamic data relating to gaseous sulfur trioxide are extensive measurements¹⁻³ of the "contact process" equilibrium,



in the temperature range 800°–1170°K. Since the heat capacity of sulfur trioxide has not been measured, purely thermodynamic calculations^{4,5} of its standard entropy and free energy at 25° have required an arbitrary choice of ΔC_p for reaction (1), and are thus subject to considerable uncertainty.

Recently this situation has been substantially improved by Stevenson,⁶ who calculated the thermodynamic properties of $\text{SO}_3(\text{g})$ statistically

from the available electron-diffraction⁷ and spectral^{8,9} data. The correctness of his results can be judged in the usual manner by examining the constancy of ΔH_0° for reaction (1) calculated from the spectroscopic values of $\Delta(F^\circ - H_0^\circ)/T$ and the experimental values of $\Delta F^\circ/T$. The three sets of equilibrium data lead to almost the same average values of ΔH_0° , and the drift of the individual values with temperature was apparently judged by Yost and Russell⁶ to be adequately small.

We were engaged in a similar calculation when Stevenson's work appeared. Desiring to obtain the best possible values, and believing the drift of ΔH_0° with temperature to be not entirely negligible, we were led to carry the investigation further. By including anharmonic contributions to the vibrational energy, we have succeeded in eliminating the trend in ΔH_0° . Our procedure and results are described below.

THE VIBRATIONAL ASSIGNMENT

A symmetrical planar XY_3 molecule has two single and two doubly degenerate normal vibra-

* Contribution No. 511 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

¹ M. Bodenstein and W. Pohl, *Zeits. f. Elektrochemie* **11**, 373 (1905).

² G. B. Taylor and S. Lehner, *Zeits. f. physik. Chemie* **30** (1931).

³ A. F. Kapustinsky and L. M. Shamovsky, *Acta Physicochimica* **4**, 791 (1936).

⁴ G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), p. 551.

⁵ K. K. Kelley, U. S. Bur. Mines Bull. **406**, 14 (1937).

⁶ D. P. Stevenson, unpublished calculations quoted by D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), p. 314.

⁷ K. J. Palmer, *J. Am. Chem. Soc.* **60**, 2360 (1938).

⁸ H. Gerding, W. J. Nijveld, and G. J. Muller, *Zeits. f. physik. Chemie* **B35**, 193 (1937).

⁹ H. Gerding and J. Lecomte, *Physica* **6**, 737 (1939).