

tities are often difficult to justify theoretically this relationship should be accepted with a great many reservations, until further verifications are made.

Thus far, we have not mentioned the possibility of cation formation by  $\gamma$ -irradiation. On theoretical grounds one may expect monopositive and mononegative ions of alternant hydrocarbons to give similar electronic spectra.<sup>9</sup> We have, however, overlooked this possibility on the assumption that cation formation requires positive charge exchange between the solute and the molecules of the matrix. Since such an exchange is restricted in polar media, positive ion formation is expected to be limited.<sup>10</sup> In fact, this was found to be the case for all hydrocarbons except perylene. Perylene (*cf.* Fig. 3) exhibits an absorption at approximately 5800 Å. which is similar to that of the monopositive ion produced in oxygenated HF, CF<sub>3</sub>COOH + BF<sub>3</sub>·H<sub>2</sub>O, or concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup> Not only that, but in solu-

(9) M. G. J. Hoijsink, Colloque International sur le Calcul des Fonctions d'ondes Moleculaires, Ed. C.N.R.S., Paris, 237 (1958).

(10) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964).

(11) (a) G. Dallinga, E. L. Mackor, and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958); (b) W. I. Aalbersberg, G. J. Hoijsink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

tion with biphenyl its optical density increases slightly (but consistently) with added biphenyl. (At 0.079, 0.158, and 0.316 mole % biphenyl the optical density of 0.04 mole % irradiated perylene is 0.68, 0.75, and 0.81, respectively.) This change in optical density cannot be explained by anion or free-radical formation. Neither can this be accounted for by formation of perylene-proton complex, since such a complex gives an entirely different spectrum.<sup>11</sup> It must, therefore, be attributed to the positive ion of perylene. This is consistent with the observation that perylene, compared with other aromatic hydrocarbons, in concentrated H<sub>2</sub>SO<sub>4</sub> or CF<sub>3</sub>COOH + BF<sub>3</sub>·H<sub>2</sub>O solutions, easily forms the monopositive ion. However, the over-all yield,  $G$  (perylene<sup>+</sup>) = 2.51,<sup>12</sup> of perylene positive ion is remarkably large for a solute at low concentration in a polar solvent and the assignment is tentative.

**Acknowledgment.**—We thank Professor John L. Magee and Dr. Paul Funabashi for useful discussions.

(12) The yield was calculated on the basis of an absorption coefficient of  $2.68 \times 10^4$  taken from the data of ref. 11a.

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIFORNIA]

## Iodine-Catalyzed Isomerization of Olefins. I. Thermodynamic Data from Equilibrium Studies of Positional and Geometrical Isomerization of 1-Butene and 2-Butene

BY DAVID M. GOLDEN, KURT W. EGGER, AND SIDNEY W. BENSON

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The kinetics and thermodynamics of the iodine atom catalyzed positional and geometrical isomerization of 1-butene and 2-butene have been studied. In this paper, first of a series, equilibrium constants ( $K$ ) for the reactions 1-butene  $\xrightleftharpoons[k_4]{k_3}$  *trans*-2-butene and *cis*-2-butene  $\xrightleftharpoons[k_6]{k_5}$  *trans*-2-butene are reported. The  $K_{3,4}$  values, measured over a wider temperature range (192 to 332°) and with greater precision than had been done earlier,<sup>1</sup> lead to  $\Delta H^\circ_{3,4} = -2.8 \pm 0.2$  kcal./mole and  $\Delta S^\circ_{3,4} = -3.1 \pm 0.4$  e.u. These values are to be compared with the less reliable data from the API tables of  $-2.6$  kcal./mole and  $-2.1$  e.u., respectively. The  $\Delta H^\circ_{5,6}$  and  $\Delta S^\circ_{5,6}$  calculated from  $K_{5,6}$  values (87 to 332°) differ from the API data by about 0.4 kcal./mole and 0.7 e.u., respectively. As anticipated, minor amounts of butadiene and *n*-butane are observed.

### Introduction

Recently Benson and co-workers<sup>1a,1b</sup> showed that in a temperature range of 200–300° catalytic amounts of iodine vapor bring about quite rapid positional as well as geometrical isomerization of olefins. Measurement of the equilibrium constants from the iodine-catalyzed reaction of olefins and their parent hydrocarbons constitutes a very valuable tool for the precise measurement of the differences in the thermodynamic properties of the reactants. Applied to the butene isomerization Benson and Bose<sup>1a</sup> obtained for the positional isomerization values for  $\Delta H^\circ$  and  $\Delta S^\circ$  that disagreed by about 0.5 kcal./mole and 1.6 e.u., respectively, with the data from the API tables.<sup>2</sup> For the geometrical

isomerization the agreement with API was excellent. The new measurements reported here were aimed at examining these differences more carefully.

Because of the absence of appreciable side reactions and the simplicity of the mechanism of iodine atom attack on olefins, the method is extremely well-adapted for studying resonance effects as well as precise thermodynamic data; toward these ends, we have begun a program of investigation into the kinetics of isomerization of simple and conjugated olefins. The present paper reports measurements of the equilibrium constants for the positional and geometrical isomerization of 2-butene and 1-butene.<sup>1c</sup>

### Experimental

The experimental procedure described herein is applicable to both equilibrium and kinetic measurements.

(a) **Materials.**—Research grade butene isomers were supplied by the Phillips Petroleum Company and were further purified by distillation under vacuum. They were stored in large glass bulbs connected to a standard-type gas handling and vacuum system. G.l.c. (gas-liquid chromatography) analysis showed less than  $10^{-3}$  mole % impurities. Reagent grade resublimed iodine was used.

(1) (a) S. W. Benson and A. N. Bose, *J. Am. Chem. Soc.*, **85**, 1385 (1963). (b) S. W. Benson, A. N. Bose, and P. Nangia, *ibid.*, **85**, 1388 (1963). (c) Subsequent papers will discuss the kinetics of the positional isomerization involving the allylic resonance in the butenyl radical and the kinetics of the *cis-trans* isomerization of 2-butene which involves the addition of the iodine atom to the double bond and the rate-controlling step of rotation of the ethyldiene radical around a single bond.

(2) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(b) **Analysis.**—Analyses of 2-ml. NTP samples of butenes were carried out by g.l.c. at 0° using a Model 720 F. and M. gas chromatograph. A 50-ft. column filled with a mixture of 20% di-2-ethylhexyl sebacate and 80% bis(2-methoxyethyl) adipate both coated (20%) on 60–80- $\mu$  Chromosorb W HMDS was used. At a flow rate of 100 ml./min., C<sub>4</sub>-hydrocarbons showed the following retention times measured from the air peak (in minutes): isobutane 9.3, *n*-butane 15.3, 1-butene (B<sub>1</sub>) 21.9, *trans*-2-butene (B<sub>t</sub>) 29.8, *cis*-2-butene (B<sub>c</sub>) 35.4, and butadiene 43.9. The procedure for analyzing the chromatograms was checked extensively with four different mixtures of butenes with known isomer ratios (from pressure–volume–temperature measurements) as well as with studies of the peak tailing on the pure compounds. The B<sub>t</sub>/B<sub>1</sub> and B<sub>t</sub>/B<sub>c</sub> ratios calculated from tailing-corrected peak heights showed the same or even less of a maximum deviation than the tailing-corrected area data computed from a recording disk integrator. Therefore peak height measurements were made using the following tailing corrections: B<sub>t</sub>/[0.4% B<sub>1</sub>], and B<sub>c</sub>/[1.1% B<sub>1</sub>]. The accuracy of the g.l.c. analysis, as obtained from a total of over 65 one-a-day test analyses over a period of 3 months using 13 different known mixtures of butene isomers, with B<sub>t</sub>/B<sub>1</sub> ratios ranging from 0.3 to 4.3 and B<sub>t</sub>/B<sub>c</sub> ratios from 0.3 to 3.2 is [B<sub>t</sub>/B<sub>1</sub>]<sub>g.l.c.</sub>  $\pm$ 0.77%, maximum deviation  $\pm$ 2%; [B<sub>t</sub>/B<sub>c</sub>]<sub>g.l.c.</sub>  $\pm$ 1.5%, maximum deviation  $\pm$ 4%. An illustrative chromatogram is shown in Fig. 1.

(c) **Apparatus.**—The measurements were carried out using a static method in cylindrical Pyrex glass vessels placed in a uniformly heated and well-insulated aluminum block furnace. The temperature was maintained to within 0.3° with a proportional controller, acting only upon about 10% of the total load. The over-all temperature gradient in the oven never exceeded 2°. The reaction vessel was connected to the pressure-measuring device and through three stopcocks to the vacuum and gas-handling system, to an iodine reservoir, and to the sampling part of the system. The total dead space (depending on the reaction vessel used) was between 15 and 27 ml. and included the pressure transducer. They were all placed in an insulated heated box and kept at 120° to avoid any precipitation of iodine or products. The stopcocks were greased with silicone grease or Apiezon H. (Neither had any effect on the rate or products of the reaction.) The pressure in the reaction system was measured using a  $\pm$ 0.1 p.s.i. Pace pressure transducer as a null instrument. The null side of the transducer was connected to a silicone oil and mercury manometer each readable to  $\pm$ 0.02 mm. The very sensitive pressure transducer was set to indicate pressure differences down to 0.04 mm. The side of the transducer exposed to the reaction system, including the diaphragm, was made of stainless steel. Viton-A O-rings were used for the seals.

Besides monitoring pressure changes with time, changes in iodine concentration during the reaction were also followed by measuring light absorption. The light from a stabilized light source was filtered through a Baird-Atomic B-9 filter (4855 Å., band width 50 Å.) roughly collimated and detected by a gas-filled phototube. The reaction vessels were constructed with parallel Pyrex windows to allow light to pass through without too much scatter. The kinetic measurements were made using two equivalent glass vessels, one of which was packed with glass tubing. The surface-to-volume ratio of the two vessels was 1:18. For the unpacked vessel with a volume of 837 ml. the maximum dead space was 15 ml. for the runs up to run 51, and thereafter it was 21.2 ml. Taking the temperature difference between dead space ( $\sim$ 400°K.) and reaction vessel ( $\sim$ 500°K.) into account, the correction never exceeded 3%. For the packed vessel, with a volume of 627.5 ml., the dead space was measured as 29 ml. or  $\sim$ 5.5%.

(d) **General Procedures.**—After evacuating the reaction system to 10<sup>-5</sup> mm., the zero readings of pressure and light intensity were recorded before admitting iodine to the reaction system. After establishing pressure equilibrium on the null side of the transducer, the manometer reading gave the initial pressure of the iodine in the system ([I<sub>2</sub>]<sub>0</sub>). At time  $t = 0$  the butene was expanded into the reaction vessel from a reservoir in the gas-handling system. This procedure gave a slight increase of the iodine concentration in the reaction vessel by the amount of iodine swept from the dead space into the reaction vessel. The pressure was again immediately equilibrated by venting air into the null side of the transducer. The new manometer reading gave the total initial pressure ( $P_{tot}$ )<sub>0</sub> in the system; by subtracting the initial iodine pressure ([I<sub>2</sub>]<sub>0</sub>) one gets the initial olefin pressure ([B]<sub>0</sub>). The  $P_{tot}$  was double-checked against another manometer reading from the gas handling system.

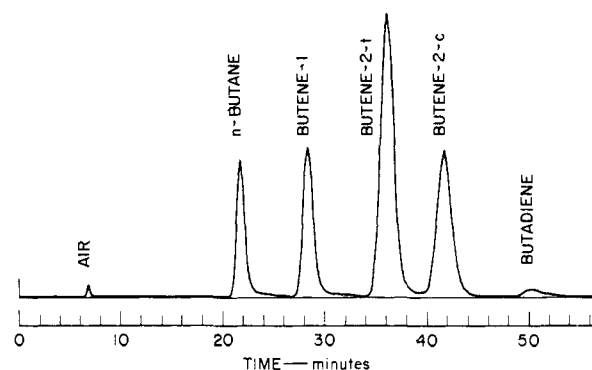


Fig. 1.—Chromatogram run 60 starting with a mixture of the three butene isomers. (Unusually high amounts of *n*-butane are due to extreme experimental conditions.)

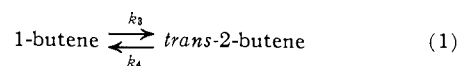
During the run, changes in pressure and light intensity were recorded. The per cent difference between initial and final optical density gave the total change in iodine pressure. The changes in iodine concentrations were usually rather small and of the order of a few per cent. However, at the highest temperatures where [I<sub>2</sub>] is necessarily low, half or more of the initial iodine concentrations may be consumed due to side reactions leading to great uncertainty in the iodine values. Errors introduced by deviations from the simple stoichiometry assumed in order to derive the rate law tend to be in the opposite direction.<sup>3</sup>

An experiment was stopped by opening a stopcock, thereby expanding the reaction mixture from the reaction vessel into the sampling system. This operation was complete within 15 to 30 sec. depending on the total pressure in the system. The shortest reaction time used was 600 sec. A liquid nitrogen trap, the last of a series of four traps, was used to remove the sample. The first trap (filled with glass beads) was kept at -40°. It removed all the iodine without condensing the butenes. The sample then passed through fine-grain KOH to remove any HI from the reaction mixture; finally the gas flowed through a -70° trap, where iodides and remaining traces of I<sub>2</sub> or impurities were caught before the butenes condensed over liquid nitrogen. The mixture of the butene isomers was then transferred into a removable sampling bulb large enough to maintain the sample as a single gas phase. (This avoids possible errors due to fractionation.) In several runs the over-all mass balance was checked by titrating the iodine and measuring the butenes. The mass balance between initial and final materials was always found to be within a few per cent.

In order to extend the temperature range to lower temperatures, equilibrium studies of the geometrical isomerization were done at 373 and 399°K. generating iodine atoms photochemically. In these experiments requisite amounts of I<sub>2</sub> and butene were put into round flasks which were then placed in a marinite box whose temperature was controlled to within  $\pm$ 0.4° with a proportional controller. A 100-w. tungsten bulb illuminated the flasks through a Pyrex window in the box. Butenes were separated from I<sub>2</sub> and analyzed as above.

## Results

(a) **The Thermodynamics of the Positional Isomerization of 1-Butene.**—The equilibrium constant for the process



is given by  $K_{3,4} = k_3/k_4 = B_t/B_1$ . The results of the measurements are listed in Table I.

In Fig. 2 are plotted the  $K_{3,4}$  values obtained from the iodine-catalyzed isomerization as shown in Table I and given by Benson and Bose.<sup>1a</sup> The values of Vogé and May<sup>4</sup> and of Bailey<sup>5</sup> for the same equilibrium using solid catalysts are included. Also shown are the results as calculated from the heat of

(3) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964).

(4) H. H. Vogé and N. C. May, *ibid.*, **68**, 550 (1946).

(5) G. C. Bailey, Research Department, Phillips Petroleum Co., Bartlesville, Okla., private communication.

TABLE I  
 COMPOSITION OF EQUILIBRATED MIXTURES OF BUTENE ISOMERS

| Temp., °C. | Run no.          | Starting compound  |       | Starting isomer                                |  | Time, min. | [I <sub>2</sub> ] <sub>0</sub> , mm. | Final equilibrium ratios      |                               |
|------------|------------------|--|-------|--|--|------------|--------------------------------------|-------------------------------|-------------------------------|
|            |                  | B <sub>1</sub> , B <sub>t</sub> , or B <sub>c</sub> <sup>a</sup> | mm.   | [B <sub>t</sub> /B <sub>1</sub> ] <sub>0</sub> | [B <sub>t</sub> /B <sub>c</sub> ] <sub>0</sub> |            |                                      | K <sub>3,4</sub> <sup>b</sup> | K <sub>5,6</sub> <sup>b</sup> |
| 87.0       | II <sup>d</sup>  | t, c   | 210   |  | 1.87   | 3848       | ~5                                   |                               | 2.35 <sup>f</sup>             |
| 95.2       | III <sup>d</sup> | t, c   | 120   |  | 1.87   | 1180       | Sat. <sup>e</sup>                    |                               | 2.74                          |
|            | IV <sup>d</sup>  | t, c   | 186   |  | 3.39   | 1205       | Sat. <sup>e</sup>                    |                               | 2.70                          |
|            | V <sup>d</sup>   | t, c   | ~300  |  | 2.57   | 1380       | Sat. <sup>e</sup>                    |                               | 2.69                          |
|            | VI <sup>d</sup>  | t, c   | 670   |  | 3.39   | 960        | Sat. <sup>e</sup>                    |                               | 2.35                          |
| 125.7      | VII <sup>d</sup> | t, c   | 200   |  | 2.57   | 960        | Sat. <sup>e</sup>                    |                               | 2.49                          |
|            | 32               | 1, t, c  | 28.1  | 4.29   | 4.29   | 5272       | 46.8                                 | 4.30                          |                               |
| 192.1      | 40               | 1, t, c  | 51.8  | 4.29   | 1.69   | 1088       | 25.5                                 | 4.40                          | 1.99                          |
|            | 41               | 1, t, c  | 122.6 | 4.42   | 1.59   | 1077       | 39.6                                 | 4.57                          | 2.00                          |
|            | 43               | 1, t, c  | 151.6 | 4.65   | 2.38   | 1212       | 44.6                                 | 4.46                          | 1.96                          |
|            | 49               | 1, t, c  | 64.6  | 4.91   | 2.10   | 1297       | 46.3                                 | 4.59                          | 2.00                          |
|            | 31 <sup>g</sup>  | 1  | 72.8  |  |  | 137        | 25.6                                 |                               | ≥ 1.82                        |
| 237.3      | 7                | 1  | 38.2  |  |  | 1230       | 8.9                                  | 3.45                          | 1.78                          |
|            | 8                | 1  | 36.4  |  |  | 1205       | 9.5                                  | 3.48                          | 1.73                          |
|            | 9 <sup>g</sup>   | 1  | 36.0  |  |  | 240        | 12.1                                 |                               | 1.72                          |
|            | 10 <sup>g</sup>  | 1  | 35.6  |  |  | 370        | 11.9                                 |                               | 1.76                          |
|            | 11 <sup>g</sup>  | 1  | 40.7  |  |  | 360        | 18.4                                 |                               | 1.79                          |
|            | 12 <sup>g</sup>  | 1  | 42.3  |  |  | 525        | 11.7                                 |                               | 1.72                          |
|            | 13               | t  | 41.5  |  |  | 284        | 24.5                                 | 3.46                          | 1.82                          |
|            | 21               | 1  | 31.8  |  |  | 293        | 25.7                                 | 2.92                          |                               |
|            | 22               | c  | 40.5  |  |  | 262        | 24.9                                 | 2.98                          | 1.71                          |
|            | 23               | 1  | 35.0  |  |  | 322        | 26.0                                 | 2.84                          | 1.74                          |
| 269.8      | 24               | t  | 235.2 |  |  | 1062       | 26.5                                 | 2.94                          | 1.69                          |
|            | 25 <sup>g</sup>  | 1  | 37.9  |  |  | 41         | 15.7                                 |                               | 1.65                          |
|            | 26 <sup>g</sup>  | 1  | 33.2  |  |  | 50         | 15.0                                 |                               | 1.65                          |
|            | 27 <sup>g</sup>  | 1  | 27.7  |  |  | 40         | 10.9                                 |                               | 1.71                          |
|            | 71 <sup>g</sup>  | t, c   | 79.0  |  | 1.36   | 12         | 2.7                                  |                               | ≥ 1.55                        |
|            | 72 <sup>g</sup>  | t, c   | 27.4  |  | 1.36   | 10         | 1.8                                  |                               | ≥ 1.60                        |
|            | 74 <sup>g</sup>  | 1  | 42.6  |  |  | 5          | 4.2                                  |                               | 1.60                          |
|            | 75 <sup>g</sup>  | 1  | 50.9  |  |  | 7          | 4.0                                  |                               | 1.59                          |
| 331.8      | 60 <sup>g</sup>  | 1, t, c  | 105.3 | 1.49   | 1.73   | 103        | 27.8                                 | 2.29                          | 1.69 <sup>h</sup>             |
|            | 61 <sup>g</sup>  | 1, t, c  | 157.7 | 2.19   | 2.08   | 45         | 3.6                                  | 2.19                          | 1.48                          |
|            | 62 <sup>g</sup>  | 1  | 118.7 |  |  | 30         | 2                                    |                               | 1.51                          |
|            | 63               | c  | 110.5 |  |  | 111        | 14.8                                 | 2.27                          | 1.54                          |
|            | 64               | 1, t, c  | 67.0  | 1.49   |  | 21         | 13.4                                 | 2.17                          |                               |
| 65         | 1, t, c          | 71.2   | 1.49  | 1.73   | 960  | Traces     | 2.22                                 | 1.50                          |                               |

<sup>a</sup> B<sub>1</sub>, B<sub>t</sub>, B<sub>c</sub> stand for 1-butene, *trans*-2-butene, and *cis*-2-butene, respectively. <sup>b</sup> See text;  $K_{3,4} = [B_t/B_1]_{final}$  and  $K_{5,6} = [B_t/B_c]_{final}$ . <sup>c</sup> Packed vessel. <sup>d</sup> Generation of iodine atom photochemically. <sup>e</sup> Saturated vapor over [I<sub>2</sub>]<sub>0</sub>. <sup>f</sup> Did not reach equilibrium, the iodine concentration being too low. <sup>g</sup> Kinetic run. The equilibrium for positional isomerization is not quite, but almost, established. <sup>h</sup> In this run high amounts of *n*-butane are formed.

formation and entropy data listed in the API tables. For an unusually extensive temperature range, all the data based on direct measurement of the composition of

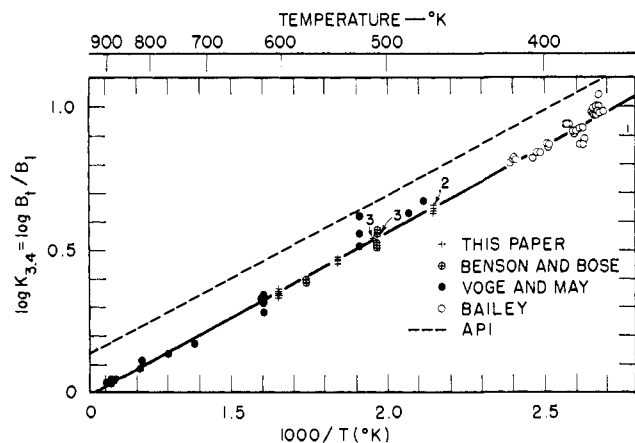
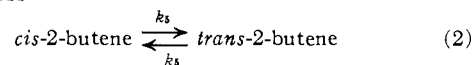


Fig. 2.—Arrhenius plot of the equilibrium constant ( $K_{3,4}$ ) for the positional isomerization of 1-butene. (Numbers indicate overlapping points.)

equilibrated mixtures of butene isomers are in very good agreement within their experimental limits with the

Arrhenius plot from this work, whereas the API values are significantly higher by a constant factor.

(b) **The Thermodynamics of the Geometrical Isomerization of 2-Butene.**—The equilibrium constant for the process



is given by  $K_{5,6} = k_5/k_6 = B_t/B_c$ . The results of these measurements are listed in Table I. Figure 3 shows an Arrhenius plot of the same data.

The data can be represented by a straight line (dashed) as well as by a slightly curved line (solid). This means that the error limits in the data make a discrimination between  $\langle \Delta C_{p5,6}^\circ \rangle = 0$  and  $\langle \Delta C_{p5,6}^\circ \rangle \lesssim 1$  e.u. impossible. The curved line is used to compute the data in Table II, thus taking into account the values of  $\Delta C_{p5,6}^\circ$  at higher temperatures, as calculated from API tables.

Figure 4 compares the results with those of Benson and Bose<sup>1a</sup> and Voge and May.<sup>4</sup> In addition the log  $K_{5,6}$  values are plotted as calculated from free-energy data in the API tables and from Scott, *et al.*<sup>6</sup>

(6) R. B. Scott, W. J. Ferguson, and F. G. Brickwedde, *J. Res. Natl. Bur. Std.*, **53**, 1 (1944).

TABLE II  
VALUES OF THE THERMODYNAMIC FUNCTIONS FOR BUTENE ISOMERIZATION (API VALUES SHOWN IN PARENTHESES)

|                           |                                       | 400°K.               | 500°K.            | 600°K.            |
|---------------------------|---------------------------------------|----------------------|-------------------|-------------------|
| Positional isomerization  | $\Delta F_{3,4}^\circ$                | $-1.58 \pm 0.05^b$   | $-1.29 \pm 0.04$  | $-0.99 \pm 0.03$  |
|                           | kcal./mole                            | (-1.79) <sup>a</sup> | (-1.56)           | (-1.35)           |
|                           | $\Delta H_{3,4}^\circ$                | $-2.8 \pm 0.2$       | $-2.8 \pm 0.2$    | $-2.8 \pm 0.2$    |
|                           | kcal./mole                            | (-2.63)              | (-2.64)           | (-2.68)           |
| Geometrical isomerization | $\Delta S_{3,4}^\circ$ , <sup>c</sup> | $-3.1 \pm 0.4$       | $-3.1 \pm 0.4$    | $-3.1 \pm 0.4$    |
|                           | e.u.                                  | (-2.09)              | (-2.16)           | (-2.22)           |
|                           | $\Delta F_{5,6}^\circ$                | $-0.694 \pm 0.03$    | $-0.582 \pm 0.03$ | $-0.489 \pm 0.02$ |
|                           | kcal./mole                            | (-0.61)              | (-0.59)           | (-0.59)           |
|                           | $\Delta H_{5,6}^\circ$                | $-1.2 \pm 0.1$       | $-1.15 \pm 0.1$   | $-0.85 \pm 0.1$   |
|                           | kcal./mole                            | (-0.81)              | (-0.66)           | (-0.56)           |
|                           | $\Delta S_{5,6}^\circ$                | $-1.2 \pm 0.2$       | $-1.1 \pm 0.2$    | $-0.6 \pm 0.2$    |
|                           | e.u.                                  | (-0.49)              | (-0.15)           | (+0.05)           |

<sup>a</sup> The API tables show a discrepancy of 0.2 kcal./mole in  $\Delta F_{3,4}^\circ$  calculated from free energy of formation tables or from separate  $\Delta H_f^\circ$  and  $\Delta S^\circ$  tables. The latter are quoted here. <sup>b</sup> The errors quoted for this work are maximum deviations; the standard errors are much smaller. <sup>c</sup> The errors in  $\Delta S^\circ$  and  $\Delta H^\circ$  are not independent.

As can be seen from Table I, the results for both equilibrium constants are quite reproducible and independent of initial composition within the error limits of the analysis.

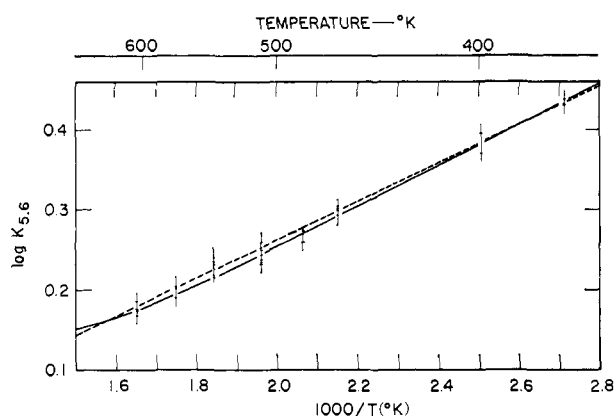


Fig. 3.—Arrhenius plot for the *cis-trans* equilibrium constant ( $K_{5,6}$ ) for the butene isomerization.

The analytical errors involved in the measurement of  $K_{5,6}$  are greater than those involved in measuring  $K_{3,4}$  as the quantitative separation of *cis*- and *trans*-2-butene is more difficult than that of 1-butene from *trans*-2-butene. The  $K_{3,4}$  values show a maximum deviation that is significantly greater than the expected deviation for the analytical procedure as reported earlier in this paper. The values of  $K_{5,6}$ , however, agree within the experimental errors. This is to be expected from the much larger temperature dependence for  $K_{3,4}$  values. It is apparent that the data of this paper do not agree with either the  $\Delta H_{5,6}^\circ$  or  $\Delta S_{5,6}^\circ$  and  $\Delta S_{3,4}^\circ$  values calculated from calorimetric measurements and spectral assignment.<sup>5,6</sup>

Table II compares the different values of  $\Delta F_{3,4}^\circ$ ,  $\Delta H_{3,4}^\circ$ ,  $\Delta S_{3,4}^\circ$ ,  $\Delta F_{5,6}^\circ$ ,  $\Delta H_{5,6}^\circ$ , and  $\Delta S_{5,6}^\circ$  at various temperatures.

### Discussion

The values of thermodynamic quantities for the three isomers in question listed in the API tables are obtained in the following manner: (1) The entropy ( $S^\circ$ ) as a function of temperature is calculated from statistical formulas based on known vibrational assignments and values of the barrier to internal rotation which are forced to fit measured entropy data over a small temperature range. (2) The heat of formation ( $\Delta H_f^\circ$ ) is obtained as a function of temperature by combining

statistical calculations of enthalpy with heat of hydrogenation or heat of combustion measurements.

The entropy values listed in the API tables for the butene isomers discussed here come from Kilpatrick and Pitzer<sup>7</sup> and are subject to errors in frequency assignments and calorimetric entropy measurements including the uncertainty in estimates of the entropy of the solid at 0°K. The frequency assignments are far from certain,<sup>8</sup> es-

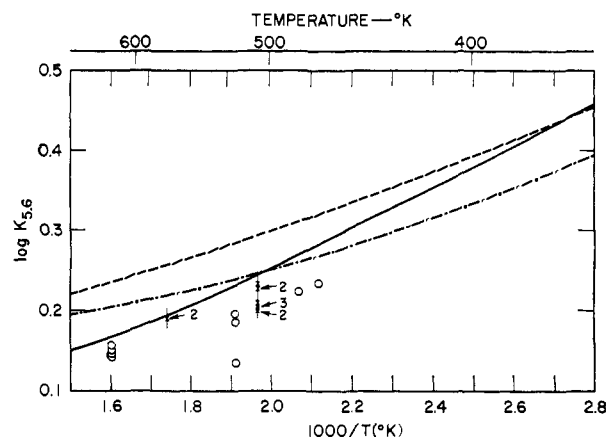


Fig. 4.—Arrhenius plot for the *cis-trans* equilibrium constant: Solid line this work, dotted line API values, dashed line from Scott, *et al.*<sup>6</sup> ○ = Voge and May,<sup>4</sup> × = Benson and Bose.<sup>1a</sup> The numbers in the graph indicate overlapping points.

pecially in the case of 1-butene where the thermodynamic calculations are based on estimated frequencies. Errors in the low frequency vibrations, which were the most difficult ones to obtain, contribute the largest discrepancies in entropy values. A conservative estimate of the error in absolute entropy for any one of the butene isomers would seem to be of the order of  $\pm 0.5$  e.u. Considering the fact that the  $\Delta S^\circ$  values are derived from differences in absolute values, they probably have error limits of at least  $\pm 0.7$  e.u.

The values of  $\Delta H_f^\circ$  listed in the API tables are based largely on the measurements of heats of combustion by Prosen, *et al.*,<sup>9</sup> and of heats of hydrogenation by Kistiakowsky, *et al.*<sup>10</sup> The quoted errors in  $\Delta H_f^\circ$  at 25° are of the order of  $\pm 0.3$  kcal./mole and would lead to an error in  $\Delta H^\circ$  of the order of  $\pm 0.4$  kcal./mole. To this

- (7) J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Std.*, **37**, 163 (1946).  
 (8) J. F. Kilpatrick and K. S. Pitzer, *ibid.*, **38**, 191 (1947).  
 (9) E. J. Prosen, F. W. Maron, and F. D. Rossini, *ibid.*, **46**, 106 (1951).  
 (10) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **67**, 876 (1935).

can be added the error involved in the enthalpy as a function of temperature.

Conclusions that can be drawn from Table II concerning the differences between API values and those of this work are limited. Most values agree within the necessarily large error limits of the API values. The discrepancy in  $\Delta S^\circ_{3,4}$  of about 1.0 e.u. probably means that the API data for the entropy of 1-butene are too low. The discrepancy in  $\Delta S^\circ_{5,6}$ , while smaller, also reflects errors in vibrational assignments, barriers to rotation, and experimental entropies.<sup>11</sup>

(11) At the temperatures and pressures employed in the present work, corrections for gas nonideality are negligible.

A good deal of the impetus for the initial calorimetric and spectroscopic work on the hydrocarbons came from interest in discovering the magnitudes of the barriers to internal rotation. It appears now that this can be done with considerably more certainty by microwave measurements. In the case of the butenes these barriers are probably the most reliably known of the spectroscopic data. As a result it appears that the measurements of  $\Delta S^\circ$  from equilibrium studies, together with the known rotation barriers, could serve to fix better the low frequencies (*i.e.*, below 1000  $\text{cm}^{-1}$ ) of the butenes. In the temperature range investigated here these are the principal contributors to  $\Delta S_{\text{vib}}$ .

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIFORNIA]

## Iodine-Catalyzed Isomerization of Olefins. II. The Resonance Energy of the Allyl Radical and the Kinetics of the Positional Isomerization of 1-Butene

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The kinetics of the iodine atom catalyzed isomerization of 1-butene to 2-butene have been studied over a wider temperature range and with greater precision than previously reported. The activation energy for the iodine atom attack on 1-butene is  $12.4 \pm 0.3$  kcal./mole. When subtracted from the value  $25.0 \pm 0.5$  kcal./mole for the analogous reaction of iodine atom with propane, this yields 12.6 kcal. for the resonance energy in 1-butene if the activation energies for the back reactions are assumed equal. The uncertainty from all sources is  $\pm 1$  kcal. The agreement with earlier work by Benson, *et al.*, is excellent and is confirmed by less direct studies of the pyrolysis of vinylcyclopropane and vinylcyclobutanes. The formation of small amounts of butadiene and other side products has been detected. It is shown that these do not alter the basic simplicity of the system.

### Introduction

A preliminary kinetic study of the iodine atom catalyzed positional isomerization of 1-butene has been previously reported by Benson, *et al.*<sup>1</sup> In the course of repeating this work to verify the operation of a new system in a new laboratory, small errors in plotting and calculation were found in the work of Benson, *et al.* In addition, the more sensitive pressure-measuring device and analytical techniques used here led to the observation of the formation of small amounts of butadiene and other side products unnoticed by these workers (see Appendix). In view of the interest in having a reliable measure of the allylic resonance energy, kinetic studies of the iodine-catalyzed isomerization of 1-butene to 2-butene were made in the temperature range of 465 to 543°K. with an 18-fold variation in surface-to-volume ratios.

Since the completion of this work Ellis and Frey<sup>2</sup> have questioned the "low" value of the allylic resonance energy deduced by Benson and co-workers from their measurements and verified in this work. In this connection the various values and their sources are discussed.

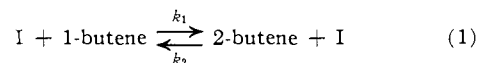
### Experimental

The techniques are similar to those of Benson, *et al.*, and have been described in great detail in a previous publication.<sup>3</sup>

### Results

Following the reasoning of Benson and co-workers the kinetic behavior of the iodine atom catalyzed posi-

tional isomerization is represented by the reversible reaction



This rests on the assumption that the *cis* and *trans* isomers of 2-butene are always in equilibrium. Measurements<sup>4</sup> show that this is not always the case, but that the validity of the assumption is upheld throughout the experiments reported here.

The rate law is (1-butene =  $B_1$ ; 2-butene =  $B_2$ )

$$-\frac{d(B_1)}{dt} = k_1(I)(B_1) \left[ 1 - \frac{(B_2)/(B_1)}{K_{1,2}} \right] \quad (2)$$

The equilibrium constant  $K_{1,2} = k_1/k_2$  is known from earlier independent measurements.<sup>3</sup> Using the stoichiometric relationship  $(B_1) + (B_2) = (B_1)_0$  and setting  $(I) = K_{I_2}^{1/2}(I_2)^{1/2}$  (where  $K_{I_2}$  is the equilibrium constant for the dissociation of  $I_2$ )<sup>5</sup> yields upon integration of (2)

$$k_1 = - \frac{K_{1,2}/(1 + K_{1,2})}{K_{I_2}^{1/2}(I_2)^{1/2}t} \left( \frac{1 + K_{1,2}}{K_{1,2}} \right) \quad (3)$$

In Table I the values of  $k_1$  obtained from eq. 3 are listed together with other pertinent information for each run.<sup>6</sup> As can be seen, the form of the derived rate law is obeyed well over a tenfold range of  $I_2$  pressures, a ninefold range in  $(B_1)_0$  pressures, and a tenfold range in  $(B_1)_0/(I_2)$ .

(4) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, submitted for publication.

(5) JANAF Interim Thermochemical Tables (Dow Chemical Co., Midland, Mich., 1960).

(6) In those runs where  $B_2$  was the starting material an equilibrium mixture of *cis*- and *trans*-2-butene was used and eq. 3 was suitably altered.

(1) S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388 (1963).

(2) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959 (1964).

(3) D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5416 (1964).