

less weight to the high moment structures in both cases, a step which is quite reasonable. It is concluded therefore that the planar configurations appear to be more acceptable in the cases of resorcinol and hydroquinone than is the concept of free or partially restricted rotation.

Summary

1. The dipole moments of catechol, resorcinol and hydroquinone have been determined in benzene and are equal to 2.62, 2.07 and 1.4 *D*, respectively.

2. The agreement between the experimental moment of catechol and the calculated value obtained by using vector addition of link moments and by assuming a *cis* planar structure involving a weak hydrogen bond is excellent.

3. Planar configurations for resorcinol and hydroquinone are more acceptable on comparison of experiment and calculation than are the structures assuming either free or partially restricted rotation of the hydroxyl groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

trans-2-Butene. The Heat Capacity, Heats of Fusion and Vaporization, and Vapor Pressure. The Entropy and Barrier to Internal Rotation

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Introduction and Discussion

The potential barrier to the rotation of a methyl group attached to an olefinic structure has been the subject of several investigations¹⁻⁶ principally concerned with the propylene molecule. In 1940 one of the present authors⁵ pointed out that while an entropy value for propylene obtained on the basis of the Third Law of Thermodynamics was uncertain because of the possibility of end for end random orientation of the molecules in the crystal, the corresponding value for *trans*-2-butene would not be uncertain because both ends of the molecule are the same. The study described below was undertaken to establish definitely the potential barrier, which would be expected to be the same for propylene and *trans*-2-butene.

The results as presented below show definitely that the potential barriers in *trans*-2-butene and propylene are in the vicinity of 2000 cal. per mole and that propylene molecules are oriented regularly in their crystals. This conclusion is in agreement with the later papers of Kistiakowsky and his collaborators^{4,7} and the work of Telfair.⁶ Apparently the hydrogenation equilibrium data of Frey and Huppke⁸ are in error by factors near two (in the equilibrium constant), which accounts for the lower potential barriers reported by one of the present authors in 1937.

While the conclusion stated above is quite definite, minor uncertainties remain in the assignment of vibration frequencies. Therefore it seems

best to postpone final statistical mechanical calculations until a later date.

Experimental

Material.—Through the kindness of Professor John G. Aston of Pennsylvania State College, there was made available to us a sample of *trans*-2-butene, whose purity, as estimated from premelting behavior, was about 99.3%. Visual examination of the just-melted compound revealed the presence of liquid-insoluble impurity which would not have appeared in the premelting. By a single distillation in a 25-plate column, the liquid-insoluble impurity was apparently removed almost completely from a middle fraction. This fraction was further purified by a single fractional crystallization *in vacuo*, with the result that the material used in the measurements contained 0.37% of impurity, assuming ideal liquid solutions and no solid solution. The weight of sample used was 52.79 g., or 0.9409 mole, the molecular weight being taken as 56.104.

Apparatus.—The calorimeter used in all the measurements was of conventional design, although a few modifications are worthy of note.

The calorimeter proper, of copper, was joined to the filling line by about 1 meter of thin-walled $\frac{1}{8}$ " german silver tubing. The german silver tube was well soldered to the heavy radiation shield, and hence heat leak down it was kept at a low value. Pure (c. p.) platinum wire, 0.1 mm. in diameter, was threaded back and forth through a bundle of thin-walled glass capillaries to give a compact strain-free resistance thermometer, which was placed in a case so situated as to be completely surrounded by the sample. Copper foil between and around the tubes afforded thermal contact with the walls of the case. Electrical connections to the thermometer were made through heavy platinum leads sealed vacuum-tight through glass beads and projecting a short distance above the upper surface of the calorimeter. The case was filled with helium at one atmosphere.

It was originally intended that the thermometer should conform to international temperature scale requirements. Unfortunately, the inclusion of some short leads of less pure platinum prevented this. However, the thermometer was compared at numerous temperatures with another thermometer which had been calibrated in the desired manner.⁹ Deviations from a linear relation between their resistances were computed and plotted on a large scale, and a temperature scale drawn up by interpolation and careful smoothing. Small changes which occurred sub-

- (1) K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).
- (2) G. B. Kistiakowsky, J. R. Lacher and W. W. Ransom, *ibid.*, **6**, 900 (1938).
- (3) T. M. Powell and W. F. Giauque, *THIS JOURNAL*, **61**, 2366 (1939).
- (4) B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells and E. B. Wilson, Jr., *ibid.*, **61**, 2980 (1939).
- (5) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).
- (6) D. Telfair, *J. Chem. Phys.*, **10**, 167 (1942).
- (7) G. B. Kistiakowsky and A. G. Nickle, *ibid.*, **10**, 78, 146 (1942).
- (8) F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

- (9) K. S. Pitzer and D. W. Scott, *THIS JOURNAL*, **65**, 803 (1943).

sequently, evidently due to incomplete annealing, were detected and corrected by calibration against the triple-point and vapor pressure of hydrogen, the upper transition, triple-point and vapor pressure of oxygen, and by comparison of the vapor pressure of butene in the calorimeter with its value in a carefully prepared ice-bath.

On the lateral surface of the calorimeter was wound a copper resistance thermometer to measure the temperature of the radiating surface. Accurate correction could then be made for heat interchange during the determination of heats of fusion and vaporization.

The vapor pressures were measured with a manometer connected directly to the calorimeter. One arm was continually evacuated, and the difference in height was observed with a Gaertner cathetometer, the vernier of which was graduated to 0.05 mm., estimation of half this distance being possible. The cathetometer scale had been compared with a standard meter bar at frequent intervals, and the deviations had been found never to exceed 0.1 mm.

Vapor Pressures.—Corrections for capillary depression were made by means of the tables of Blaisdell.¹⁰ The pressures were corrected to 0°C., and to standard gravitational acceleration. Table I contains the observed pressures, and the deviations from the equation

$$\log_{10} p_{\text{cm.}} = -1757.283/T - 0.0171296 T + 1.88411 \times 10^{-6} T^2 + 11.57265 \quad (1)$$

The boiling point calculated from this equation is 274.04°K. (0°C. = 273.16°K.).

TABLE I

VAPOR PRESSURE OF *trans*-2-BUTENE
0°C. = 273.16°K.

T, °K.	$p_{\text{obs.}}$, cm.	$p_{\text{obs.}} - p_{\text{calcd.}}$
201.703	1.492	0.006
212.617	3.276	-.015
222.042	6.064	-.016
230.261	9.883	-.017
235.801	13.451	.002
244.857	21.437	-.002
252.159	30.358	-.004
258.901	41.047	.006
263.202	49.286	-.007
269.233	63.038	.009
274.142	76.297	-.013

Melting Point.—The melting point was observed as a function of the fraction melted by the usual procedure of introducing measured quantities of energy and allowing time for the temperature to become essentially constant. Table II contains the results at the four highest points, comparatively little premelting having occurred below the first temperature given. If Raoult's law is obeyed, the temperature plotted against the reciprocal of the fraction melted should give a straight line whose intercept at zero (infinite dilution) is the true melting point, and whose slope is proportional to the mole fraction of impurity. Figure 1 shows such a plot. The true melting point is found to be 167.61 ± 0.05°K.; the slope leads to the value 0.368% impurity, which was used to correct the heat capacities for pre-melting. Table III compares the results of this research with other values of the melting and

(10) Blaisdell, *J. Math. Phys.*, **3**, 186 (1919).

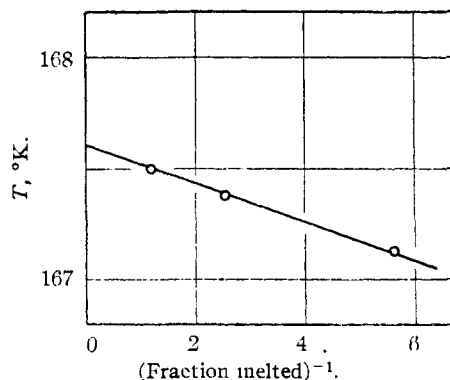


Fig. 1.

boiling points to be found in the literature. The discrepancy between the melting point of Todd and Parks and the present value is inexplicable on the basis of any reasonable limits of error in our temperature scale. Since they give no account of their method of treatment of premelting heat and extrapolation to the melting point, the difference could be ascribed to this source.

TABLE II

MELTING POINT OF *trans*-2-BUTENE

Fraction melted	T, °K.
0.030	164.759
.178	167.126
.394	167.373
.847	167.498
True melting point	167.61 ± 0.05°K.

TABLE III

MELTING AND BOILING POINTS OF *trans*-2-BUTENE

M. p. T, °K.	B. p. T, °K.	Observer
167.3	Todd and Parks ¹¹
167.3	274.09	Kistiakowsky, <i>et al.</i> ¹²
....	274.07	Lamb and Roper ¹³
167.61 ± 0.05	274.04 ± 0.05	This research
167.72 ± 0.10	Glasgow and Rossini ¹⁴

Heat Capacities.—The heat capacities were measured from about 15°K. to the boiling point in several series. Except at the extreme temperatures and in the premelting region, the error should not exceed 0.2%. In all measurements on the liquid, the calorimeter was always kept colder than its surroundings, to prevent distillation. In consequence, the radiation corrections were larger than at lower temperatures, and the accuracy less. The liquid heat capacities were corrected for vaporization into the filling line. This correction amounted to about 8% at the highest point, and decreased rapidly at lower temperatures. The experimental values, in terms of a defined calorie equal to 4.1833 Int. joules, are contained in Table

(11) S. S. Todd and G. S. Parks, *THIS JOURNAL*, **58**, 134 (1936).

(12) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935).

(13) A. B. Lamb and E. E. Roper, *ibid.*, **62**, 896 (1940).

(14) A. R. Glasgow, Jr., and F. D. Rossini, *Natl. Bur. of Standards, unpublished data.*

TABLE IV
HEAT CAPACITY OF *trans*-2-BUTENE

T, °K.	C _p , cal./deg.	T, °K.	C _p , cal./deg.
14.56	0.608	110.08	15.95 ^a
16.46	0.878	110.41	15.88 ^a
17.95	1.136	113.46	16.24 ^a
19.16	1.342	117.48	16.85 ^a
20.26	1.553	119.09	17.04 ^a
21.03	1.711	122.26	17.60 ^a
22.91	2.097	127.92	18.41 ^a
25.18	2.571	134.13	19.21 ^a
27.70	3.119	141.32	20.50 ^a
30.52	3.703	142.93	20.78 ^a
33.58	4.404	149.82	22.22 ^a
37.00	5.004	151.79	22.64 ^a
40.82	5.767	154.42	23.28 ^a
44.96	6.517	160.40	24.17 ^a
49.83	7.402	Melting point	
55.48	8.373	170.66	26.41
57.42	8.684	177.04	26.47
61.19	9.268	184.32	26.56
63.56	9.648	193.51	26.70
65.94	9.977	196.31	26.86
71.74	10.83	203.19	26.89
72.06	10.87	213.14	27.23
78.71	11.80	222.51	27.51
79.19	11.88	231.72	27.77
86.95	12.92	244.19	28.21
95.24	13.98	253.81	28.59
100.89	14.71	262.55	28.97
101.62	14.77	269.20	29.16
107.12	15.58 ^a	271.03	29.08

^a Corrected for premelting.

IV, and are plotted in Fig. 2. Heat capacities at rounded temperatures read off a smooth curve through these points are given in Table V, together with a comparison with the values of Todd and Parks.¹¹

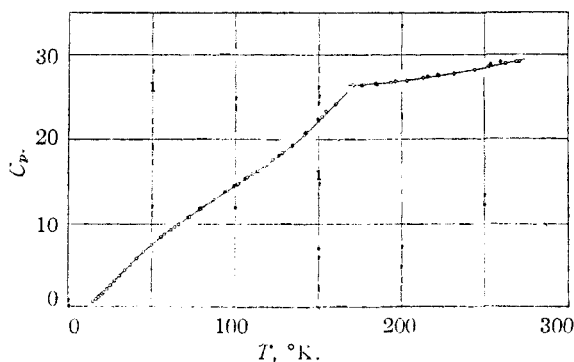


Fig. 2.

Heat of Fusion.—The customary method of determination of the heat of fusion was used, the measurements being started somewhat below the melting point and ending shortly above it. The results are summarized in Table VI.

Heat of Vaporization.—With the calorimeter slightly cooler than its surroundings, butene

TABLE V
HEAT CAPACITY OF *trans*-2-BUTENE AT ROUNDED TEMPERATURES

T, °K.	C _p , cal./deg.	Dev., (T. and P.) — (This research), %	T, °K.	C _p , cal./deg.	Dev., (T. and P.) — (This research), %
15	0.669		140	20.32	-0.1
20	1.504		150	22.34	.4
25	2.533		160	24.22	
30	3.594		Melting point		
35	4.600		170	26.40	-.4
40	5.607		180	26.53	-.3
45	6.543		190	26.67	-.1
50	7.423		200	26.89	-.1
60	9.087		210	27.14	.1
70	10.57		220	27.43	.3
80	11.99		230	27.71	.6
90	13.31	0.2	240	28.04	.8
100	14.58	.4	250	28.43	.9
110	15.85	.7	260	28.84	1.1
120	17.22	.7	270	29.24	1.3
130	18.66	.3			

TABLE VI
HEAT OF FUSION OF *trans*-2-BUTENE

Temperature interval, °K.	Cor. heat input, cal./mole	Pre-melting, cal./mole	$\int C_p dT$, cal./mole	ΔH , cal./mole
154.797-167.626	2754.8	20.7	439.7	2335.8
161.054-170.024	2610.2	36.5	315.6	2331.1
161.439-167.580	2503.6	38.5	213.4	2328.7
161.130-169.259 ^a	2579.6	37.3	285.0	2331.9
Mean			2331.9 ± 2.0	
Todd and Parks ¹¹			2356	

^a Using outside thermometer as heater.

was vaporized at a temperature near the boiling point, and condensed through a capillary system in small weighed bulbs which were cooled by liquid air. Correction was made for heat gain by radiation, for the small change in the contents of the line, and for the change in heat content of the calorimeter and liquid remaining in it, due to slight inequality of the initial and final temperatures. The butene weight was corrected to vacuum. The heats of vaporization were corrected from their average temperature to the boiling point, using the gas heat capacities of Kistakowsky and Rice.¹⁵ The results are found in Table VII. Determination 5 was given no weight because it was subject to a large uncertainty in the amount of butene vaporized. Determination 6 was given more weight than the others because conditions were such that all corrections could be made more accurately for it.

Since equation of state data have been determined for *trans*-2-butene by Roper,¹⁶ it is possible to calculate an accurate heat of vaporization from the vapor pressure Eq. 1 and the Clausius-

(15) G. B. Kistakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 618 (1940).

(16) E. E. Roper, *J. Phys. Chem.*, **44**, 836 (1940).

Clapeyron equation. This value is included, as is also the value calculated by this method from the vapor pressure equation of Kistiakowsky, *et al.*¹² The agreement is quite satisfactory.

TABLE VII
HEAT OF VAPORIZATION OF *trans*-2-BUTENE

Av. temp., °K.	Heating time, min.	Moles vap.	Cor. heat input, cal.	ΔH at T , cal./mole	ΔH at 274.04°, cal./mole
273.75	15	0.08579	465.3	5424	5421
274.24	15	.08253	448.9	5439	5441
272.44	20	.08005	434.1	5423	5409
272.88	20	.08839	482.2	5455	5445
274.60	15	.08725 ^a	478.2	5481	5486
274.61	15	.08581	467.5	5448	5453
Weighted average					5439 \pm 15
Calculated from Equation 1 and Roper's equation of state ¹⁶					5448
Calculated from the vapor pressure equation of Kistiakowsky, <i>et al.</i> , ¹² and Roper's equation of state ¹⁶					5444

^a Uncertain.

Entropy from Calorimetric Data.—For the purpose of extrapolation of the heat capacity below the lowest temperature of measurement, a Debye function of six degrees of freedom was fitted to the data. The agreement in this case was surprisingly good. The first fourteen heat capacity values extending up to 45°K. are all fitted within approximately their experimental error.

The calculation of the entropy by the usual method of graphical integration is summarized in Table VIII, which includes the corresponding values of Todd and Parks¹¹ for comparison.

TABLE VIII
THE ENTROPY OF *trans*-2-BUTENE FROM CALORIMETRIC DATA

	This research	Todd and Parks ¹¹
0–14°, $2 \times D(166/T)$	0.185	
14–167.61°, graphical	21.471	
Solid at melting point	21.66	21.41
Fusion, 2331.9/167.61	13.913	
Liquid at melting point	35.57	35.48
167.61–274.04°, graphical	13.502	
Liquid at boiling point	49.07	49.09
Vaporization, 5439/274.04	19.85	
Actual gas at boiling point	68.92	69.50
Gas imperfection	0.20	
Ideal gas at boiling point	69.12 \pm 0.3	
	cal./deg. mole	

The correction for gas imperfection was made using the data of Roper referred to previously.¹⁶ The estimate by Todd and Parks of the entropy increment from 0°K. to 90°K. is in fair agreement with the experimental value, but fortuitously so, since a later and supposedly improved estimate¹⁷ increased the extrapolation by 10%.

Comparison with Calculated Entropy.—As was explained above, the assignment of vibration frequencies is still being studied. When that work is complete the final statistical mechanical entropy calculations can be made. At present it can be said that, using the most reasonable vibration frequency values, the calorimetric entropy from Table VIII leads to a potential barrier of 1960 cal. per mole restricting the rotation of each methyl group. Dynamical calculations show that this potential barrier should give a separation of energy levels for the torsional mode of symmetry B_g very close to the value 210 cm.^{-1} observed in the Raman spectrum.¹⁸ This is strong confirmation of this barrier and is interesting also because spectral observations of torsional modes in hydrocarbons are very rare.

It has already been shown^{4,5} that a barrier near 2000 cal. per mole is in agreement with the measured entropy of propylene. Thus it is concluded that the propylene molecules are regularly oriented in their crystals. It remains to be determined how long a 1-olefin molecule must be before random orientation will occur in the crystal.

Summary

Since *trans*-2-butene is symmetrical, its entropy from low temperature calorimetry and the Third Law of Thermodynamics is free from any uncertainty due to random orientation in the crystal. The results indicate a potential barrier to methyl group rotation near 2000 cal. per mole. This confirms the similar value which has been reported for propylene, and shows that the latter molecule is regularly oriented in its crystals.

Heat capacities of solid and liquid are reported from 15 to 270°K. and vapor pressures from 200 to 274°K. The following values were obtained: melting point, 167.61 \pm 0.05°K.; heat of fusion, 2331.9 \pm 2 cal. per mole; heat of vaporization 5439 \pm 15 cal. per mole at the boiling point, 274.04 \pm 0.05°K.; entropy of ideal gas at boiling point, 69.12 \pm 0.3 cal. per degree mole.

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(17) G. S. Parks, C. H. Shomate, W. D. Kennedy and B. L. Crawford, *J. Chem. Phys.*, **5**, 339 (1937).

(18) H. Gershinowitz and E. B. Wilson, Jr., *ibid.*, **6**, 247 (1938)