

Assuming the cross sectional area of the molecule to be about 20 sq. Å., then $ab \sin \beta$ must be divided by four to give a value of 19.5 sq. Å. This unit cell, therefore, has eight molecules. Within a few tenths of an ångström, the calculated length of two fully extended molecules of hexanolamine oleate, based on analogous work on the saturated fatty acids, sodium soaps and sodium acid soaps, agrees with the value of $c \sin \beta$ here reported. The value of $\sin \beta$ is therefore close to unity. By analogy with the sodium salts of the fatty acids, this form may appropriately be called the alpha form.

The density, calculated from the unit cell parameters and $\sin \beta$ of unity, is 1.096 g./cc.—a result in agreement with known data on sodium soaps.

Summary

1. Two forms of sodium oleate are distinguished by X-ray powder diagrams.
2. The unit cell parameters of a pure sample of one of these forms of sodium oleate are obtained after fibrillation of the sample, produced by extrusion through a small orifice under pressure. The parameters agree with values previously found for the gamma forms of saturated sodium soaps.
3. Samples of sodium oleate used in previously published physicochemical investigations in this laboratory are identified by X-ray diffraction.
4. The parameters of the unit cell of hexanolamine oleate are obtained after fibrillation of the sample, as already described.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Isomerization Equilibria among the *n*-Butenes

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Knowledge of the equilibria among the three *n*-butenes at a series of temperatures is of value in the industrial use of these hydrocarbons, and also serves to verify and augment basic thermodynamic data. Equilibrium determinations for vapor phase isomerization over several catalysts, covering the range 200 to 630°, are reported in this paper. The measurements were greatly facilitated by an infrared absorption method of analysis, recently developed.¹ This method is a marked improvement over earlier methods of analysis such as distillation; the latter is difficult to do with precision because of the small differences in boiling points (1-butene, -6.3°; *trans*-2-butene, 0.9°, and *cis*-2-butene 3.6°).

Previous observations of the isomerization of *n*-butenes by McCarthy and Turkevich² at 400 and 450° using an alumina catalyst gave values for the 1-butene contents at equilibrium but did not show the amounts of *cis*- and *trans*-2-butenes. Determinations of the *cis-trans*-equilibria in thermal isomerization at 347 and 390° were made by Kistiakowsky and Smith.³ Twigg⁴ gave a value of 7% for the equilibrium content of 1-butene at about 100° (65–126°) based on isomerization over nickel in the presence of hydrogen. Approximate equilibrium ratios of all three *n*-butenes at 350 to 450° were given by Frey and Huppke⁵ on the basis of low temperature distillation analyses of the

products from dehydrogenation of *n*-butane over chromic oxide. None of these studies, however, furnished accurate equilibrium distributions, or results over a wide range of temperature.

Experimental

Isomerizations were effected by flowing the *n*-butenes over granular catalysts in an electrically heated tube. Temperatures were automatically controlled, and were held within 3° of the specified values in the outlet portion of the catalyst bed. Catalyst volumes varied from 15 to 100 cc. Flow rates were chosen, with the help of experimental results not reported here in detail, to produce essentially equilibrium conversions. The pressure was atmospheric throughout. After the gases had passed through the catalyst they were separated from the small amount of liquid product, if there was any, and analyzed. In most runs a butene fraction for infrared analysis was separated by low temperature distillation, but in some experiments the amount of side reaction was so small that this proved to be unnecessary. Thus, products from experiments at 250° and LHSV 1, at 350° and LHSV 4, and at 450° and LHSV 8, were not usually distilled prior to analysis (LHSV = liquid hourly space velocity = flow rate, volumes *n*-butene as liquid per volume of catalyst per hour).

Side reactions observed were polymerization at the lower temperatures, cracking and isomerization to isobutene at the higher temperatures, and dehydrogenation at the highest temperature. The extent of side reactions was below 20%, and often below 2%, except in the experiments at 630°, where there was about 30% side reaction, chiefly dehydrogenation to butadiene. The extents to which these side reactions cause the apparent equilibria to differ from true equilibria are difficult to estimate without rate data. From unreported experiments in which isomerization was incomplete, it is estimated that the slowest of the six isomerization rates was at least ten times as fast as the rate of disappearance of *n*-butenes through side reactions. Therefore, according to the considerations of Bates,⁶ the equilibrium constants cannot be in error by more than 10%.

(1) R. R. Brattain, R. S. Rasmussen and A. M. Cravath, *J. Applied Phys.*, **14**, 418 (1943); R. R. Brattain and O. Beek, *ibid.*, **13**, 699 (1942).

(2) W. W. McCarthy and J. Turkevich, *J. Chem. Phys.*, **12**, 405 (1944).

(3) G. B. Kistiakowsky and W. R. Smith, *THIS JOURNAL*, **58**, 766 (1936).

(4) G. H. Twigg, *Proc. Roy. Soc. (London)*, **A178**, 106 (1941).

(5) F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

(6) J. R. Bates, "Effect of Side Reactions on Experimental Isomerization Equilibria," Petroleum Division Papers, American Chemical Society Meeting, New York, September, 1944.

Feed stock compositions are given in Table I. Three catalysts were used, identified as follows. Catalyst A was a silica-alumina-magnesia catalyst of the type used for cracking hydrocarbons, obtained from the National Aluminate Corporation, Chicago. It was designated Nalco No. 300 by the manufacturer. Our analysis showed 17.1% Al₂O₃ and 7.7% MgO. B was "Porocel" bauxite from the Porocel Corporation, Philadelphia. It was an 8 to 14 mesh size, and was calcined for one hour at 700° before use. C was a catalyst effective for the dehydrogenation of *n*-butenes to butadiene. Catalyst B could have been used at 610-630° in place of C, if steam had been omitted and an LHSV of about 20 employed.

TABLE I

No. Mole %	<i>n</i> -BUTENE FEEDS FOR ISOMERIZATION							
	→ 1	2	3	4	5	6	7	8
<i>i</i> -C ₄ H ₈	1.0	0.0	0.7	..	0.3
1-C ₄ H ₈	93.0	1.7	99.3	..	.1	24	1	0
<i>i</i> -2-C ₄ H ₈	5.1	85.5	0.0	5.3	65.2	19	58	19
<i>c</i> -2-C ₄ H ₈	0.6	12.4	.0	94.7	33.9	57	41	81
C ₄ H ₁₀	.3	0.4	.0	..	0.5

Discussion

Results of experiments are summarized in Table II, and the distributions of the gaseous olefins are plotted in Fig. 1. The equilibria are well

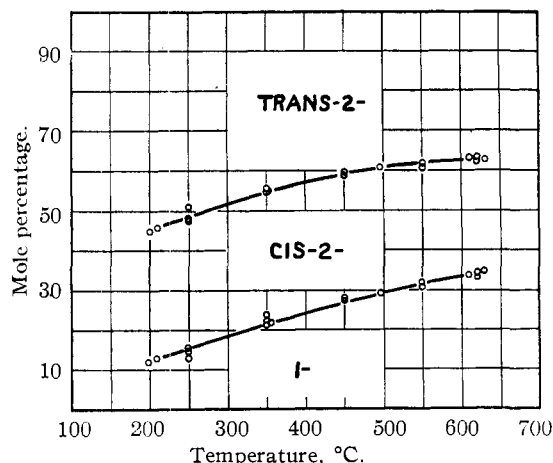
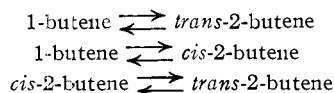


Fig. 1.—Distribution of isomeric *n*-butenes at equilibrium.

defined for practical purposes. Values reported by others are in fair agreement with those found here. McCarthy and Turkevich² gave 25.5% 1-butene at 450°, and the present result is 27.0%. The points of Twigg⁴ and of Frey and Huppke⁵ also fall fairly well in line. Kistiakowsky and Smith³ reported a value of 1.12 for the ratio of *trans* to *cis*, based on melting point determinations on products from thermal isomerization at 390°, while our result is 1.3 to 1.4 at the same temperature; their analysis may have been affected by slight thermal conversion to 1-butene.

The three reactions involved in the isomerization of the *n*-butenes are



For these we may write

$$\begin{aligned}
 K_{1t} &= [\textit{trans}\text{-}]/[1\text{-}] \\
 K_{1c} &= [\textit{cis}\text{-}]/[1\text{-}] \\
 K_{ct} &= [\textit{trans}\text{-}]/[\textit{cis}\text{-}] = K_{1t}/K_{1c}
 \end{aligned}$$

Here [*trans*-] stands for the activity of *trans*-2-butene, etc. The measured partial pressures are used to represent activities with adequate accuracy. Free energy changes for the reactions may be computed from the equations $\Delta F_{it}^\circ = -RT \ln K_{1t}$, etc. Figures 2, 3 and 4 show the resulting ΔF° values as functions of temperature.

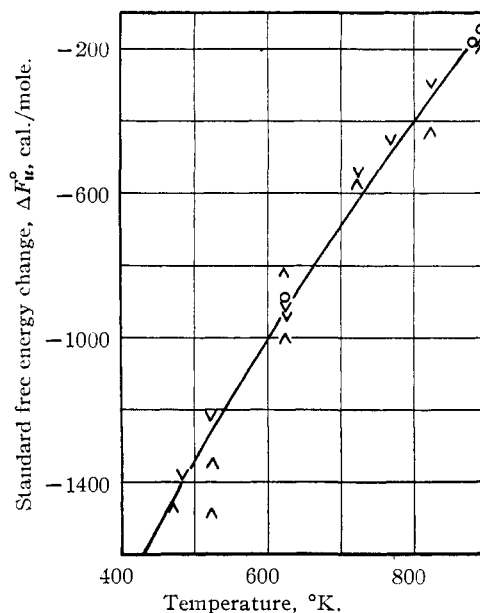


Fig. 2.—Free energy change for the reaction 1-butene → *trans*-2-butene.

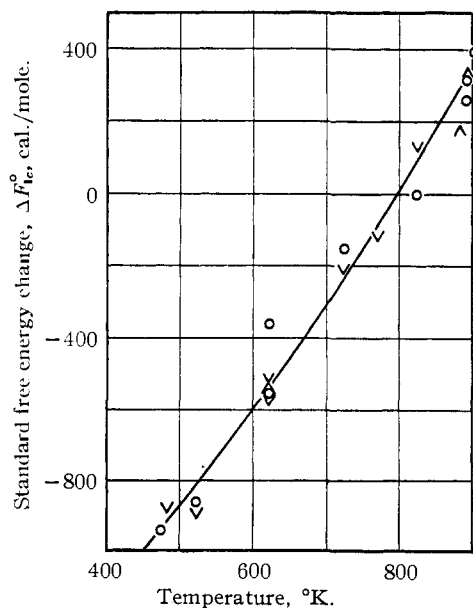


Fig. 3.—Free energy change for the reaction 1-butene → *cis*-2-butene.

TABLE II
 RESULTS OF *n*-BUTENE ISOMERIZATION EXPERIMENTS

Temp., °C.	No.	Feed Type	Catalyst	Flow rate, as LHSV ^a	Gas product, mole % on <i>n</i> -butene basis			Free energy change in cal./mole		
					1-C ₄ H ₈	<i>t</i> -2-C ₄ H ₈	<i>c</i> -2-C ₄ H ₈	ΔF_{it}°	ΔF_{ic}°	ΔF_{ct}°
200	5	<i>t</i> -2	A	0.5	11.8	55.7	32.5	-1460	-955	-505
210	1	1	A	0.5	12.8	54.6	32.6	-1400	-900	-500
250	2	<i>t</i> -2	B	1	14.5	52.3	33.2	-1340	-870	-470
250	2	<i>t</i> -2	B	1	12.7	52.9	34.4	-1480	-1040	-440
250	3	1	B	1	15.0	49.0	36.0	-1230	-910	-320
350	3	1	B	4	21.4	44.8	33.8	-910	-570	-340
352	1	1	B	1	21.4	45.9	32.7	-950	-530	-420
350	5	<i>t</i> -2	B	1	20.9	46.3	32.8	-985	-560	-425
350	2	<i>t</i> -2	B	4	23.6	45.0	31.4	-800	-360	-440
350	4	<i>c</i> -2	B	4	21.7	44.7	33.6	-895	-540	-355
450	2	<i>t</i> -2	B	8	27.9	41.2	30.9	-560	-150	-410
450	3	1	B	8	27.4	40.5	32.1	-560	-230	-330
495	3	1	B	19	29.0	39.4	31.6	-465	-135	-330
550	5	<i>t</i> -2	B	16	30.4	39.3	30.3	-415	0	-415
553	1	1	B	16	31.9	38.5	29.6	-310	120	-430
610	6	<i>c</i> -2	C	2 ^b	33.2	37.0	29.8	-180	195	-375
620	8	<i>c</i> -2	C	2 ^b	34.4	37.5	28.1	-150	350	-500
620	7	<i>t</i> -2	C	2 ^b	34.0	37.8	28.2	-185	335	-520
620	7	<i>t</i> -2	C	2 ^b	33.9	36.8	29.3	-150	265	-415
630	7	<i>t</i> -2	C	2 ^b	34.8	37.5	27.7	-140	400	-540

^a Liquid hourly space velocity at which hydrocarbon was fed to the catalyst. ^b For butenes. Steam diluent also present.

The points drawn as arrowheads indicate the direction of approach to equilibrium; the tips of the arrowheads represent the actual values. Unreported experiments that did not reach equilibrium showed that starting with 1-butene led to an approach to the *cis-trans* equilibrium from the *cis* side. Circular points are used where the direction of approach is uncertain. Thus, when *trans*-2-butene was fed, the direction of approach in the 1- to *cis* conversion was not certain. There was evidence, however, that *cis* was produced from *trans* about as fast as was the 1-butene, and therefore equilibrium in the *trans* to 1-reaction meant that the 1- to *cis* reaction was also close to equilibrium. The deviations of points that do not fall on the curves in the figures may be explained by failure to reach equilibrium in some experiments, and by analytical errors in others.

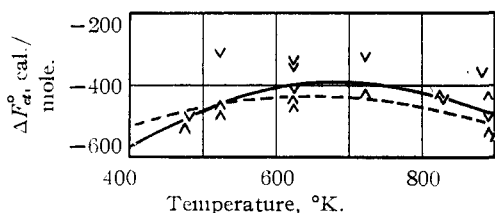


Fig. 4.—Free energy change for the reaction *cis*-2-butene \rightarrow *trans*-2-butene. The solid line is drawn to represent the experimental points. The dotted line is from the equation $\Delta F_{ct}^{\circ} = -1395 + 2.64T - 1.49T \ln(T/298)$.

The isomerization results reported here are useful in computing reaction equilibria for other reactions involving the *n*-butenes. For example,

in computing equilibrium in the dehydrogenation of *n*-butane from free energy values, it is necessary to consider that all three forms of *n*-butene are in equilibrium if the reaction conditions cause isomerization. It is then convenient, and often most accurate, to do this by first computing the equilibrium between *n*-butane and the one *n*-butene for which the best basic thermodynamic data exist. Subsequently the effect of the existence of the other *n*-butenes can be taken into account by making proper use of the isomerization equilibrium constants. For convenience, Table III gives values of these constants taken from the smooth free energy curves of Figs. 2, 3 and 4.

TABLE III
EQUILIBRIUM CONSTANTS FOR ISOMERIZATION
Smoothed values from ΔF° curves.

Temperature °K.	Temperature °C.	Equilibrium constants		
		K_{it}	K_{ic}	K_{ct}
400	127	8.26	4.09 ^a	2.02 ^a
500	227	3.86	2.43	1.59
600	327	2.31	1.65	1.40
700	427	1.64	1.25	1.31
800	527	1.29	0.99	1.30
900	627	1.08	.82	1.32

^a Extrapolated.

Although Fig. 2 and 3 indicate some curvature for the free energy changes as functions of temperature in the 1- to *trans* and 1- to *cis* isomerizations, the accuracy of the data does not warrant attempts to draw further conclusions from this curvature in the absence of accurate ΔC_p values.

Linear equations that furnish good approximations are

$$\Delta F_{1i}^{\circ} = -2875 + 3.05T$$

$$\Delta F_{1c}^{\circ} = -2370 + 3.00T$$

If these are considered to be of the form

$$\Delta F^{\circ} = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ}$$

which is valid over a moderate temperature range if $\Delta C_p = 0$, then the constant terms may be compared with the ΔH° values from thermochemistry. The comparison below shows fair agreement, considering the possible errors of about ± 200 calories for both sets of data.

Reaction	Constant term in ΔF° eqn.	Thermo- chemical ΔH_{298}° , cal./mole ⁷
1- \rightarrow <i>trans</i> -	-2875	-2720
1- \rightarrow <i>cis</i> -	-2370	-1770
<i>cis</i> - \rightarrow <i>trans</i> - (by diff.)	- 505	- 950

Actually the ΔC_p values are not likely to be zero. For the *cis* and *trans* isomers experimental values are available for the range 25 to 98° from the work of Kistiakowsky and Rice,⁸ and these values lead to a constant ΔC_p of 1.49 for the reaction *cis* \rightarrow *trans*. Accurate heat capacity measurements have not been made on 1-butene. If it is assumed that ΔC_p for the *cis* to *trans* isomerization is constant over a wider range than 25-98°, then the equation

$$\Delta F_T^{\circ} = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ} + \Delta C_p(T - 298) - T \Delta C_p (\ln T - \ln 298)$$

may be used. Substituting the thermochemical value of -950 for ΔH_{298}° , this equation leads to $\Delta S_{298}^{\circ} = -1.0$ to -1.3 , which is between -0.6 proposed by Pitzer and -2.0 derived from Parks' third law determinations.⁹ Taking $\Delta S_{298}^{\circ} = -1.15$ as an average, the above equation becomes

$$\Delta F_{ci}^{\circ} = -1395 + 2.64T - 1.49T \ln (T/298)$$

which is plotted as a dotted line in Fig. 4, and seems to represent the experimental results fairly well.

Recently third law measurements and spectro-

(7) F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940).

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

(9) See K. S. Pitzer, *ibid.*, **5**, 473 (1937); R. H. Ewell, *Ind. Eng. Chem.*, **32**, 781 (1940).

scopic calculations for *cis*-2-butene were published by Scott and co-workers,¹⁰ and were combined by them with similar but unpublished data for *trans*-2-butene to give free energy changes for the isomerization reaction. These computations show a maximum in the free energy change at about 600°K. like that represented in Fig. 4, but the value of ΔF° at 600°K. is -675 cal. instead of -400 cal. found in the present work. The computed equilibrium constants are therefore appreciably greater than those observed here. It is disappointing that this careful treatment by Scott and co-workers does not give results agreeing as well with experiment as the more arbitrarily derived sets of free energy data published previously.¹¹ Distributions of the *n*-butenes calculated from these older sets of data agree fairly well with the experimental values in Fig. 1,¹² especially for the data of Frost^{11d} and Ewell.^{11b}

Acknowledgment of the collaboration of Messrs. R. R. Brattain and R. S. Rasmussen, of these Laboratories, who supervised the infrared analyses, is gratefully recorded.

Summary

1. Isomerization equilibria among the three *n*-butenes have been measured in the vapor phase at 200 to 630°. *trans*-2-Butene is the most stable isomer at the lower temperature, but 1-butene and *cis*-2-butene are nearly as stable at the higher temperature.

2. Equilibrium constants and free energy changes for the isomerization reactions are given. The results are compared with thermochemical measurements and with data derived from the third law of thermodynamics and spectroscopic observations.

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(10) R. B. Scott, W. J. Ferguson and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **33**, 1 (1944).

(11) (a) A. W. Francis in "Science of Petroleum," Vol. III, Oxford Univ. Press, 1938; p. 2088; (b) R. H. Ewell, *Ind. Eng. Chem.*, **32**, 778 (1940); (c) C. M. Thacker, H. O. Folkins and E. L. Miller, *ibid.*, **33**, 584 (1941); (d) A. V. Frost, *J. Gen. Chem. U.S.S.R.*, **9**, 1813 (1939); *Refiner Natural Gasoline Mfr.*, Jan. (1941).

(12) NOTE ADDED IN PROOF: The recent data compiled by the A.P.I. Research Project 44 at the National Bureau of Standards are in very good agreement with the present measurements (Table 8x, Dec. 31, 1944). The data just published by Aston, *et al.*, *J. Chem. Phys.*, **14**, 67 (1946), do not agree as well.