

The Isomerization of nButane-1C13

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be about thirty fringes from flat. The angle was reduced 0.3 percent to $18^{\circ} 33'$ although the deviation for a given wave-length was almost the same as before, corresponding to a change in index ($\lambda = 5770\text{\AA}$) from 2.6396 to 2.6444. The quality of the visible spectrum was considerably reduced. This deterioration plus the wide slits used reduced the resolving power to about 10 wave numbers at 30 microns. The deterioration of KRS-5 certainly warrants further study if it is to be used extensively as a prism material.

† Assistance is gratefully acknowledged to the Engineer Research and Development Laboratories under a contract between them and the Baird Associates, and to the Office of Naval Research under Contract NSori-76, T.O. V., with Harvard University. Our first prism was obtained through the kindness of Dr. P. H. Egli of the Naval Research Laboratory while the one currently in use, obtained from the Baird Associates, was cut and polished by F. Cooke (see J. Opt. Soc. Am. **37**, 984(A) (1947)) from ERDL Batch No. 23-2.

¹ O. F. Tuttle and P. H. Egli, J. Chem. Phys. **14**, 571 (1946).

² E. K. Plyler, J. Chem. Phys. **15**, 885 (1947).

³ Gershinowitz and Wilson, J. Chem. Phys. **6**, 247 (1938).

The Isomerization of *n*-Butane-1-C¹³

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May 24, 1948

IN a recent note,¹ data were presented showing that propane-1-C¹³ is reversibly converted into propane-2-C¹³ by an exclusively intramolecular mechanism in the presence of a water promoted aluminum bromide catalyst at *ca.* 25°C. An investigation of the reactions of *n*-butane-1-C¹³ in the presence of such a catalyst and at the same temperature has been carried out, using the same general methods previously outlined. The mass spectrometric analyses were supplemented, as needed, by low temperature distillation through a high efficiency Podbielniak column and infra-red spectrophotometric analyses.

The compositions of the initial normal butane and of the product after 12 and 1180 hours contact with the catalyst are given in Table 1. The product recovered after 12 hours reaction corresponds to 11.6 percent conversion of normal to isobutane, while that after 1180 hours corresponds approximately to the accepted equilibrium composition at 25°C.

It will be noted that the concentration of butane-C₂¹³ underwent no change in 1180 hours. Since at intermolecular redistribution equilibrium the concentration of butane-C₂¹³ would be 0.0131, it is apparent that, as was found to be the case for propane isomerization, the butane isomerization is exclusively intramolecular with respect to carbon atoms.

Comparison of the composition of the 12-hour product with the initial material reveals the *n*-butane-2-C¹³, *i*-butane-1-C¹³, and *i*-butane-2-C¹³ to have been formed from the *n*-butane-1-C¹³ in the ratios 2:3:1, respectively. These relative rates of formation of the three isomers of *n*-butane-1-C¹³ are in the ratio of their random statistical weights. Such rates of formation are most easily explained

TABLE I. The isomerization of butane, catalyzed by aluminum bromide at 25°C.

Substance	Mole fraction		
	<i>t</i> = 0 hours	12 hours	1180 hours
<i>n</i> -C ₄ H ₁₀ -C ₉ ¹³	0.809	0.715	0.166
<i>i</i> -C ₄ H ₁₀ -C ₉ ¹³	0.000	0.094	0.643
<i>n</i> -C ₄ H ₁₀ -1-C ₁ ¹³	0.169 ₈	.136 ₈	0.020 ₄
<i>n</i> -C ₄ H ₁₀ -2-C ₁ ¹³	0.016 ₄	.027 ₇	0.017 ₃
<i>i</i> -C ₄ H ₁₀ -1-C ₁ ¹³	0.000 ₀	0.016 ₂	0.110 ₉
<i>i</i> -C ₄ H ₁₀ -2-C ₁ ¹³	0.000 ₀	0.005 ₄	0.036 ₉
C ₄ H ₁₀ -C ₂ ¹³	0.005 ₂	0.005 ₂	0.095 ₃

in terms of a single activated complex which may rearrange at random into the four butane-C¹³ isomers.

The results of these experiments provide no experimental basis for theories of the paraffin isomerization reaction which postulate attack of the molecule at a particular point, followed by the migration of a methyl group. Rather the experiments point toward a general activation of the molecule as a whole.

A comprehensive paper describing the synthesis of the various isotopic propanes and butanes, the analytical methods, and isomerization experiments is in preparation and will be submitted for publication in the near future.

¹ O. Beeck *et al.*, J. Chem. Phys. **16**, 255 (1948).

Free Volumes of the Metallic Elements at Their Melting Points

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May 17, 1948

THE free volume model for the liquid and solid state has found application in various semi-empirical treatments of physico-chemical phenomena.¹⁻⁵ Eyring and co-workers^{1,3,4} have given several equations for the free volume of a liquid, whereas Lennard-Jones² has derived an expression for the free volume of a solid in terms of the characteristic vibration frequency of the solid. The Kincaid-Eyring⁴ formula for the free volume leads to results identical with those calculated from the Lennard-Jones equation² for a number of metallic elements at room temperature.⁶

It has been shown recently that the Lennard-Jones expression for the free volume can be obtained from a rate process treatment of melting by requiring that the free volume model for a liquid leads to the same result as a treatment based on the Einstein approximation of the solid.⁶ This derivation of the Lennard-Jones formula for the free volume of a solid suggests application of this formula to a determination of the free volume at the melting point. Accordingly the free volumes v_f at the melting point have been calculated for a number of metallic elements by use of the relation

$$v_f = (RT/2\pi M\nu^2)^{1/3}, \quad (1)$$

where R is the molar gas constant, T is the absolute temperature, M represents the atomic weight, and ν is the

TABLE I. The free volumes of the metallic elements at their melting points.

Element	Melting Point (°K)	$v_f \times 10^{27}$ (cc)	$v \times 10^{24}$ (cc)	$(v_f/v) \times 10^3$
Li	459	22.3*	21.7**	1.0**
Na	371	102	38.7	2.6
K	335	133	78.6	1.7
Cu	1356	16.7	13.3	1.3
Ag	1234	20.6	19.2	1.1
Au	1336	19.1	19.0	1.0
Be	1557	12.0	8.10**	1.5**
Mg	924	50.9	25.2	2.0
Ca	1083	61.2	42.9**	1.4**
Sr	1073	46.3	56.0**	0.83**
Zn	693	11.7	15.7	0.75
Cd	594	12.7	23.3	0.54
Hg	234	7.56	23.5	0.32
Cr	1888	10.2	12.5**	0.81**
Mn	1533	18.2	12.7**	1.4**
Fe	1808	13.2	13.4	0.98
Co	1753	15.1	11.0**	1.4**
Ni	1725	16.0	11.0**	1.5**
Mo	2893	16.0	15.6**	1.0**
Ru	>2223	>8.47	14.0**	>0.61**
Rh	2228	10.6	14.1**	0.75**
Pd	1828	18.1	16.1	1.1
Al	933	18.2	18.8	0.97
Ga	304	24.7	19.6**	1.3**
In	428	38.2	25.9**	1.5**
Tl	577	25.1	30.9	0.81
La	1099	35.0	37.5**	0.93**
Ti	2073	35.2	17.7**	2.0**
Zr	1973	24.3	23.7**	1.0**
Hf	>1975	>20.2	22.3**	>0.90**
Ge	1232	15.2	22.5**	0.68**
Pb	601	38.4	33.4	1.1
Sb	904	39.1	30.9	1.3
Bi	544	22.3	34.4	0.65
Ta	3123	25.9	18.1**	1.4**
W	3643	15.7	15.8**	0.99**
Re	3713	17.5	14.5	1.2
Os	2973	21.0	14.1**	1.5**
Ir	2623	11.5	14.3	0.80**
Pt	2028	15.6	17.1	0.91

* Since Seitz (See reference 7.) does not give the value for the characteristic vibration frequency of lithium, the value given in the Landolt-Börnstein Tabellen was used.

** Calculated by use of the room-temperature value for the density.

characteristic vibration frequency of the element under discussion. The value of ν was obtained from a compilation of the Debye characteristic temperatures given by Seitz.⁷

The total volume per molecule v , at the melting point, is given by the relation

$$v = M/N\rho \quad (2)$$

where N is the Avogadro number and ρ is the density at the melting point. The calculated values of v_f , v , and the ratio v_f/v are summarized in Table I. For the elements for which the densities at the melting point were not readily available, the densities at room temperature were used. Use of room-temperature values for the density will yield values for v which are too small and values for v_f/v which are too large but will not alter the order of magnitude of the calculated results.

Reference to the values listed in Table I shows that the calculated free volumes at the melting point generally lie between 10×10^{-27} and 50×10^{-27} cc, whereas the free volumes per molecule at the melting point divided by the respective total volumes per molecule at the melting point are of the order of 10^{-3} for all of the elements listed. Some of the alkali metals have relatively large free volumes at the melting point, whereas mercury, cadmium, and germanium have relatively small free volumes at the melting point. A more detailed analysis indicates some regularities in the dependence of v_f/v on atomic number. Reference to Table I shows that for the elements of the first and second groups of the periodic system the ratio v_f/v decreases regularly with increasing atomic number except for the first member of each series. The behavior of the elements in the other groups of the periodic system appears to be less regular although some of the discrepancies may be removed if the densities at the melting points are used for each of the elements.

¹ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, New York, 1941).

² J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)* **A163**, 53 (1937); *ibid.* **A165**, 1 (1938); *ibid.* **A169**, 317 (1939); *ibid.* **A170**, 464 (1939); J. E. Lennard-Jones, *Proc. Phys. Soc. (London)* **52**, 729 (1940).

³ H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.* **41**, 249 (1937).

⁴ J. F. Kincaid and H. Eyring, *J. Chem. Phys.* **6**, 620 (1938).

⁵ T. L. Hill, *J. Phys. and Colloid Chem.* **51**, 1219 (1947).

⁶ S. S. Penner, to appear shortly in the *Journal of Physical and Colloid Chemistry*.

⁷ F. Seitz, Table XXXIV, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, New York, 1940).