concentration of deuterium is in accord with the experiments with maleic acid, and the same mechanism may be responsible. Such high deuterium concentration in the β position is most striking, as the keto–enol mechanism would tend to introduce normal hydrogen from the water into this position. The β hydrogen atoms of the dissolved keto glutaric acid seem to have exchanged with the deuterium of the gas phase.

DEPARTMENT OF BIOCHEMISTRY D. RITTENBERG
COLLEGE OF PHYSICIANS AND SURGEONS S. RATNER
COLUMBIA UNIVERSITY HENRY D. HOBERMAN
NEW YORK CITY

RECEIVED JULY 20, 1940

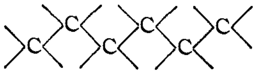
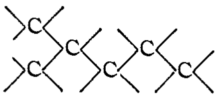
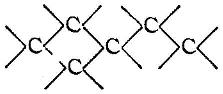
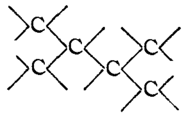
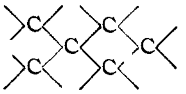
ENERGIES OF ISOMERIZATION OF THE FIVE HEXANES

Sir:

Data obtained in this Laboratory on the heats of combustion of each of the five isomeric hexanes[1] lead to the values given in Table I for the energies of isomerization at 25°, for both the liquid and the gaseous states, expressed in terms of the relative energy content referred to normal hexane as zero, with each substance in its thermodynamic standard state.

TABLE I

RELATIVE ENERGY CONTENTS OF THE FIVE HEXANES AT 25°

Isomer	Skeleton structure	Relative energy content[a] $E°$ (isomer) − $E°$ (n-hexane) Liquid, kcal./mole	Gas, kcal./mole
n-Hexane		0	0
2-Methylpentane		−1335 ± 160	−1748 ± 200
3-Methylpentane		− 754 ± 160	−1069 ± 200
2,3-Dimethylbutane		−1964 ± 160	−2546 ± 200
2,2-Dimethylbutane		−3446 ± 160	−4375 ± 200

[a] See footnotes *a* and *b* of Table II.

These data (see column 1 of Table II for the same quantities converted to 0°K.) indicate that (1) as was expected on the basis of the data previously reported for the butanes[2] and the pentanes,[3,4] there are important differences in the energy contents of these isomers; (2) contrary to what might have been expected on the basis of the values previously reported for normal butane and 2-methylpropane (isobutane) and for normal pentane and 2-methylbutane, there is a significant difference in energy content between 2-methylpentane and 3-methylpentane; (3) the difference in energy content between normal hexane and 2,3-methylbutane is roughly the sum of the differences in energy content between normal hexane and 2-methylpentane and between normal hexane and 3-methylpentane; (4) the difference in energy content between normal hexane and 2,2-dimethylbutane is roughly the same as that between normal pentane and 2,2-dimethylpropane (tetramethylmethane or neopentane).

When combined with the appropriate values of $H - H_0°$ and of $(H_0° - F°)/T$ as calculated by Pitzer,[5] these data yield the thermodynamic values given in Table II. Columns 2, 3, 4, and 5 give, for 0, 298, 600, and 1000°K., values for $H°$ (isomer) − $H°$ (n-hexane), which is the increment in heat content for the reaction, $n\text{-}C_6H_{14} = i\text{-}C_6H_{14}$; columns 6, 7, and 8 give, for 298, 600, and 1000°K., values for $F°/T$(isomer) − $F°/T$ (n-hexane), which when multiplied by

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[1] E. J. R. Prosen and F. D. Rossini, forthcoming paper in *J. Research Natl. Bur. Standards.*

(2) F. D. Rossini, *J. Research Natl. Bur. Standards*, **15**, 357 (1935).

(3) F. D. Rossini, *ibid.*, **13**, 21 (1934).

(4) J. W. Knowlton and F. D. Rossini, *ibid.*, **22**, 415 (1939).

(5) K. S. Pitzer, *Chem. Rev.*, **27**, August (1940).

TABLE II

SUMMARY OF THERMODYNAMIC VALUES FOR THE FIVE HEXANES IN THE GASEOUS STATE[a,b]

Isomer	$H°$ (isomer) − $H°$ (n-hexane), cal./mole 0°K.	298°K.	600°K.	1000°K.	$F°/T$ (isomer) − $F°/T$ (n-hexane), cal./deg. mole 298°K.	600°K.	1000°K.	Relative amounts present at equilibrium 298°K.	600°K.	1000°K.
n-Hexane (g)	0	0	0	0	0	0	0	1.0	1.0	1.0
2-Methylpentane (g)	−1108 ± 220	−1748 ± 200	−1468	−1248	−3.56 ± 0.77	−0.85	+0.17	6.0 ± 2.3	1.5	0.9
3-Methylpentane (g)	− 399 ± 220	−1069 ± 200	− 759	− 339	−1.18 ± 0.77	+0.43	+0.88	1.8 ± 0.7	0.8	0.7
2,3-Dimethylbutane (g)	−1856 ± 220	−2546 ± 200	−2016	−1596	−2.67 ± 0.77	+1.20	+2.52	3.8 ± 1.5	0.6	0.3
2,2-Dimethylbutane (g)	−3535 ± 220	−4375 ± 200	−4095	−3375	−8.00 ± 0.77	−0.80	+1.75	56 ± 22	1.5	0.4

[a] The values of energy are given in terms of the artificial calorie defined as equal to 4.1833 international joules. [b] The uncertainty in the difference in heat content or free energy between any two isomers is substantially the same as that given here for the difference between normal hexane and each of the other isomers.

T become values for the standard free energy change for the reaction, $n\text{-}C_6H_{14} = i\text{-}C_6H_{14}$; columns 9, 10, and 11 give values for the relative amounts of each of the five isomers present at equilibrium with one another at 298, 600, and 1000°K., with the amount of normal hexane taken as unity. Estimated uncertainties are assigned to the values for 0 and 298°K., the uncertainties for 600 and 1000°K. will be greater.

NATIONAL BUREAU OF STANDARDS FREDERICK D. ROSSINI
WASHINGTON, D. C. EDWARD J. R. PROSEN

RECEIVED JULY 5, 1940

UNSATURATED FAT OXIDASE

Sir:

In 1928 R. Bohn and L. W. Haas found that the soy bean, navy bean and other beans contain an enzyme which oxidizes carotene and unsaturated fats. They obtained and assigned patents to the J. R. Short Milling Company of Chicago for bleaching of wheat flour by this method. Recently J. B. Sumner and A. L. Dounce [*Enzymologia*, **7**, 190 (1939)] verified the claims of Bohn and Haas and stated that the carotene oxidase present in soy meal also oxidizes xanthophyll of egg yolk.

The following experiments show that carotene oxidase as described by these authors does not exist and that the oxidation of carotene is caused indirectly by an "unsaturated fat oxidase." To 30 cc. of water, 2 g. of soy meal and 0.15 cc. of commercial carotene in vegetable oil (a mixture of α- and β-carotene) was added. A second enzyme sample was prepared containing 0.03 mg. of crystalline β-carotene in 0.15 cc. of mineral oil and to a third sample containing 0.03 mg. of crystalline β-carotene in 0.15 cc. of mineral oil, 0.15 cc. of olive oil was added. All samples of course contained 2 g. of soy meal. To all samples 10 cc. of 0.1 M phosphate of pH 6.5 was added and they were mechanically shaken in open containers at 23°. The sample with the commercial carotene in vegetable oil was completely oxidized (disappearance of yellow color) in thirty minutes. The sample with crystalline carotene and added olive oil was oxidized in sixty minutes, whereas the sample which contained crystalline carotene without olive oil remained unchanged for at least three hours. In the presence of fat gaseous oxygen was taken up rapidly when the reaction was measured in the Warburg–Barcroft respirometer. When crystalline β-carotene in mineral oil was employed, however, no oxygen was consumed and the color of the enzyme solution remained yellow.

These results show that the oxidation of carotene, and probably also the oxidation of xanthophyll, is dependent upon the simultaneous oxidation of unsaturated fats. The unsaturated fats are oxidized (probably to peroxides) by the *unsaturated fat oxidase* and the products of oxidation in turn oxidize the carotenoids.

I am grateful to Professor L. Zechmeister of the California Institute of Technology for a generous sample of crystalline β-carotene, and to the Short Milling Company for supplying me with soy meal.

LONG ISLAND CITY, N. Y. HENRY TAUBER

RECEIVED JUNE 12, 1940

IMPROVED SYNTHESIS OF PANTOTHENIC ACID

Sir:

A method of synthesis of pantothenic acid has been described[1,2] in which β-alanine ester was

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(1) Woolley, Waisman and Elvehjem, THIS JOURNAL, **61**, 977 (1939).

(2) Woolley, *J. Biol. Chem.*, **134**, 461 (1940).