

To compute the contributions to the thermodynamic functions of tautomerism and anharmonicity, it was necessary to evaluate three parameters from experimental values of C_p° at four temperatures. The parameters selected simultaneously to fit the calorimetric data were: $\Delta H(\text{chair} \rightarrow \text{boat}) = 4020 \text{ cal. mole}^{-1}$, $\nu = 1025 \text{ cm.}^{-1}$ and $Z = 8.17 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. Comparisons of the experimental and calculated values of S° and C_p° are made in Table XI. Because the calculated values of C_p° were not sensitive to simultaneous variations of the adjustable parameters, the division of the total contribution of anharmonicity and tautomerism into the individual contributions listed in Table XI was somewhat arbitrary. However, the value used for $\Delta H(\text{chair} \rightarrow \text{boat})$ is of the same order of magnitude as that used for cyclohexane, 5600 cal. mole⁻¹.³⁰ Also, if the effect of anharmonicity was neglected, no choice of $\Delta H(\text{chair} \rightarrow \text{boat})$ gave

satisfactory agreement between the calculated and experimental values of C_p° .

The Chemical Thermodynamic Properties.—

The vibrational assignment, product of principal moments of inertia and other parameters discussed in the preceding sections were used to compute values of the thermodynamic functions of thiacyclohexane at selected temperatures to 1000°K. The results of these calculations are given in Table XII.

The data of Tables IX and XII were used with thermodynamic data for C(graphite),²³ H₂(gas)²³ and S₂(gas)²⁶ to compute values of the standard heat, ΔH_f° , standard free energy, ΔF_f° , and common logarithm of the equilibrium constant, $\log_{10} K_f$, for the formation of thiacyclohexane from the elements. Values of these functions at selected temperatures to 1000°K. are included in Table XII.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Physical and Thermodynamic Properties of Terpenes. II. The Heats of Combustion of Some Terpene Hydrocarbons

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The heats of combustion of α -pinene, β -pinene, dipentene, *d*-limonene, *cis*-alloöcimene and myrcene, in the liquid state, were measured in a bomb calorimeter. The samples, of known purity, were enclosed in thin glass bulbs, placed in a platinum crucible in an illium bomb together with 30 atmospheres of oxygen, and ignited by means of an iron fuse wire. The amount of reaction was based on the weight of carbon dioxide formed in the combustion. Tests were made for incomplete combustion by analyzing for carbon monoxide. The calorimeter was calibrated with benzoic acid. The heats of combustion were reported in kcal./mole at 25° for the reactants and products in their standard states. The following values were obtained: α -pinene, $1483.0 \pm 0.25 \text{ kcal./mole}$; β -pinene, $1485.1 \pm 0.34 \text{ kcal./mole}$; *d*-limonene, $1473.9 \pm 0.27 \text{ kcal./mole}$; dipentene, $1474.7 \pm 0.24 \text{ kcal./mole}$; *cis*-alloöcimene, $1481.2 \pm 0.60 \text{ kcal./mole}$; myrcene, $1490.4 \pm 0.24 \text{ kcal./mole}$.

Introduction

A search of the literature revealed only a few references dealing with the experimentally determined heats of combustion of terpene hydrocarbons. This work was done in the early part of this century² before thermochemical standards had been established and before many of the errors inherent in the combustion experiments had been analyzed. There is also a question of the purity of the compounds used in the measurements. In view of this, it appeared desirable to obtain the information presented herein. This paper presents the combustion data on six terpenes, of known purity, determined in a calorimeter capable of attaining a precision of a few hundredths of one per cent.

Method

The method used is a substitution one whereby the heat released in an unknown reaction is compared to that released in a known one, with the calorimeter serving as an absorber and comparator of the energies involved. The energy equivalent of the calorimeter was determined in a series of experiments using benzoic acid supplied by the Bu-

reau of Standards (Standard sample 39f). Sufficient benzoic acid was used to give a temperature rise in the calorimeter of about 1.5°, and the unknown reactions were adjusted to produce substantially the same temperature change. The energy equivalent of the calorimeter and all the corrections were evaluated directly in terms of the resistance change of the platinum resistance thermometer used.

Unit of Energy and Molecular Weights

The unit of energy upon which the values of this investigation are based is the absolute joule in terms of which the heats of combustion of benzoic acid are known. The heat of combustion of benzoic acid was taken as $26433.8 \pm 2.6 \text{ abs. j./g.}$ under standard conditions of the bomb process.³⁻⁵

To convert to the conventional thermochemical calorie, the relation was used

$$4.1840 \text{ abs. j.} = 1 \text{ calorie}$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken to be 44.010, and the molecular weight of the C₁₀H₁₆ terpenes was taken to be 136.23.

(3) R. S. Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(4) E. J. Prosen and F. D. Rossini, *ibid.*, **33**, 439 (1944).

(5) E. C. Crittenden, NBS Circular 450 (1947), U. S. Government Printing Office, Washington, D. C.

(1) This paper is abstracted from a portion of a dissertation submitted by Warren T. Eriksen to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1952.

(2) K. Auwers, W. A. Roth and F. Eisenlohr, *Ann.*, **385**, 102 (1911).

Source and Purity of Compounds Used

α -Pinene.—Crude α -pinene was obtained through the courtesy of the Glidden Company of Jacksonville, Florida. It was carefully fractionated through a 120-plate distillation column of the Lecky-Ewell type.⁶ After purification it had a refractive index at 25° of 1.4631, f.p. -75.51°, b.p. 52° (20 mm.). An estimation of the purity from freezing point measurements indicated a purity of 99.6%.

β -Pinene.—Crude β -pinene was obtained from the same source and treated in the same fashion as the α -pinene. The purified product had a refractive index at 25° of 1.4763, f.p. -61.54°, b.p. 60° (20 mm.). Freezing point measurements indicated a purity of 98.7%.

***d*-Limonene.**—The *d*-limonene was obtained through the courtesy of the Minute Maid Corporation of Plymouth, Florida. After fractionation it had a refractive index at 25° of 1.4701, f.p. -75.03°, b.p. 71° (20 mm.). Freezing point measurements indicated a purity of 98.0%.

Dipentene.—The dipentene was obtained from a vapor phase pyrolysis of α -pinene.⁷ After fractionation it had a refractive index at 25° of 1.4701, f.p. -89.03°, b.p., 71° (20 mm.). Freezing point measurements indicate a purity of 99.3%.

***cis*-Alloöcimene.**—The *cis*-alloöcimene was also obtained from the vapor phase pyrolysis of α -pinene. After distillation and fractional crystallization it had a refractive index at 25° of 1.5420, f.p. -25.64°. Freezing point measurements indicated a purity of 93.7%.

Myrcene.—A sample was obtained from the Glidden Company of Jacksonville, Florida. After fractionation it had a refractive index at 25° of 1.4680. Due to glass formation it was impossible to obtain an estimate of the purity of the compound from freezing point measurements.

The impurities in all the compounds will almost certainly be isomeric with the main component and as such will have small effect on the heat of combustion. In the case of *cis*-alloöcimene, the impurity is almost certainly the *trans* isomer, which is present in the natural product.⁸ On the assumption that the *trans* isomer differs in heat of combustion from the *cis* by less than 5 kcal./mole an uncertainty of 0.02% was added to the heat of combustion of the *cis*-alloöcimene. The same uncertainty was also added to the heat of combustion of the *d*-limonene. For the other compounds it was assumed that the uncertainty in the heat of combustion due to the impurity was within the experimental error. Further information on the determination of the purity and the freezing points of these samples will be presented in another report.

Experimental

The experimental procedure followed closely was that given in detail by E. J. Prosen and F. D. Rossini in a series of publications from the National Bureau of Standards.^{9,10} Owing to a larger calorimeter the temperature range in this investigation was 1.5 degrees, 25° to 26.5°, instead of the 3 degrees described by Rossini and Prosen. The thermometric system consisted of a 25-ohm platinum resistance thermometer connected to a Mueller resistance bridge. The sensitivity of the system was such that a bridge unbalance of 0.0001 ohm gave a deflection on the galvanometer scale of 3 mm. which meant that the temperature could be read to 0.0001°.

The bomb was made of illum. It weighs 4443.5 g. and has an internal volume of 390 ml. A teflon gasket was used. The calorimeter and water weighed 5395.0 g.

The calorimeter was built by the Precision Scientific Company according to specifications outlined by the thermochemical section of the National Bureau of Standards. The thermostat controlling the temperature of the constant temperature jacket consisted of a toluene bulb and a vacuum tube relay circuit providing on-off control. The temperature of the jacket could easily be controlled to $\pm 0.002^\circ$.

The calorimeter water was weighed on a Metro-gram balance to 0.05 g. This balance had a capacity of 10 kg. and a sensitivity at full load of at least 0.02 g. With the

calorimeter can and water on the balance (5,395 g.) a drop of water from a small pipet gave a measurable deflection on the balance indicator. All other weighings were made on a semi-micro balance sensitive to 0.01 mg. The samples were enclosed in thin-walled glass ampoules which were flattened on two sides in order to withstand the pressure when the bomb was filled with oxygen.

The oxygen used to fill the bomb and to flush it out after the combustion was purified by passing it through a heated tower of copper oxide to oxidize any impurities in it. It was then passed to a tower of Ascarite to absorb the carbon dioxide formed in the foregoing oxidation.

After completion of the combustion measurements the bomb was placed in the analytical train. Its contents were permitted to escape, at the rate of 200 ml./min. into an absorption tube containing Ascarite. When atmospheric pressure was reached oxygen, purified as described in the above paragraph, was flushed through the bomb for an hour at the same rate. The escaping gases were then passed through a heated tower of copper oxide. In this tower any products of incomplete combustion, such as carbon monoxide, were oxidized to carbon dioxide which was then absorbed in another bulb of Ascarite. Any experiments in which this last bulb gained appreciably in weight were discarded because of incomplete combustion.

Calculations and Results

The calculations involved in arriving at the heat released in the combustion from the time-temperature data have been described elsewhere.¹¹ The heat, K , added to the calorimeter system by transfer from the jacket and the heat, U , added by stirring, were determined from two 20-minute rating periods (one before and one after the 16-minute reaction period) and a knowledge of the mean temperature (with respect to time) of the calorimeter during the reaction period. This mean temperature was evaluated from the area between the time-temperature curves of the calorimeter and jacket during the reaction period.

The jacket was kept constant at a temperature slightly higher than the final temperature of the calorimeter. During the first five minutes of the reaction period the time was recorded in seconds at the moment the resistance of the thermometer reached certain preselected values. During the last eleven minutes of the reaction period the resistance of the thermometer was recorded on the even minutes. The area was then determined by use of the trapezoidal rule operating on the even resistances of the first five minutes and on the even times of the last eleven minutes. The areas were checked in several experiments by plotting the data and counting squares. The areas determined by the two methods checked within the experimental error.

The correction, Δr_i , for the heat added by the combustion of the iron fuse wire was obtained from the weight of wire burned and the heat of combustion of iron, 7.5 kJ./g.¹¹

The correction, Δr_n , for the heat added by the formation of nitric acid from nitrogen present in the oxygen was obtained by titrating the bomb washings with 0.1 *N* NaOH. The acid content so determined was used to calculate the correction using the value of 57.8 kg./mole for the heat of formation of nitric acid.

The value of the heat released, after the foregoing corrections had been applied, was then corrected to heat released at constant pressure and 25° with all the products and reactants at their thermodynamic

(6) R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 503 (1942).

(7) L. A. Goldblatt and S. Palkin, *THIS JOURNAL*, **63**, 3517 (1941).

(8) J. J. Hopfield, S. A. Hall and L. A. Goldblatt, *ibid.*, **66**, 115 (1944).

(9) F. D. Rossini and E. J. Prosen, *J. Research Natl. Bur. Standards*, **27**, 289 (1941).

(10) F. D. Rossini and E. J. Prosen, *ibid.*, **33**, 255 (1944).

(11) E. J. Prosen, NBS Report No. 1119 (1951).

standard states.¹¹ The uncertainties in the reported values of the heats of combustion were arrived at by taking the square root of the sum of the squares of the uncertainty in the energy equivalent of the calorimeter, the uncertainty in the experimentally determined heats, a 0.01% uncertainty in the reduction to standard conditions, and the uncertainty due to impurities in the compounds where necessary.

Table I gives a summary of the experimental data. In Table II are listed: $-\Delta U_B$ (26.5°), the heat developed in the bomb process; $-\Delta U^0$ (26.5°), the energy of combustion in the ideal bomb process; and $-\Delta H^0$ (25°), the heat of combustion at constant pressure and 25° with all the reactants and products in their thermodynamic standard states. $-\Delta U_B$ (26.5°) in kcal./mole of terpene

TABLE I

RESULTS OF CALORIMETRIC COMBUSTION EXPERIMENTS							
Expt. No.	Mass of CO ₂	k	K	U	Δr_i	Δr_n	$\Delta R_c/CO_2$
Benzoic acid							
1	4.04519	0.00179	0.00013	0.00032	0.00022	0.00003	0.050113
2	3.97604	.00178	.00215	.00039	.00021	.00004	.050113
3	3.74097	.00178	.00222	.00041	.00021	.00000	.050093
4	3.76588	.00173	.00130	.00057	.00022	.00000	.050112
5	3.78400	.00179	.00128	.00047	.00016	.00002	.050095
							Mean 0.050105
							S.D. of mean ± 0.000010
α -Pinene							
1	2.89466	.00135	.00244	.00046	.00019	.00001	.067392
2	2.97137	.00134	.00204	.00054	.00022	.00001	.067382
3	3.18004	.00181	.00211	.00039	.00024	.00001	.067368
4	3.55890	.00183	.00090	.00049	.00027	.00002	.067369
5	3.48047	.00185	.00087	.00062	.00027	.00003	.067372
							Mean 0.067377
							S.D. of mean ± 0.000010
β -Pinene							
1	2.77750	.00183	.00270	.00045	.00027	.00000	.067488
2	2.80456	.00175	.00462	.00059	.00025	.00000	.067492
3	2.68398	.00192	.00196	.00059	.00027	.00001	.067488
4	2.83760	.00192	.00060	.00047	.00027	.00002	.067451
5	3.06250	.00193	.00128	.00034	.00027	.00001	.067451
6	2.84102	.00187	.00141	.00066	.00021	.00001	.067469
							Mean 0.067473
							S.D. of mean ± 0.000019
Dipentene							
1	3.4193	.00183	.00105	.00022	.00027	.00003	.066958
2	3.4605	.00177	.00018	.00038	.00027	.00003	.066961
3	3.45355	.00181	.00117	.00046	.00025	.00003	.066975
							Mean 0.066965
							S.D. of mean ± 0.000009

Limonene

1	3.05989	.00182	.00080	.00042	.00027	.00003	.067008
2	3.24917	.00176	.00112	.00054	.00027	.00003	.066988
3	3.54780	.00191	.00069	.00027	.00027	.00003	.066999
4	3.12560	.00196	.00130	.00024	.00027	.00003	.066998
							Mean 0.066998
							S.D. of mean ± 0.000008

Myrcene

1	3.03047	.00181	.00126	.00057	.00027	.00003	.067695
2	2.66890	.00184	.00152	.00045	.00027	.00001	.067709
3	2.83050	.00181	.00169	.00026	.00025	.00002	.067719
4	2.75632	.00178	.00196	.00058	.00027	.00001	.067724
5	3.17430	.00182	.00166	.00060	.00019	.00001	.067700
							Mean 0.067709
							S.D. of mean ± 0.000012

cis-Alloöcimene

1	2.72452	.00185	.00188	.00037	.00020	.00001	.067290
2	2.98010	.00180	.00114	.00044	.00027	.00003	.067280
3	3.17092	.00184	.00064	.00038	.00027	.00001	.067299
4	3.36110	.00183	.00083	.00032	.00027	.00002	.067332
5	2.71720	.00176	.00155	.00038	.00027	.00002	.067260
							Mean 0.067293
							S.D. of mean ± 0.000029

TABLE II

Compound	VALUES OF THE HEATS OF COMBUSTION		
	$-\Delta U_B$ (26.5°), j./g.	$-\Delta U^0$ (26.5°), kcal./mole	$-\Delta H^0$ (25°), kcal./mole
α -Pinene	45503.0 \pm 4.5	1480.5 \pm 0.15	1483.0 \pm 0.25
β -Pinene	45567.8 \pm 8.6	1482.6 \pm .28	1485.1 \pm .34
Dipentene	45247.8 \pm 4.1	1472.3 \pm .13	1474.7 \pm .24
<i>d</i> -Limonene	45225.2 \pm 3.6	1471.4 \pm .11	1473.9 \pm .27
Myrcene	45729.1 \pm 4.6	1487.9 \pm .14	1490.4 \pm .24
<i>cis</i> -Alloöcimene	45448.1 \pm 11.3	1478.7 \pm .36	1481.2 \pm .60

hydrocarbons is obtained by multiplying the ratio of the mean value of $\Delta R_c/g. CO_2$ (from Table I) for each of the terpene hydrocarbons to that of benzoic acid by the appropriate factor

$$(26423.4 \times 122.118 \times 10)/(4184.0 \times 7)$$

where 26423.4 is the heat of combustion of benzoic acid in the actual bomb process in j./g., 122.118 is the molecular weight of benzoic acid, 4184.0 is the conversion factor from joules to kcal., and 10 and 7 are the moles of carbon dioxide per mole of compound for the terpenes and benzoic acid, respectively. $-\Delta U^0$ was derived from $-\Delta U_B$ by correction to the ideal bomb process.¹¹ $-\Delta H^0$ was derived from $-\Delta U^0$ by correction to constant pressure ($\Delta H^0 = \Delta U^0 - nRT$) and to 25° (using $\Delta C_p = 0.073$ kcal./mole⁰).

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