

The entropy associated with the "hump" at 287.8°K. in the specific heat curve of calcium nitrate was determined by actual summation,  $\sum_{i=1}^n C_{p_i} \Delta T/T$ , of a series of short-interval specific-heat determinations with little or no intervening temperature gaps. Minor corrections were applied to bring the final temperature of each determination into exact coincidence with the initial temperature of the immediately following determination. The total entropy increase from 281.8 to 291.7°K is 1.267 E. U., and the total heat absorption in this interval, also obtained by summation  $\sum_{i=1}^n C_{p_i} \Delta T$ , is 363.4 calories per mole. If a smooth curve is drawn, joining the results just above the "hump" with those below 200°K., the excess entropy in the "hump" is computed to be 0.24 E. U. No real significance should be attached to this figure, but it is of interest to compare it with a similarly obtained value, only 0.01 E. U., for the 88.5° "hump." The abnormal specific heat in both "humps" is too great to be attributed to effects of impurities.

#### Free Energies of Formation

The heats, entropies, and free energies of formation of the elements are listed in Table IV. The heats of formation are those recently determined by Young.<sup>6</sup> The entropies of formation combine the values in Table III with the entropies of the elements.<sup>11</sup> Free energies of formation are com-

(11) Kelley, Bureau of Mines Bulletin 434, 1941; estimate for barium, *ibid.*, 384, 1935.

puted from the relationship,  $\Delta F^0 = \Delta H^0 - 298.16 \Delta S^0$ .

TABLE IV

THERMAL DATA AT 298.16°K.

Sub- stance	$\Delta H_{298.16}^0$ , cal./mole	$\Delta S_{298.16}^0$ , E. U./mole	$\Delta F_{298.16}^0$ , cal./mole
Mg(NO <sub>3</sub> ) <sub>2</sub>	-188,770 ± 310	-161.5 ± 0.5	-140,620 ± 340
Ca(NO <sub>3</sub> ) <sub>2</sub>	-224,050 ± 360	-156.6 ± .7	-177,360 ± 420
Ba(NO <sub>3</sub> ) <sub>2</sub>	-236,990 ± 380	-157.8 ± 1.1	-189,940 ± 500
Al(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O	-680,890 ± 460	-518.7 ± 1.9	-526,230 ± 730

#### Summary

Specific heats of the anhydrous nitrates of magnesium, calcium, and barium, and of aluminum nitrate hexahydrate, were measured throughout the temperature range 52 to 298°K. Anhydrous calcium nitrate has two anomalies in its specific-heat curve, one peak occurring at 287.8°K. and another small peak at 88.5°K.

The following molal entropies at 298.16°K. were computed: magnesium nitrate, 39.2 ± 0.5; calcium nitrate, 46.2 ± 0.7; barium nitrate, 51.1 ± 0.3; and aluminum nitrate hexahydrate, 111.8 ± 1.9.

Combination of the above entropies with related thermal data yields the following free energies of formation from the elements at 298.16°K.: magnesium nitrate, -140,620 ± 340; calcium nitrate, -177,360 ± 420; barium nitrate -189,940 ± 500; and aluminum nitrate hexahydrate, -526,230 ± 730 cal./mole.

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## The Heats of Combustion of Some Substituted Eicosanes, Heneicosanes and Docosanes<sup>1</sup>

BY JOHN W. KNOWLTON<sup>2</sup> AND HUGH M. HUFFMAN<sup>3</sup>

### Introduction

The Petroleum and Natural Gas Division of the Bureau of Mines has recently inaugurated a program of research to determine the thermodynamic properties of petroleum hydrocarbons and certain of their derivatives. As a part of this general program the authors have determined the heats of combustion of ten hydrocarbons that appear in the light-lube range of petroleum. These data have been utilized in conjunction with existing data to calculate the heats of formation of these compounds.

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(2) Physical chemist, Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla.

(3) Principal physical chemist, Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla.

### Experimental

**Calorimetric Method.**—The calorimetric method has been described previously,<sup>4</sup> and the same apparatus was used in this investigation, with no significant changes. The combustion apparatus was loaned to the Bureau of Mines by the California Institute of Technology and was moved to and set up in Bartlesville, Okla. All combustions were carried out in a Parr dual-valve bomb having a volume of 0.358 liter, with an initial oxygen pressure of 30 atmospheres, and with 0.1 ml. of water in the bomb.

The energy equivalent of the calorimetric system was determined during the course of the investigation by frequent calibration with benzoic

(4) (a) Huffman and Ellis, *THIS JOURNAL*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, *ibid.*, **60**, 1171 (1938).

TABLE I  
 EXPERIMENTAL AND DERIVED DATA AT 25°

Substance	Formula	Mole % purity <sup>a</sup>	Num- ber of com- bus- tion expts.	Average $-\Delta U_B/m$ , cal./g.	Mean dev. from mean, cal./g.	Max. dev. from mean, cal./g.	$-\Delta U_R$ kcal./mole	$-\Delta H_R$ kcal./mole	$-\Delta H_f^0$ kcal./mole
3-Phenyleicosane (s)	C <sub>26</sub> H <sub>46</sub>	98.2	6	10817	±1	3	3878.3	3885.1	131.6
9-Phenyleicosane (l)	C <sub>26</sub> H <sub>46</sub>	99.5	7	10866	2	3	3895.7	3902.5	114.2
3-Cyclohexyleicosane (l)	C <sub>26</sub> H <sub>52</sub>	<sup>c</sup>	7	11120	2	3	4054.3	4062.0	159.6
9-Cyclohexyleicosane (l)	C <sub>26</sub> H <sub>52</sub>	<sup>c</sup>	6	11115	1	2	4052.4	4060.1	161.5
11-Cyclopentylheneicosane (l)	C <sub>26</sub> H <sub>52</sub>	97.1	6	11132	1	2	4058.5	4066.2	155.5
11-Phenylheneicosane (l)	C <sub>27</sub> H <sub>48</sub>	97.6	6	10872	1	2	4050.4	4057.5	121.5
11-Cyclohexylheneicosane (l)	C <sub>27</sub> H <sub>54</sub>	<sup>c</sup>	13	11121	2	5	4210.7	4218.7	165.3
5- <i>n</i> -Butyldocosane (l)	C <sub>26</sub> H <sub>54</sub>	97.6	6	11213	1	2	4111.0	4119.0	171.0
11- <i>n</i> -Butyldocosane (l)	C <sub>26</sub> H <sub>54</sub>	95-97 <sup>b</sup>	6	11212	1	2	4110.4	4118.4	171.5
11- <i>n</i> -Decylheneicosane (l)	C <sub>31</sub> H <sub>64</sub>	95-97 <sup>b</sup>	6	11192	2	3	4887.9	4897.3	204.4

<sup>a</sup> Reported by Schiessler, private communication. The following notes, (b) and (c), are his. <sup>b</sup> Estimated. <sup>c</sup> Melting curve method inadequate because of geometrical isomerism. Since these compounds were prepared by hydrogenation of the corresponding aromatic derivatives, they should be of the same order of purity.

acid. The material used for this was National Bureau of Standards Standard Sample 39f, having for its isothermal heat of combustion under standard conditions<sup>5</sup> and at 25° the value of  $-\Delta U_B/m = 26,428.4$  N. B. S. international joules.<sup>6</sup> The conditions in our bomb are not quite standard, necessitating a correction<sup>6</sup> of this value to 26,426.1 N. B. S. international joules.

The energy equivalent of the calorimetric system was taken as 3232.1 cal./degree, the mean of nineteen calibration experiments, with a standard deviation of 0.008% and an extreme deviation of 0.02%. The results of all the combustion experiments are expressed in terms of the arbitrary calorie, which is defined as 4.1833 N. B. S. international joules, and refer to the isothermal process at 25° and for true mass. The molecular weights are computed from data in the 1943 table of atomic weights.

**Materials and Heats of Combustion.**—The samples of hydrocarbons used in this work were prepared at The Pennsylvania State College under Research Project 42 of the American Petroleum Institute.<sup>7</sup> The purity of the compounds was estimated by the workers on A. P. I. Project 42, when possible, from the data obtained when determining the melting point, and is given in Table I.

All the substances burned were liquid at 25°, with the exception of 3-phenyleicosane, whose melting point was reported to be 29.3.<sup>7c</sup> The low vapor pressure of these materials (1 mm. at 200°<sup>7c</sup>) permitted direct weighing of the samples into the platinum crucible used in the bomb. Because it was desired to obtain the thermal data on all the hydrocarbons with reference to the liquid state (for purposes of intercomparison), as well as for the standard state, several attempts were made

to burn samples of supercooled liquid 3-phenyleicosane at 25°, but none of the experiments was certainly successful.

The products of combustion from one experiment of each series were examined for the presence of carbon monoxide by means of the gallo-tannic acid blood-saturation method of Sayers and Yant,<sup>8</sup> as modified by Cook.<sup>8b</sup> No significant amount was found as the result of any of the combustions. Separate experiments showed this method to be sensitive to 0.002% carbon monoxide (equivalent to about 0.008% of the heat evolved in the calorimeter). These control experiments on the determination of carbon monoxide were carried out under conditions comparable to those of the examination of the gas from the bomb following a combustion.

The mean results of the combustions of these compounds are given in Table I. The usual corrections to true mass, for nitric acid formed, and for the isothermal reaction were applied. The hydrocarbons burned were not of high purity, hence details of each combustion are not presented. Included in Table I are calculated values of  $-\Delta U_R$ ,  $-\Delta H_R$  and  $-\Delta H_f^0$ . To obtain the heats of formation of the hydrocarbons, we have used for the heats of formation of water and of carbon dioxide at 25°, the values 68,317.3<sup>9</sup> and 94,052<sup>10</sup> cal./mole, respectively.

## Discussion

Insofar as the authors are aware, there are no previous data on the heats of combustion of these compounds, and while the reported order of purity precludes the acceptance of our thermal data as more than preliminary values, we believe that they should be placed on record. It should be

(5) Washburn, *Bur. Standards J. Research*, **10**, 552 (1933).

(6) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(7) (a) Whitmore, Cosby and Sutherland, *THIS JOURNAL*, **64**, 1360 (1942); (b) Whitmore, Cosby, Sloatman and Clarke, *ibid.*, **64**, 1801 (1942); (c) Schiessler, Cosby, Clarke, Rowland, Sloatman and Herr, *Proc. Am. Petroleum Inst.*, **23** [III], 15 (1942).

(8) (a) Sayers and Yant, *Bur. Mines Tech. Paper* 373 (1927); (b) Cook, *Ind. Eng. Chem., Anal. Ed.*, **12**, 661 (1940); (c) Spitzer, Ph.D. Thesis, California Institute of Technology, 1941.

(9) Rossini, *J. Research Natl. Bur. Standards*, **22**, 407 (1939). This is corrected to the value of 1.0080 for the atomic weight of hydrogen.

(10) Rossini, private communication.

noted that these are extremely large molecules and hence a small percentage error leads to a large absolute error. Consequently any small differences in energy content due to structural modifications could easily be masked by the experimental uncertainties.

### Summary

1. The isothermal heats of combustion at

25° of 3-phenyleicosane, 9-phenyleicosane, 3-cyclohexyleicosane, 9-cyclohexyleicosane, 11-cyclopentylheneicosane, 11-phenylheneicosane, 11-cyclohexylheneicosane, 5-*n*-butyldocosane, 11-*n*-butyldocosane, and 11-*n*-decylheneicosane have been determined.

2. From the above data the heats of formation have been calculated.

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## Kinetics of the Acid-catalyzed Esterification of Phenyl- and Cyclohexyl-substituted Aliphatic Acids in Methanol

BY HILTON A. SMITH AND JAMES BURN

In a series of papers<sup>1</sup> a study of the effect of position and nature of certain substituents on the velocity of esterification of aliphatic acids and of acid and base catalyzed hydrolysis of their ethyl esters has been reported. The purpose of the present paper is to report the results of further experiments dealing with the effect of phenyl and cyclohexyl substituents on the rate of acid-catalyzed esterification.

### Experimental

**Cyclohexylacetic acid** was prepared from cyclohexyl bromide by a malonic ester synthesis carried out in the usual manner. The crude acid was fractionated under reduced pressure in a 5-ft. (1.5 meter) Vigreux column. The samples used distilled at 135° under a pressure of 12 mm., melted at 29.7°, and analyzed 99.8% by titration with standard base.

**$\beta$ -Cyclohexylpropionic acid,  $\gamma$ -cyclohexylbutyric acid, and dicyclohexylacetic acid** were prepared by hydrogenation of hydrocinnamic,  $\gamma$ -phenylbutyric, and diphenylacetic acids, respectively. The hydrogenations were carried out in acetic acid solution using Adams catalyst. When hydrogenation was complete, the acids were thrown out of solution by addition of water, or were separated from the solvent by distillation. The  $\beta$ -cyclohexylpropionic acid was fractionated in a 5-ft. (1.5-meter) Vigreux column under reduced pressure. The samples used distilled at 141° at 9 mm. pressure, froze at 17.8° (cor.), and analyzed 99.8%. The  $\gamma$ -cyclohexylbutyric acid was fractionated in a small 25-cm. Vigreux column. The samples used distilled at 169° at 20 mm. pressure, froze at 31° (cor.), and analyzed 100.0%. The dicyclohexylacetic acid was recrystallized from ether. It melted at 138.6°, and analyzed 99.9%.

**Phenylethylacetic acid**, obtained from the Eastman Kodak Company, was fractionated under reduced pressure in a 5-ft. (1.5-meter) Vigreux column. The best samples from the fractionation (m. p. 39.6–41.4°) were recrystallized from ligroin. The purified material melted at 41.6–42.0°, and analyzed 99.9%.

**$\delta$ -Phenylvaleric acid** was prepared from  $\gamma$ -phenylpropyl bromide by a malonic ester synthesis carried out in the usual manner. The product was fractionated under vacuum, and the best samples (m. p. 57.7–58.2°) were recrystallized from ligroin. The resulting crystals melted at 58.2–58.7° (cor.), and analyzed 99.8%.

**Diphenylacetic and triphenylacetic acids** were used directly as obtained from the Eastman Kodak Company.

The diphenyl compound melted at 148.2–148.7° (cor.), and analyzed 99.5%. The triphenyl compound melted at 265.6°.

**Methanol** was obtained in a pure, dry state, as in previously reported work, by careful fractionation of methyl alcohol through a 5-ft. (1.5-meter) spiral column. The material used distilled at a constant head temperature. A check sample was prepared according to the directions of Lund and Bjerrum.<sup>2</sup> When used in esterification, this methanol gave results identical with those obtained using methanol which had been fractionated only.

The method used to obtain rate constants was essentially that previously described.<sup>3</sup> Corrections were made for solvent expansion.

### Experimental Results and Calculations

The rate constants were calculated from Goldschmidt's equation

$$k = \frac{(r + a) \ln [a/(a - x)] - x}{(\text{catalyst})rt}$$

where  $a$  is the original concentration of organic acid,  $x$  is the concentration of ester formed after time  $t$ , and the catalyst is hydrogen chloride. The values of the constant,  $r$ , used were those obtained in earlier work with normal aliphatic acids.<sup>1,4</sup> All of the acids except dicyclohexylacetic and triphenylacetic acids esterified sufficiently fast to make correction for reaction of the catalyst with the solvent unnecessary. The results of a typical run are given in Table I.

For several of the runs, the value of the rate constant fell off toward the end of the reaction somewhat more than in previous work. For this reason, only constants obtained in the interval represented by 20–60% reaction were averaged.

The calculated reaction rate constants are given in Table II. For these runs, the initial concentration of organic acid was 0.500 mole per liter, and the concentration of the catalyst, HCl, was 0.005 *M*. The plot of  $\log k$  versus  $1/T$  for the esterification of these acids is shown in Fig. 1. The activation energies in Table II are calculated from the slopes of these lines, and were checked

(2) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(3) Smith, *This Journal*, **61**, 254 (1939).

(4) Smith and Reichardt, *ibid.*, **63**, 605 (1941).

(1) For the latest, see Smith and Myers, *This Journal*, **64**, 2362 (1942).