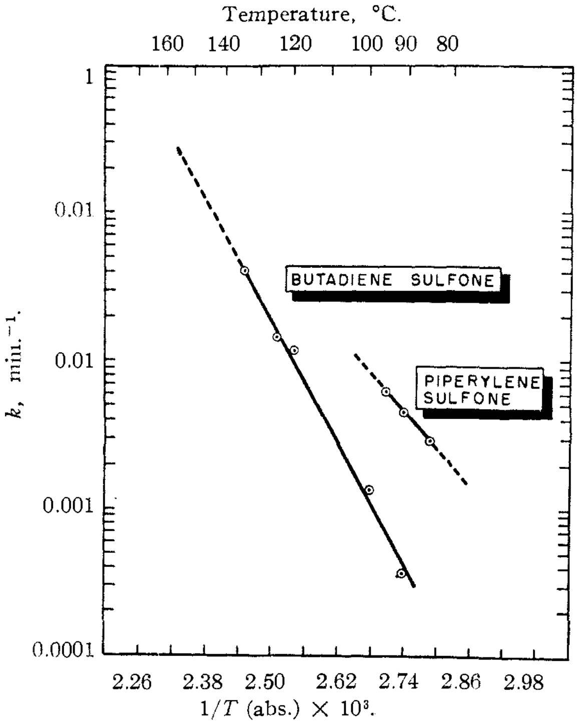

Fig. 2.—Specific reaction rate constant *vs.* temperature.

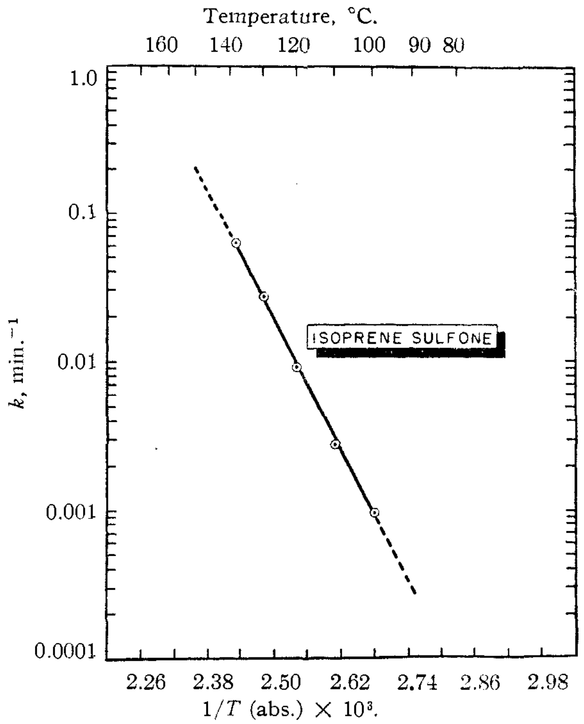

Fig. 3.—Specific reaction rate constant *vs.* temperature.

The calculated heats of formation and activation energy of decomposition for the sulfones of butadiene, piperylene and isoprene are summarized in Table VIII.

TABLE VIII

Monosulfone of	Heat of formation cal./g. mole	Activation energy of decomposition cal./g. mole
Butadiene	−26,600	27,300
Piperylene	−14,900	19,450
Isoprene		32,900

Summary

1. The reaction of a conjugated diene and sulfur dioxide in the presence of an inhibitor to form the monosulfone is an equilibrium reaction.

2. The heats of formation of butadiene sulfone and piperylene sulfone from the diene and sulfur dioxide have been measured and found to be −26,600 and −14,900 cal./g. mole, respectively.

3. The energy of activation for the decomposition of butadiene sulfone, piperylene sulfone and isoprene sulfone have been determined and found to be 27,300, 19,450 and 32,900 cal./g. mole, respectively.

MIDLAND, MICHIGAN RECEIVED[7] AUGUST 12, 1946

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[7] Original manuscript received August 20, 1945.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XXIII. Modern Combustion Data for Fourteen Hydrocarbons and Five Polyhydroxy Alcohols

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The accurate determination of the heats of combustion of organic compounds has constituted one of the important lines of experimental work in this Laboratory during the past decade. Four papers,[1] presenting some of the thermochemical results thereby obtained, have already been published. Since 1940 five additional studies within this field have been initiated. Of these, two have been brought to a state of fairly satisfactory completion, while the other three studies have been seriously interrupted by the various wartime activities of the individuals involved. As the resumption of these latter studies is still very uncertain, it now appears desirable to publish briefly our present combustion data, since these are in most cases more reliable than the corresponding data now available in the literature.

Accordingly, we shall here summarize our determinations of the heats of combustion of four-

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[1] Richardson and Parks, THIS JOURNAL, **61**, 3543 (1939); Moore and Parks, *ibid.*, **61**, 2561 (1939); Moore, Renquist and Parks, *ibid.*, **62**, 1505 (1940); Parks and Moore, *J. Chem. Phys.*, **7**, 1066 (1939).

teen hydrocarbons and five polyhydroxy alcohols and with these results shall derive values for the corresponding enthalpies of formation from the elements.

Experimental

Apparatus and Method

The apparatus and general method were essentially the same as in the previous studies.[1] Six cylinders of oxygen were used in this investigation and with each a new series of calibrations of the calorimeter, involving four to eight combustions, was carried out with standard benzoic acid (samples 39e and 39f) supplied by the United States Bureau of Standards. For these samples Jessup[2] has reported a mean combustion value of 26,428.4 international joules (equal to 6317.6 cal.) per gram mass for the standard calorimetric conditions of Washburn,[3] which also approximated our own working conditions. In all, more than seventy highly consistent calibrations of our calorimeter have thus yielded a mean value of 3210.5 (±0.3) cal. for the energy equivalent per degree at 25.0°.

The combustions were made with our Parr bomb (capacity 390 ml.) filled with oxygen to a pressure of 30 atm. at 23° and with 1 ml. of water initially in the bomb. In all cases most of the air originally in the bomb was washed out by two preliminary fillings with oxygen to a pressure of 5 atm. and thus the correction for nitric acid formation was generally kept down to less than 0.02% of the total heat involved. The magnitude of the thermal correction for this nitric acid was calculated on the basis of 14,340 cal. per mole of aqueous acid formed, in accordance with the recent study of Jessup. No tests for carbon monoxide were made in this work, but the high degree of concordance obtained in the various sets of determinations really constitutes excellent evidence as to the completeness of the reported combustions. In four or five exceptional cases, however, in which ignition difficulties occurred or small amounts of carbon were produced within the bomb, the experimental data were immediately discarded without computation of the corresponding combustion values.

Except in the case of ethylene glycol, the samples of substance to be burned, in pellet or liquid form, were placed directly in the platinum combustion crucible within the bomb. The ethylene glycol, which boils at 197°, was the most volatile of the several materials studied. While it could probably have been handled in the same manner as the other substances, we enclosed our samples within small glass capsules as a precautionary measure and burned them after the procedure of Moore, Renquist and Parks.[1]

As the five polyhydroxy alcohols have rather low heats of combustion per gram, it was found expedient to use an auxiliary material to aid in attaining complete combustion. The standard benzoic acid was generally employed for this purpose and in such cases represented from 2 to about 10% of the total heat evolved.

Units.—The unit of energy used throughout this paper is the defined conventional calorie which has been derived from the international joule by dividing by the factor 4.1833 The unit of mass is the gram true mass which has been derived from the weight in air against brass weights by use of a suitable correction factor for buoyancy. In cases where the density of the material in question was not available in the literature, we have made rough estimates from the mass and volume of the pelleted substances. The molecular weights are based on the 1941 table of atomic weights.[4]

Materials

A special effort was made to obtain high grade materials, inasmuch as the purity of the samples probably constitutes in most cases the limiting factor in determining the accuracy of present day combustion results such as ours. In this connection small amounts of water or dissolved air are particularly objectionable impurities, since these are inert and contribute nothing to the heat of combustion. Accordingly, all samples to be burned were kept in vacuum desiccators over anhydrous magnesium perchlorate for periods of three to twenty days prior to the measurements and these desiccators were repeatedly evacuated to a pressure of about 1 mm. Ash determinations were carried out on all samples but, except with the substances noted hereafter, the results were quite negligible. Suitable corrections were made in the experimental combustion values in these cases of materials with small contents of water or with ash residues.

Several of the hydrocarbon samples undoubtedly contained isomers or other closely related compounds. Thus the purity of the 11-*n*-decylheneicosane has been estimated[5] as only 96.6 mole per cent. However, the impurities here undoubtedly have nearly the same heat of combustion as the compound in question and the resulting uncertainty in our present value is probably only a very few hundredths of 1%.

Pentamethylbenzene and Hexamethylbenzene.—These were samples of materials which had been kindly given to us a number of years ago by Professor Lee Irvin Smith of the University of Minnesota. Details concerning them will not be given here, as their preparation and properties have been fully described elsewhere.[6] Their respective melting points were 54.3 and 165.5°, and in each case the character of the fusion process indicated a highly satisfactory degree of purity. Ash determinations yielded 0.023 and 0.020%, respectively.

Diphenylmethane.—Our starting material, obtained from the Eastman Kodak Co., was subjected to three fractional crystallizations. The resulting product melted at 25.1° to a liquid, which could be undercooled readily over a range of several degrees.

Anthracene.—Spectral anthracene with "blue-violet fluorescence," prepared by the Eastman Kodak Co., was used in its original form as Sample 1. It contained 0.005% non-combustible matter. Sample 2, prepared from the same material by washing with benzene, yielded heats of combustion identical with those for sample 1.

Dibenzyl.—Eastman Kodak Co. material (m. p. 50.8°) was subjected to three fractional crystallizations. The resulting product (m. p. 51.2°; ash content, 0.003%) became our sample 1. Some of this sample was next crystallized from ethyl alcohol and then washed with benzene. These crystals were in turn melted and the liquid was placed in a vacuum desiccator in order to remove all of the benzene, such a procedure being repeated three times. This final product constituted our sample 2.

***n*-Octadecane.**—Sample 1 was the Eastman Kodak Co. product (m. p. 26°). Sample 2 was prepared from some of this same material by recrystallization from pure *n*-heptane. The product was heated at 100° for several hours to remove residual traces of this heptane and then placed, while still liquid, in a desiccator under a high vacuum. Specific heat determinations,[7] made upon a comparable product, yielded a melting point of 27.7° with a purity, as estimated from the fusion process, of about 95 mole per cent. The crystalline samples, when they were burned by us, undoubtedly contained a small fraction of premelted substance and accordingly, in computing our present data for the crystals, we have reduced our actual results by 2.8 cal./g. to allow for about 5% of premelting.

Triphenylmethane.—Our sample 1 was the Eastman Kodak Co. product (m. p. 94°). Sample 2 was prepared from this material by three crystallizations from benzene and a subsequent drying for several days in a vacuum desiccator.

11-Phenylheneicosane, 11-Cyclohexylheneicosane, 13-Phenylpentacosane, 13-Cyclohexylpentacosane and 11-*n*-

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

(3) Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

(4) Baxter, Guichard, Hönigschmid and Whytlaw-Gray, THIS JOURNAL, **63**, 845 (1941).

(5) Fischl, Naylor, Ziemer, Parks and Aston, *ibid.*, **67**, 2075 (1945).

(6) Smith and MacDougall, *ibid.*, **51**, 3001 (1929).

(7) An unpublished investigation by Parks and Naylor.

Decylheneicosane.—The samples of these hydrocarbons were prepared at the Pennsylvania State College under Research Project 42 of the American Petroleum Institute.[8] They were judged to represent the highest feasible degree of purity for such complex hydrocarbons, and we merely subjected them to prolonged evacuations in vacuum desiccators in order to remove dissolved air. Their properties, as communicated by the American Petroleum Institute, are given in Table I.

TABLE I

SOME PHYSICAL PROPERTIES OF FIVE COMPLEX HYDROCARBONS

	M. p., °C.	$n^{20}{}_D$	$d^{20}{}_4$
11-Phenylheneicosane	20.8	1.4788	0.8531
11-Cyclohexylheneicosane	−7.2	1.4639	.8373
13-Phenylpentacosane	33	....	....
13-Cyclohexylpentacosane	−1.7	1.4654	.8390
11-*n*-Decylheneicosane	8.7	1.4540	.8115

Dicetyl (Dotriacontane).—Eastman Kodak Co. product (m. p. 69.5°) was used without further purification. Ash determinations on this sample showed 0.016% noncombustible matter.

Polyisobutylene.—This sample, which had been prepared in the laboratories of the Standard Oil Development Co., was kindly given to us by Dr. Waldo L. Semon of the B. F. Goodrich Co. A representative portion yielded an ash content of 0.033%. The sample was somewhat like crape rubber in appearance and was reported to approximate 200,000 in molecular weight.

Ethylene Glycol.—A 500-ml. lot of C. P. material was carefully fractionated and the middle 200 ml. therefrom constituted our sample 1. A comparable fractionation of this middle portion then yielded our second sample, from which in turn our third sample was similarly prepared. All three samples yielded essentially the same combustion values.

Glycerol.—The middle fraction from the distillation of Eastman Kodak Co. glycerol at 10 mm. pressure was used for these combustions. Its specific gravity was $d^{23.6}{}_{23.6}$ 1.2620, corresponding to 0.08% water content on the basis of the density tables of Bosart and Snoddy.[9]

***i*-Erythritol, *d*-Mannitol and Dulcitol.**—These were C. P. products from the Pfanstiehl Chemical Co. They were oven-dried at 110° and then stored over anhydrous magnesium perchlorate in evacuated desiccators for at least a week. Ash determinations indicated 0.009, 0.003 and 0.007% incombustibles, respectively.

The Heats of Combustion and Derived Data

Table II contains a summary of our experimental combustion data together with some important thermal data calculated therefrom. The number of combustions made on each particular compound is given in the fifth column. The resulting mean values for the energy evolved in the isothermal bomb process per g. at 25.0°, represented by the term $-\Delta U_B/m$, and the mean deviations of the individual combustions from these mean values, represented by Δ, appear in the succeeding column. The values of the bomb process were then calculated per mole and corrected to the standard constant-volume process where the reactants and products are each at 1 atmosphere by means of the equations of Washburn.[3] The energy evolved in this hypothetical standard process is designated in the table by the symbol $-\Delta U_R$. From this quantity $-\Delta H_R$, the heat evolved in the isobaric process at 1 atm., was obtained by addition of the proper work term. Finally, $-\Delta H_f^0$, the heat of formation of the compounds from the elements (gaseous hydrogen, graphitic carbon and gaseous oxygen) was calculated from $-\Delta H_R$ by use of 68,317.4 cal.[10] and 94,051.8 cal.[11] for the heats of formation of water and carbon dioxide, respectively.

It is rather hard to estimate the uncertainties that should be attached to these tabulated values of $-\Delta U_R$ and $-\Delta H_R$. The actual "reaction error" for the combustion of the several compounds was not over 0.02% except in the cases of ethylene glycol and erythritol. Inclusion of a "calibration error" of 0.010% and an "assigned error" of 0.010% for the combustion value of the standardizing substance thus yields precision errors, as described by Rossini,[12] which do not exceed 0.025% except in the two instances just noted. However, in many cases the purity of the samples of the various substances studied is probably at least an equally important source of uncertainty in our final results and one which is harder to evaluate properly. Accordingly, we here suggest as our final uncertainty percentages 0.03 to 0.04% for the hydrocarbons and 0.06% for the polyhydroxy alcohols.

Previous Work.—The literature contains no experimental combustion values for *n*-octadecane, 13-phenylpentacosane and 13-cyclohexylpentacosane.

Recently Knowlton and Huffman[13] have made precise determinations on portions of these API samples of 11-phenylheneicosane, 11-cyclohexylheneicosane and 11-*n*-decylheneicosane with results that are lower than ours by 0.02, 0.01 and 0.06%, respectively. Likewise, for dicetyl Beckers[14] has reported a value which, converted to our present standards, is only 0.02% lower than ours. In this connection it may be noted that unpublished data (obtained in our Laboratory) for the hypothetical heats of fusion of *n*-octadecane and dicetyl at 25°, when combined with our tabulated values for $-\Delta H_R$, yield 2869.44 kcal. and 5058.77 kcal. for these two compounds in the hypothetical liquid state at 25°. The corresponding values predicted on the basis of the combustion regularities deduced by Prosen and Rossini[15] are 2870.16 and 5057.85 kcal., respectively, which differ by +0.025 and −0.018% from our data.

Our present combustion values for pentamethylbenzene, hexamethylbenzene and dibenzyl

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[8] Whitmore, Cosby, Sloatman and Clarke, THIS JOURNAL, **64**, 1801 (1942); Shiessler, Cosby, Clarke, Rowland, Sloatman and Herr, *Proc. Am. Petroleum Inst.*, **23** [III], 15 (1942).

[9] Bosart and Snoddy, *Ind. Eng. Chem.*, **19**, 506 (1927).

[10] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[11] Prosen, Jessup and Rossini, *ibid.*, **33**, 447 (1944).

[12] Rossini, *Chem. Rev.*, **18**, 252 (1936).

[13] Knowlton and Huffman, THIS JOURNAL, **66**, 1492 (1944).

[14] Beckers, *Bull. soc. chim. Belg.*, **40**, 518 (1931).

[15] Prosen and Rossini, *J. Research Natl. Bur. Standards*, **34**, 263 (1945).

TABLE II

SUMMARY OF EXPERIMENTAL AND DERIVED DATA AT 25°

Substance	Formula	Mol. wt.	Density	No. of comb.	$-\Delta U_B/m$ and Δ, cal. g.$^{-1}$	$-\Delta U_R$ kcal. mole^{-1}	$-\Delta H_R$ kcal. mole^{-1}	$-\Delta H_f^0$ kcal. mole^{-1}
			Hydrocarbons					
Pentamethylbenzene (s)	$C_{11}H_{16}$	148.238	0.92	4	10,435.6 ± 0.3	1546.30	1548.67	32.44
Hexamethylbenzene (s)	$C_{12}H_{18}$	162.264	0.92	6	10,490.9 ± 0.6	1701.63	1704.29	39.19
Diphenylmethane (l)	$C_{13}H_{12}$	168.226	1.006	5	9,822.2 ± 1.9	1651.44	1653.22	−20.64
Anthracene (s)	$C_{14}H_{10}$	178.220	1.25	5	9,445.6 ± 0.9	1682.36	1683.84	−25.53
Dibenzyl (s)	$C_{14}H_{14}$	182.252	1.00	5	9,901.1 ± 0.6	1803.40	1805.48	−10.53
n-Octadecane (s)	$C_{18}H_{38}$	254.484	0.90	8	11,199.8 ± 2.2	2849.41	2855.04	135.92
Triphenylmethane (s)	$C_{19}H_{16}$	244.318	1.05	9	9,706.1 ± 1.4	2369.86	2372.23	−38.71
11-Phenylheneicosane (l)	$C_{27}H_{48}$	372.654	0.8531	5	10,874.4 ± 2.1	4051.08	4058.19	120.83
11-Cyclohexylheneicosane (l)	$C_{27}H_{54}$	378.702	.8373	4	11,122.4 ± 1.0	4210.90	4218.90	165.07
13-Phenylpentacosane (s)	$C_{31}H_{56}$	428.758	.95	5	10,862.5 ± 1.7	4655.88	4663.79	164.71
13-Cyclohexylpentacosane (l)	$C_{31}H_{62}$	434.806	.8390	4	11,121.5 ± 1.2	4834.35	4843.53	189.92
11-*n*-Decylheneicosane (l)	$C_{31}H_{64}$	436.822	.8115	6	11,198.8 ± 2.1	4890.57	4900.04	201.72
Dicetyl (s)	$C_{32}H_{66}$	450.848	.941	5	11,143.2 ± 1.7	5022.54	5032.31	231.82
Polyisobutylene	$(C_4H_8)_n$	*n*(56.104)	.95	3	11,176.3 ± 2.0	626.85	628.04	21.44
			Polyhydroxy Alcohols					
Ethylene glycol (l)	$C_2H_6O_2$	62.068	1.115	7	4,578.2 ± 2.3	284.03	284.32	108.73
Glycerol (l)	$C_3H_8O_3$	92.094	1.262	3	4,295.2 ± 0.3	395.33	395.63	159.80
Erythritol (s)	$C_4H_{10}O_4$	122.120	1.451	9	4,096.0 ± 1.3	499.89	500.18	217.61
Mannitol (s)	$C_6H_{14}O_6$	182.172	1.489	6	3,969.5 ± 0.8	722.63	722.93	319.61
Dulcitol (s)	$C_6H_{14}O_6$	182.172	1.466	5	3,956.9 ± 0.6	720.34	720.63	321.90

differ by +0.06, +0.05 and −0.12% from the corresponding results of Banse and Parks,[16] obtained in 1932 and estimated to be good within 0.1%. Our new value for anthracene differs by −0.10% from the value recently reported by Richardson and Parks,[1] who also made a detailed comparison with earlier data. We believe that the presumably superior purity of this present sample of anthracene warrants the substitution of our new result for the previous one. In the case of polyisobutylene, our present value is 0.05% less then that reported by Richardson and Parks for a sample of this material of about 4900 molecular weight. The small difference, of course, is in line with the greater degree of polymerization of our present sample.

Stohmann and other early workers[17] have also reported values for six of these hydrocarbons and for the five polyhydroxy alcohols. However, this early work is frequently in error by more than 0.5%, and any detailed comparison of such values with our present data is not really worth while.

Summary

1. A bomb calorimeter has been used for accurate measurements of the heats of combustion of the following fourteen hydrocarbons and five polyhydroxy alcohols at 25° and constant volume: pentamethylbenzene, hexamethylbenzene, diphenylmethane, anthracene, dibenzyl, *n*-octadecane, triphenylmethane, 11-phenylheneicosane, 11-cyclohexylheneicosane, 13-phenylpentacosane, 13-cyclohexylpentacosane, 11-*n*-decylheneicosane, dicetyl (dotriacontane), polyisobutylene, ethylene glycol, glycerol, *i*-erythritol, *d*-mannitol and dulcitol.

2. From these experimental results the corresponding heats of combustion and heats of formation at constant pressure have been calculated.

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[16] Banse and Parks, THIS JOURNAL, **53**, 3223 (1933).

[17] Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1587.