[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS.
IX. A STUDY OF THE EFFECT OF UNSATURATION ON THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SOME HYDROCARBONS AND OTHER COMPOUNDS[1]

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RECEIVED JUNE 27, 1930 PUBLISHED NOVEMBER 5, 1930

In the three papers[4] of this series immediately preceding the present one, we presented data for the heat capacities, entropies and free energies of more than thirty hydrocarbons. These results were utilized in determining the effect (1) of increasing the length of the chain in an aliphatic hydrocarbon, (2) of inserting side branches on the main chain and (3) of introducing one or more phenyl groups. The present investigation is essentially similar in character to those which have gone before it but deals particularly with the problem of unsaturation, *i. e.*, the effect of the C=C bond on the heat capacities, entropies and free energies of hydrocarbons and other compounds. In this study we have used many of the data previously obtained and also have made new heat capacity measurements on the following twelve compounds: fumaric acid, maleic acid, succinic acid, pentene-2, trimethylethylene, *n*-pentane, cyclohexene, methylcyclohexane, di-isobutylene, stilbene, dibenzoylethylene and dibenzoylethane.

Materials

Fumaric Acid, Maleic Acid, Succinic Acid, Dibenzoylethylene and Dibenzoylethane.—These substances were supplied to us in pure form by Professor James B. Conant of Harvard University. Concerning them he writes as follows.

"The fumaric acid was a commercial material (presumably prepared by the catalytic oxidation of benzene) which I recrystallized three or four times from water. The succinic acid was a high-grade commercial product which I personally recrystallized twice.

"The maleic acid was prepared by redistilling in glass maleic anhydride. This anhydride was then dissolved in distilled water and crystallized by concentration *in vacuo*. This is the only method which gives a really pure maleic acid free from fumaric. The melting point given in the literature is 130–131°. If slowly heated in the ordinary melting point apparatus, the acid I am sending you melts at this temperature. It shows a somewhat higher melting point if rapidly heated. Personally I am inclined to

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] Parks, Huffman and Thomas, THIS JOURNAL, 52, 1032 (1930); Huffman, Parks and Daniels, *ibid.*, 52, 1547 (1930); Huffman, Parks and Thomas, *ibid.*, 52, 3241 (1930).

think that this higher value may be nearer the truth, in spite of the statements in the literature.

"The dibenzoylethane ($C_6H_5CO(CH_2)_2COC_6H_5$) and ethylene (*trans*-$C_6H_5COCH=CHCOC_6H_5$) were prepared according to the methods described by Lutz and myself.[5] They were purified by repeated recrystallization from alcohol. In this connection it should be noted that the ethane sample was very kindly donated by Professor Lutz of the University of Virginia."

Pentene-2, Trimethylethylene, *n*-Pentane and Di-isobutylene.—These four hydrocarbons were very carefully prepared for us by Dr. H. E. Buc of the Standard Oil Development Company. Their preparation is difficult, and none of them could be obtained in the open market in a state of purity sufficient for our work.

The pentene-2, $CH_3CH=CHC_2H_5$, was prepared by dehydration of secondary amyl alcohol. The product was dried with alkali and then refractionated over anhydrous copper sulfate. Two additional fractionations in a special still gave a final product which boiled between 36.27 and 36.31° at 765 mm. In spite of the very small boiling range of this material, we were never able to crystallize it completely in the course of our specific heat measurements. The explanation of this fact is probably to be found in geometrical isomerism, since pentene-2 may exist in *cis* and *trans* forms similar to maleic and fumaric acids. Undoubtedly one of these forms of pentene-2, probably the *trans*, is somewhat more stable thermodynamically than the other; but it is quite possible that some of each was produced in the present synthesis and was carried through the fractional distillations into the final product. In this event we were really working upon a solution rather than on a pure compound. However, the specific heats of the two forms should not differ greatly, and therefore we believe that our data for this substance in the liquid state are fairly reliable. The incomplete crystallization prevented us from obtaining accurate values for the crystals or for the heat of fusion.

The trimethylethylene, $(CH_3)_2C=CHCH_3$, was prepared from a cruder sample of this material by fractional distillation. Fifteen successive fractionations, starting with about 1800 cc. and ending with 200 cc., gave a final product which boiled at 38.5–38.6°, 765 mm. This material crystallized in satisfactory fashion and was evidently fairly pure. It is interesting to note that the compound does not admit of geometrical isomerism.

The *n*-pentane was similarly prepared from a sample of crude "normal pentane" (a petroleum product) by an elaborate series of fractional distillations. It boiled at 35.75–35.80° (746 mm.) and, when cooled by liquid air, produced crystals which exhibited a very sharp melting point at 143.4°K. Without doubt this was one of the purest hydrocarbon samples that we have ever studied.

The di-isobutylene was prepared by polymerization of isobutylene and subsequent fractionation. It presumably has the formula $(CH_3)_3CCH=C(CH_3)_2$. On being cooled with liquid air, it first formed a glass, which crystallized completely as it warmed up. While the melting point of the crystals was not sharp, we believe that our thermal data for this substance are fairly reliable, although probably not of the same order of accuracy as for the other compounds.

Cyclohexene and Methylcyclohexane.—High grade Eastman products were subjected to a series of fractional distillations and to successive dryings with anhydrous copper sulfate. The final sample of cyclohexene boiled at 83.0°, 765 mm.; that of the methylcyclohexane boiled at 100.95–101.00°, 763 mm. Both substances exhibited sharp melting points after crystallization with liquid air.

Stilbene.—Eastman's stilbene (m. p. 120°) was subjected to four crystallizations from ethyl alcohol. The final product melted at 124.2°. It is considered to be the *trans* form.

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[5] Conant and Lutz, This Journal, 45, 1303 (1923).

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[6] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in a hydrocarbon sample, such as that of di-isobutylene, may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie[7] and with all weights reduced to a vacuum basis, appear in Tables I and II.

TABLE I

SPECIFIC HEATS

FUMARIC ACID: Crystals

Temp., °K	91.3	97.2	104.7	112.5	135.0	144.1	155.6	175.2
C_p per g	0.128	0.135	0.141	0.148	0.168	0.174	0.183	0.199
Temp., °K	184.9	193.5	215.2	234.6	255.7	275.6	288.0	297.1
C_p per g	0.206	0.212	0.231	0.246	0.261	0.275	0.285	0.292

MALEIC ACID: Crystals

Temp., °K	91.0	97.5	103.4	124.0	136.4	149.7	163.5	177.7
C_p per g	0.124	0.130	0.134	0.150	0.160	0.170	0.180	0.190
Temp., °K	189.0	199.6	220.7	247.1	275.1	281.5	287.9	294.4
C_p per g	0.198	0.207	0.222	0.241	0.262	0.268	0.273	0.279

SUCCINIC ACID: Crystals

Temp., °K	93.4	100.9	113.7	125.5	139.7	154.7	185.1	215.0
C_p per g	0.134	0.141	0.152	0.162	0.174	0.187	0.211	0.237
Temp., °K	244.3	260.0	265.9	272.4	274.6	276.0	283.4	289.8
C_p per g	0.262	0.277	0.289	0.344	0.295	0.289	0.296	0.303

PENTENE-2: Liquid

Temp., °K	136.1	152.8	169.0	201.2	230.8	260.5	275.1	289.1
C_p per g	0.436	0.439	0.443	0.458	0.474	0.492	0.504	0.515

TRIMETHYLETHYLENE: Crystals

Temp., °K	92.7	93.9	97.3	101.0	104.8	107.5	111.3
C_p per g	0.238	0.240	0.247	0.254	0.261	0.266	0.277

Liquid

Temp., °K	143.9	152.8	173.4	183.8	201.4	203.4	213.7	231.5
C_p per g	0.448	0.448	0.449	0.452	0.459	0.461	0.466	0.471
Temp., °K	233.5	253.5	263.4	275.4	283.4	289.0	293.9	
C_p per g	0.473	0.485	0.491	0.498	0.505	0.508	0.512	

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[6] Parks, THIS JOURNAL, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[7] The factor 0.2390 has been used in converting from the joule to the 15° calorie.

TABLE I (*Continued*)

n-PENTANE: Crystals

Temp., °K	92.8	97.9	102.7	108.6	114.8	121.0	126.7	132.2
C_p per g	0.233	0.243	0.251	0.261	0.271	0.282	0.292	0.306

Liquid

Temp., °K	149.9	154.1	162.4	169.9	185.5	200.4	214.9
C_p per g	0.465	0.465	0.468	0.468	0.473	0.479	0.485
Temp., °K	231.2	244.5	260.2	274.8	279.2	284.7	290.0
C_p per g	0.494	0.501	0.514	0.528	0.531	0.536	0.540

CYCLOHEXENE: Crystals I

Temp., °K	92.0	99.2	105.7	112.6	119.3	125.7	131.8
C_p per g	0.155	0.164	0.171	0.178	0.185	0.192	0.199

Crystals II

Temp., °K	146.5	151.2	157.1	162.8
C_p per g	0.280	0.286	0.294	0.312

Liquid

Temp., °K	175.2	177.1	185.4	197.1	211.9	227.0
C_p per g	0.336	0.337	0.342	0.349	0.358	0.368
Temp., °K	243.8	256.7	275.8	280.6	286.9	293.2
C_p per g	0.382	0.390	0.407	0.411	0.419	0.423

METHYLCYCLOHEXANE: Crystals

Temp., °K	93.2	99.2	105.5	111.6	112.2	118.2	124.5	130.0
C_p per g	0.154	0.162	0.170	0.178	0.179	0.186	0.195	0.205

Liquid

Temp., °K	151.4	157.1	170.3	182.6	199.4	214.3
C_p per g	0.339	0.343	0.351	0.359	0.368	0.378
Temp., °K	229.4	244.9	260.0	275.4	285.2	294.2
C_p per g	0.389	0.400	0.412	0.426	0.436	0.443

DI-ISOBUTYLENE: Crystals

Temp., °K	92.1	94.5	97.0	103.3	110.0	124.2	125.5	131.3
C_p per g	0.188	0.195	0.202	0.217	0.226	0.247	0.249	0.260

Liquid

Temp., °K	183.0	189.1	210.5	230.1	251.8	275.2	281.2	296.0
C_p per g	0.407	0.410	0.425	0.439	0.454	0.475	0.481	0.497

STILBENE:[a] Crystals

Temp., °K	92.3	93.9	101.7	109.8	124.3	134.0	148.3	164.9
C_p per g	0.116	0.118	0.123	0.129	0.140	0.148	0.159	0.174
Temp., °K	179.6	198.8	211.7	227.6	254.4	264.8	276.4	292.8
C_p per g	0.188	0.206	0.219	0.235	0.262	0.273	0.284	0.301

DIBENZOYLETHYLENE: Crystals

Temp., °K	88.8	97.5	107.8	127.0	138.6	151.5	165.0	178.5
C_p per g	0.111	0.117	0.126	0.141	0.150	0.161	0.172	0.183
Temp., °K	192.5	206.3	230.3	251.8	258.5	277.6	284.0	291.9
C_p per g	0.196	0.208	0.231	0.251	0.257	0.277	0.284	0.290

TABLE I (*Concluded*)

DIBENZOYLETHANE: Crystals

Temp., °K.	93.2	99.8	107.8	117.1	124.0	134.1	145.8	156.0
C_p per g.	0.115	0.121	0.128	0.135	0.141	0.151	0.161	0.171
Temp., °K.	164.6	169.5	172.7	180.3	182.4	186.2	190.6	194.4
C_p per g.	0.179	0.183	0.188	0.203	0.207	0.219	0.200	0.200
Temp., °K.	214.0	243.8	255.4	276.0	276.3	281.9	289.0	296.0
C_p per g.	0.215	0.241	0.252	0.272	0.272	0.277	0.284	0.292

[a] In this connection we wish to acknowledge our indebtedness to Mr. A. C. Daniels of this Laboratory, who very kindly made the measurements on stilbene for us.

TABLE II

FUSION DATA[a]

Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2d result	Mean
Trimethylethylene	138.9	25.82	25.66	25.74
n-Pentane	143.4	27.75	27.75	27.75
Cyclohexene	169.0	9.56	9.58	9.57
Methylcyclohexane	146.2	16.25	16.24	16.24
Di-isobutylene	172	16.83	...	16.83

[a] In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

TABLE III

TRANSITION DATA

Substance	Transition temperature, °K.	Heat of transition (cal. per g.) 1st result	2nd result	Mean
Cyclohexene	138.7	12.19	11.53	11.86

For comparison with these values the literature[8] contains only very meager data. Our extrapolated specific heat curve for succinic acid is about 6% above the value obtained by Hess at a mean temperature of 25° and 3.5% above that of deHeen at 35°. For *n*-pentane Schlesinger has made determinations on the liquid at −78 and 0°. His results are below our curve by 0.2 and 2.3%, respectively. The specific heat value of Nadejdin for "isoamylene," presumably trimethylethylene, at a mean temperature of −3.5° is only 0.4% above our curve for this substance.

Cyclohexene was found to exist in two crystalline forms with a fairly definite transition temperature at 138.7°K., and the heat of transition was measured by the same procedure used in the fusion determinations. The data thus obtained are recorded in Table III. In this connection it is noteworthy that the heat of transition is about 25% greater than the heat of fusion.

In the cases of succinic acid and dibenzoylethane the specific heat curve for the crystals show a small maximum or "hump." Such a phenomenon

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[8] Landolt–Börnstein–Roth–Scheel, "Tabellen," Julius Springer, Berlin, **1923**, pp. 1267 and 1271.

has been observed for several other compounds which have been studied in this Laboratory and is undoubtedly real, although its explanation is not apparent. For dibenzoylethane the hump comes at about 187°K. (see Fig. 1) and the heat effect in excess of the normal specific heat amounts to 0.22 cal. per g. or 52 cal. per mole. The two parts of the heat capacity curve below and above this transition region fit together quite smoothly, indicating that the same crystalline form probably exists over the entire temperature range. A similar hump was found for succinic acid at about 272°K. with a heat effect of 41 cal. per mole.

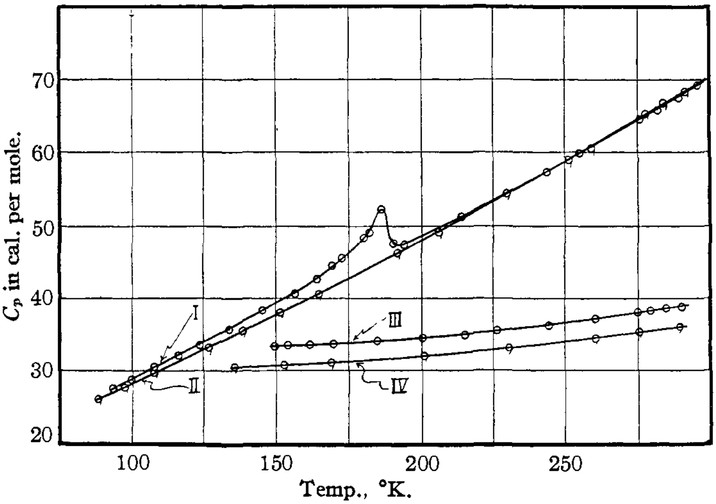

Fig. 1.—Curve I refers to dibenzoylethane; II to dibenzoylethylene; III to *n*-pentane; IV to pentene-2.

A careful study of the thermal data indicates that the withdrawal of a mole of hydrogen, with the resulting production of an ethylenic double bond in the parent compound, ordinarily lowers somewhat the molal heat capacity at a given temperature. Outside of the hump region the effect is hardly noticeable in the case of crystalline dibenzoylethane and dibenzoylethylene, where the change in the molecular weight is less than 1%, while it is quite appreciable with liquid *n*-pentane and pentene-2, where the change in molecular weight is about 3%. These examples are, perhaps, rather extreme cases, and, accordingly, we have represented them graphically in Fig. 1.

The lowering in molal heat capacity on formation of an olefin is undoubtedly due to the decreased vibrations (as a result of the increased constraints) of the carbon atoms adjacent to the double bond rather than to a loss of the thermal energy associated with the vibrations of the two hydrogen atoms. This last is probably negligible at all temperatures up to that of the room.

Discussion

Entropies of the Compounds.—Using the data contained in Tables I, II and III in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for all the compounds except pentene-2. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[9] for estimating the entropy increase for the crystals, Col. 2 of Table IV, from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading S_{298} in the last column. In the case of stilbene, which is normally crystalline, we have roughly calculated the entropy of fusion[10] at 298° so as to obtain a value for its entropy as a liquid, even though the liquid state is unstable at this temperature.

TABLE IV

ENTROPIES OF THE SUBSTANCES PER MOLE

Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298}
Fumaric acid	12.31	27.34	...	...	39.7
Maleic acid	12.10	25.97	...	...	38.1
Succinic acid	13.17	28.86[a]	...	...	42.0
Trimethylethylene	13.12	8.37	12.99	25.00	59.5
n-Pentane	13.53	9.09	13.95	25.42	62.0
Cyclohexene	11.76	18.13[b]	4.65	17.28	51.8
Methylcyclohexane	13.08	8.77	10.90	26.59	59.3
Di-isobutylene	15.24	18.03	10.96	27.12	71.4
Stilbene (solid)	19.81	40.16	...	...	60.0
Stilbene (liquid)	...	...	15.7	...	75.7
Dibenzoylethylene	24.88	51.42	...	...	76.3
Dibenzoylethane	24.79	52.81[c]	...	...	77.6

[a] This value includes 0.15 E. U. for the entropy of the hump at 272°K.

[b] This value includes the entropy increase for both crystalline forms as well as the entropy effect (7.11 E. U.) for the transition between them.

[c] This value includes 0.28 E. U. for the entropy of a hump at 187°K.

We now possess entropy values for a number of unsaturated compounds and are in a position to compare these with the entropies of the corresponding saturated substances. We have made such a comparison in Table V.

In eight cases out of the nine cited the entropy of the unsaturated compound is appreciably less than that of the corresponding saturated one.

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[9] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

[10] This approximate calculation of the entropy of fusion was made by the equation $\Delta S_{298} = (\Delta H \text{ fusion})/T_M - \Delta C_p \ln (T_M/298)$, where ΔH and T_M are, respectively, the molal heat of fusion and the melting point. In this case ΔC_p, the difference between the molal heat capacity of the liquid and crystals, was assumed to be approximately 9 cal. For ΔH, we have used 7200 cal. per mole ("International Critical Tables," Vol. V, p. 134).

TABLE V

A COMPARISON OF THE ENTROPIES OF SOME SATURATED AND UNSATURATED ORGANIC COMPOUNDS

Entropy of the saturated compound		Entropy of the unsaturated compound		Entropy decrease with unsaturation, E. U.
Succinic acid	42.0	Fumaric acid	39.7	2.3
Succinic acid	42.0	Maleic acid	38.1	3.9
Dibenzoylethane	77.6	Dibenzoylethylene	76.3	1.3
2-Methylbutane	60.8	Trimethylethylene	59.5	1.3
2,2,4-Trimethylpentane	75.2	Di-isobutylene	71.4	3.8
Dibenzyl	64.6	Stilbene	60.0	4.6
Cyclohexane	49.2	Cyclohexene	51.8	−2.6
Cyclohexane	49.2	Benzene	41.9	2.4 × 3
Methylcyclohexane	59.3	Toluene	52.4	2.3 × 3

In these eight comparisons the differences, while by no means constant, average 2.7 E. U. per double bond, or mole of hydrogen withdrawn. In the cyclohexane–cyclohexene comparison, however, the entropy of the latter is actually greater by 2.6 E. U. In our opinion this anomaly is to be attributed to an abnormally low entropy value for cyclohexane, which (like benzene) possesses great molecular symmetry and is somewhat unique in character.

In a preceding paper[11] it was shown that the entropy of a liquid paraffin or benzenoid hydrocarbon could be calculated quite accurately by the empirical equation, $S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$. Here n and p represent, respectively, the number of aliphatic carbon atoms and phenyl groups in the molecule, and r ordinarily refers to the number of methyl branches attached on the main aliphatic chain. In order to apply the equation to olefin hydrocarbons we might now add the term $-2.7e$, where e represents the number of ethylenic double bonds within the acyclic portion of the compound. The equation for liquid olefins then becomes, $S_{298} = 25.0 + 7.7n - 4.5r - 2.7e + 19.5p$. Using it, we calculate the following entropies: trimethylethylene, 56.3 E. U.; di-isobutylene, 70.4 E. U.; and stilbene, 76.7 E. U. These values differ from the experimental results of Table IV by −3.2, −1.0 and +1.0 E. U., respectively. Thus the above formula, though not precise, may be useful in roughly estimating the entropies of olefin hydrocarbons.

The Free Energies of the Compounds

We have also calculated the free energies of these eleven compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

The essential data are given in Table VI. For obtaining the ΔH of formation for succinic acid we have used the heat of combustion reported by Verkade, Hartman and Coops,[12] and for dibenzoylethylene and dibenzoyl-

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[11] Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1553 (1930).

[12] Verkade, Hartman and Coops, *Rec. trav. chim.*, **47**, 608 (1928).

ethane we have employed some unpublished values, recently obtained in our Laboratory by Mr. T. R. Lumb. In the cases of the remaining eight compounds we have taken the heats of combustion as given in the "International Critical Tables."[13] For our present purpose we have converted all these combustion data to 298.1°K. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.[4] for the heats of combustion of hydrogen and graphitic carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respective entropies of carbon and hydrogen were taken as 1.3 and 14.8 E. U.[4] per gram atom.

TABLE VI

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	Heat of combustion at constant pressure	ΔH_{298} Cal.	ΔS_{298} E. U.	ΔF°_{298} Cal.
Fumaric acid (S)	319,900	−193,800	−122.7	−157,200
Maleic acid (S)	326,000	−187,700	−124.3	−150,600
Succinic acid (S)	356,900	−225,100	−150.0	−180,400
Trimethylethylene	795,700	− 17,300	− 95.0	+ 11,000
n-Pentane	833,100	− 48,300	−122.1	− 11,900
Cyclohexene	891,700	− 15,600	−104.0	+ 15,400
Methylcyclohexane	1,091,400	− 46,800	−157.0	0,000
Di-isobutylene	1,252,000	− 48,800	−175.8	+ 3,600
Stilbene (S)	1,764,600	+ 34,800	−135.8	+ 75,300
Dibenzoylethylene (S)	1,885,300	− 33,000	−171.1	+ 18,000
Dibenzoylethane (S)	1,920,700	− 65,900	−199.4	− 6,500

The molal free energies appear in the last column of the table. For comparative purposes the accuracy of these values is largely limited by the accuracy of the combustion data employed. In the cases of di-isobutylene and stilbene the present combustion values may be in error by as much as five thousand calories; and therefore the free energies are uncertain to this extent. On the other hand, in the cases of the three dibasic acids the combustion results are accurate to about three hundred calories. For the remaining compounds the values are probably reliable to one or two thousand calories.

The results for maleic and fumaric acids provide quantitative thermodynamic evidence on the interesting problem of geometrical isomerism. It is well known that the *cis* form, maleic acid, tends to change over into the *trans* isomer, fumaric acid, and the present data show that for the transformation $\Delta F_{298} = -6600$ cal. Hence, the reaction should go virtually to completion. Furthermore, such a marked difference in the values for two geometrical isomers serves to emphasize the specific influence of structure in determining the free energies of unsaturated compounds.

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[13] "International Critical Tables," Vol. V, p. 163.

To develop further this last thesis, we have calculated from the data of this and the immediately preceding papers the free energy changes accompanying a number of reactions in which a saturated compound loses hydrogen and yields an olefinic or benzenoid compound. The results appear in Table VII. For completeness we have also included a value for the conversion of ethane into ethylene derived by Pease and Durgan.[14] It is evident that ΔF_{298} for the process of forming an olefin varies greatly, and no generalization concerning this quantity can be made with any certainty. However, the respective values for the production of ethylene, trimethylethylene and di-isobutylene indicate that ΔF for the dehydrogenation process probably decreases rapidly as we proceed up the series of olefin hydrocarbons.

In the two parallel cases involving the production of benzene and toluene from cyclohexane and methylcyclohexane, respectively, it is noteworthy that the ΔF values are practically identical, *i. e.*, about 24,000 cal. for the loss of three moles of hydrogen. Here the average ΔF_{298} per mole of hydrogen withdrawn (8000 cal.) is considerably less than in the case of any olefin compound except di-isobutylene.

TABLE VII

FREE ENERGY CHANGES ACCOMPANYING SOME DEHYDROGENATION REACTIONS

Saturated compound		Unsaturated compound	ΔF°_{298}, cal.
Succinic acid	=	H_2 + Maleic acid	+29,800
Succinic acid	=	H_2 + Fumaric acid	23,200
Dibenzoylethane	=	H_2 + Dibenzoylethylene	24,500
Ethane	=	H_2 + Ethylene	22,600
2-Methylbutane	=	H_2 + Trimethylethylene	17,600
2,2,4-Trimethylpentane	=	H_2 + Di-isobutylene	9,200
Dibenzyl	=	H_2 + Stilbene	15,200
Cyclohexane	=	H_2 + Cyclohexene	11,700
Cyclohexane	=	$3H_2$ + Benzene	8,000 × 3
Methylcyclohexane	=	$3H_2$ + Toluene	8,000 × 3

Before concluding, the authors wish to thank the Research Laboratory of the Standard Oil Development Company and Professor James B. Conant of Harvard University for the valuable compounds which made this research possible.

Summary

1. The specific heats of twelve organic compounds, including seven hydrocarbons, have been measured over a wide range of temperatures. The heats of fusion of five of the hydrocarbons and the heat of transition of cyclohexene have also been determined.

2. The entropies of eleven of the compounds have been calculated from these heat capacity data. In general the entropy of an unsaturated sub-

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[14] Pease and Durgan, THIS JOURNAL, 50, 2715 (1928).

stance was found to be slightly less than that of the corresponding saturated compound.

3. The corresponding free energies have also been calculated. The free energy change in dehydrogenation reactions was found to vary greatly, and it is apparent that the effect of unsaturation in determining the free energy value of an organic compound is very specific.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ALCOHOLYSIS OF CERTAIN 1,3-DIKETONES AND BETA-KETONIC ESTERS

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RECEIVED JULY 3, 1930 PUBLISHED NOVEMBER 5, 1930

This investigation was undertaken originally for the purpose of studying the influence of structure on the extent of formation and cleavage of carbon to carbon linkages in organic compounds. The ideal condition for a study of this nature would be a perfectly reversible reaction in which the concentration of various sets of reactants at the equilibrium point could be measured accurately. The quantitative work which has been done previously in connection with this problem has been concerned chiefly with the extent of dissociation of hexa-substituted ethanes. The interpretation of the experimental data in terms of the relation of structure to the strength of the carbon to carbon linkage between the substituted methyl groups is complicated by the fact that the dissociated radical is apparently in equilibrium with compounds having a quinoid structure. In addition to the rather large volume of literature upon the hexa-substituted ethanes there has been, also, a paper by Miss Edith Usherwood[1] upon the position of the equilibrium point in the aldolization of isobutyric aldehyde.

The Claisen or acetoacetic ester condensation since the publication of Dieckmann's work[2] has been considered to be a reversible reaction, and it seemed upon preliminary consideration to be better suited than any other reaction for an investigation of the relationship of the structure of a compound to the strength of carbon to carbon linkages. In general terms the Claisen synthesis may be considered to involve the elimination of a molecule of alcohol through the reaction of the alkoxy group of an ester with a hydrogen on a carbon atom alpha to a carbonyl or other activating group in the presence of such reagents as sodium, sodium ethoxide or sodamide. The type reaction may be represented as

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[1] Usherwood, *J. Chem. Soc.*, **123**, 1917 (1923).

[2] Dieckmann, *Ber.*, **33**, 2670 (1900).