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# Enthalpies of Combustion and Formation of 11 Isomeric Nonanes

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**The enthalpies of combustion of 11 isomeric nonanes were determined by oxygen-bomb combustion calorimetry. Enthalpies of combustion were computed from measurements of mass of samples burned and mass of carbon dioxide produced. The following values, in kilocalories per mole based on the mass of sample, are reported for the standard enthalpy of combustion, $\Delta Hc^{\circ}_{298.15}$, of these compounds in the liquid state: *n*-nonane, −1463.96 ± 0.13; 2,2-dimethylheptane, −1460.74 ± 0.20; 2,2,3-trimethylhexane, −1462.05 ± 0.18; 2,2,4-trimethylhexane, −1462.01 ± 0.20; 2,2,5-trimethylhexane, −1459.50 ± 0.20; 2,3,3-trimethylhexane, −1462.43 ± 0.20; 2,3,5-trimethylhexane, −1461.73 ± 0.20; 2,4,4-trimethylhexane, −1462.65 ± 0.18; 3,3,4-trimethylhexane, −1463.28 ± 0.18; 2,2-dimethyl-3-ethylpentane, −1464.44 ± 0.18; and 2,4-dimethyl-3-ethylpentane, −1465.15 ± 0.18. The experimental results for these compounds were compared to values predicted by current correlative procedures.**

THE BUREAU OF MINES is conducting thermodynamic studies on selected hydrocarbons under American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum." One of the experimental goals of this program is the provision of basic thermodynamic data on a limited number of carefully selected compounds. From these basic data the thermodynamic properties for many other compounds can be calculated by correlation. As part of this continuing program, the enthalpies of combustion of 11 isomeric nonanes were determined and are reported. Johnson *et al.* (*12*) have contributed experimental enthalpies of combustion of five other highly branched nonanes. The present research adds 10 experimental values for branched-chain nonanes in addition to a new value for *n*-nonane, so experimental values now are available for 16 of the 35 nonanes.

The API Research Project 44 tables (*2*) contain experimental enthalpy-of-formation data for the alkanes of molecular weight as high as the octanes with a few exceptions. Data for two of the heptanes, 2-methylhexane and 3-methylhexane, are correlated values. New experimental evidence (*14*) also indicates that the older experimental enthalpy-of-formation data for the pentanes, particularly neopentane, need adjustment in the tables.

Many attempts have been made to correlate the enthalpy-of-formation data of the alkanes with their molecular structure. Some of these correlations have been more successful than others, and perhaps the most successful of the recent correlative procedures have been the Allen (*1*) method, the modification of the Allen method by Skinner (*20*), the Rossini-Greenshields (*9*) method, and the Somayajulu-Zwolinski (*21*) method. All of these correlative methods meet severe tests at about the $C_7$ to $C_8$ level in the alkanes. At this level steric effects in the more compact molecules become critical; also current research indicates that even the best of these methods fail for some molecular configurations of the $C_9$ alkanes.

## EXPERIMENTAL

**Apparatus and Procedures.** Experimental measurements of the enthalpy of combustion followed a procedure previously reported (*6*). The rotating-bomb calorimeter BMR II (*7*) and platinum-lined bomb Pt-3b (*5*), internal volume $0.349_4$ liter, have been described. Rotation of the bomb was not necessary for these experiments. One milliliter of water was added to the bomb, and the bomb was flushed and charged to 30 atm. with pure oxygen. The high purity of the oxygen used in these experiments made the formation of nitric acid negligible. Each experiment was started at 23° C., and because of the masses of combustibles chosen, the final temperatures were very nearly 25° C.

The 11 nonanes were divided into two groups for experimental study to avoid extending a single series of experiments over a long time. This division was a safeguard against ampoule breakage (from thermal expansion and contraction of the confined liquids) and possible loss of calibration of the calorimeter by equipment failure. Fortunately, the safeguards were unnecessary. Both groups of measurements were calibrated by means of benzoic acid combustion experiments, and *n*-nonane was burned along with both groups of experiments, establishing a firm connection between these experimental measurements and the accepted values for the normal alkanes. Compounds studied in the first group (Series I) were *n*-nonane, 2,2,3-trimethylhexane, 2,3,3-trimethylhexane, 3,3,4-trimethylhexane, and 2,2-dimethyl-3-ethylpentane. The second group (Series II) consisted of *n*-nonane, 2,2-dimethylheptane, 2,2,4-trimethylhexane, 2,2,5-trimethylhexane, 2,3,5-trimethylhexane, 2,4,4-trimethylhexane, and 2,4-dimethyl-3-ethylpentane.

**Materials.** The 11 nonanes were samples of API research hydrocarbons purified and made available by the American Petroleum Institute Research Project 58B at the Carnegie-Mellon University. Sample designations and impurities are listed in Table I. All compounds were dried by vapor passing over freshly activated molecular sieve. Ampoules were filled in a vacuum system and sealed as previously described (*6, 8*).

The sample of benzoic acid used for calibration was National Bureau of Standards Sample 39I. The material had a heat of combustion of 26.434 ± 0.003 absolute kilojoules per gram under certificate conditions. Conversion to standard conditions (*10*) gives −6313.02 ± 0.72 cal. per gram for $\Delta Ec°/M$, the energy of the idealized combustion reaction.

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$. A recent determination of this formula favors this composition over the $CH_{1.891}$ formerly used. The most recent determination of $\Delta Ec°/M$ for this material gave $-10{,}984.3_0 \pm 0.1_5$ cal. per gram (mean and standard deviation), a value that has held remarkably constant for 15 years.

For the cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta Ec°/M$ was −4050 cal. per gram.

**Units of Measurements and Auxiliary Quantities.** All data reported are based on the 1961 atomic weights (*3*) and the 1963 definitions of the thermodynamic temperature scale and of the thermochemical calorie (*4*).

For reducing weights in air to weights in vacuo, converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states, the values summarized in Table II were used for density, $\rho$, and $(\partial E/\partial P)_T$. Values of the density of the nonanes are from the API Research Project 44 tables (*2*). Values of $(\partial E/\partial P)_T$ were calculated from the temperature dependence of density (*2*) by using the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$. An estimate of 0.5 cal. gram$^{-1}$ °K.$^{-1}$ was used for the heat capacity of all the nonanes.

**Calibration.** Calibration experiments with benzoic acid were done with both Series I and Series II. $\varepsilon$(calor.) for Series I was found to be 4004.97 ± 0.007 cal. per deg. (mean and standard deviation). $\varepsilon$(calor.) for Series II was found to be 4004.62 ±0.09 cal. per deg. (mean and standard deviation). A minor repair accounting for the change in the value of $\varepsilon$(calor.) was made to the calorimeter between experiments of Series I and II. Excellent evidence for the validity of the two calibration series is the good agreement of the values for the enthalpy of combustion of *n*-nonane.

**Carbon Dioxide Recovery.** Carbon dioxide was recovered in both the calibration and combustion experiments. Anhydrous lithium hydroxide was used as the carbon dioxide absorbent (*6*). The carbon dioxide recoveries are summarized in Table III. The results for benzoic acid afford a check on the accuracy of the carbon dioxide recovery method. The certificate supplied with benzoic acid (Standard Sample 39I) indicates that the purity of the

### Table I. Compound Description

| | Impurity, Mole % |
|---|---|
| *n*-Nonane (B) | 0.051 ± 0.004 |
| 2,2-Dimethylheptane | 0.13 ± 0.10 |
| 2,2,3-Trimethylhexane | (0.25 ± 0.20) est. |
| 2,2,4-Trimethylhexane | 0.25 ± 0.20 |
| 2,2,5-Trimethylhexane | 0.14 ± 0.04 |
| 2,3,3-Trimethylhexane | 0.07 ± 0.06 |
| 2,3,5-Trimethylhexane | (0.25 ± 0.20) est. |
| 2,4,4-Trimethylhexane | 0.27 ± 0.11 |
| 3,3,4-Trimethylhexane | 0.13 ± 0.10 |
| 2,2-Dimethyl-3-ethylpentane | 0.08 ± 0.08 |
| 2,4-Dimethyl-3-ethylpentane | 0.14 ± 0.11 |

### Table II. Physical Properties at 298.15° K.

| | $\rho$, G./Ml. | $(\partial E/\partial P)_T$, Cal./Atm./G. |
|---|---|---|
| *n*-Nonane | 0.71381 | −0.0107 |
| 2,2-Dimethylheptane | 0.7066 | −0.0111 |
| 2,2,3-Trimethylhexane | 0.7257 | −0.0104 |
| 2,2,4-Trimethylhexane | 0.7118 | −0.0108 |
| 2,2,5-Trimethylhexane | 0.70322 | −0.0116 |
| 2,3,3-Trimethylhexane | 0.7345 | −0.0081 |
| 2,3,5-Trimethylhexane | 0.7179 | −0.0113 |
| 2,4,4-Trimethylhexane | 0.72007 | −0.0104 |
| 3,3,4-Trimethylhexane | 0.7414 | −0.0104 |
| 2,2-Dimethyl-3-ethylpentane | 0.7310 | −0.0103 |
| 2,4-Dimethyl-3-ethylpentane | 0.7341 | −0.0101 |
| Auxiliary oil | 0.87 | −0.0061 |
| Benzoic acid | 1.320 | −0.00278 |
| Fuse | 1.5 | −0.007 |

### Table III. Carbon Dioxide Recovery

| | % Recovered |
|---|---|
| Benzoic acid (16)[a] | 99.997 ± 0.006[b] |
| *n*-Nonane, Series I (6) | 100.003 ± 0.020 |
| *n*-Nonane, Series II (6) | 100.000 ± 0.015 |
| 2,2-Dimethylheptane (6) | 99.997 ± 0.014 |
| 2,2,3-Trimethylhexane (6) | 99.991 ± 0.006 |
| 2,2,4-Trimethylhexane (6) | 100.001 ± 0.005 |
| 2,2,5-Trimethylhexane (6) | 100.002 ± 0.011 |
| 2,3,3-Trimethylhexane (6) | 100.010 ± 0.010 |
| 2,3,5-Trimethylhexane (6) | 99.997 ± 0.013 |
| 2,4,4-Trimethylhexane (6) | 99.996 ± 0.011 |
| 3,3,4-Trimethylhexane (6) | 99.998 ± 0.010 |
| 2,2-Dimethyl-3-ethylpentane (6) | 99.987 ± 0.010 |
| 2,4-Dimethyl-3-ethylpentane (6) | 99.994 ± 0.011 |

[a] Number of experiments. [b] Average deviation of mean.

sample is 99.997 mole % as measured by the freezing point method, and the moisture content is stated to be 0.002%. The essentially quantitative carbon dioxide recoveries for the nonanes indicated that the impurities in these materials are hydrocarbons, probably isomeric. The effect of such impurity on the heat of combustion should be negligible.

**Calorimetric Results.** Typical combustion experiments for the compounds in the two series of experiments are summarized in Table IV. It is impractical to list summaries for all experiments, but values of $\Delta Ec°/M$ for all experiments are tabulated in Table V. Standard deviations of the mean are given. All values of $\Delta Ec°/M$ in Tables IV and V refer to the gram of sample as the measure of the amount of reaction. Equation 1 represents the combustion reaction:

$$C_9H_{20}(\text{liq.}) + 14O_2(g) = 9CO_2(g) + 10H_2O(\text{liq.}) \qquad (1)$$

Derived molal enthalpies of combustion and formation for the liquid hydrocarbons are given in Table VI. One set of values employs the sample mass as the measurement of the amount of reaction. The second set was based on the carbon dioxide recoveries. It was assumed that the auxiliary oil and fuse burned completely. The sample mass was derived from the carbon dioxide recovery through the stoichiometry of the combustion reaction, a procedure that should give reliable results. Experiments are rejected if unburned carbon remains in the bomb, and carbon monoxide has never been detected. The molal values of $\Delta Ec°$ and $\Delta Hc°$ in Table VI refer to Equation 1. The molal values of $\Delta Hf°$ refer to Equation 2.

$$9C(\text{c, graphite}) + 10H_2(g) = C_9H_{20}(\text{liq.}) \qquad (2)$$

Uncertainties expressed are the "uncertainty interval" (*17*). The enthalpies of formation of gaseous $CO_2$ and liquid water were taken to be −94.051 and −68.315 kcal. per mole, respectively (*22*). Uncertainties assigned to gaseous carbon dioxide (*19*) and liquid water (*18*) were 0.011 and 0.010 kcal. per mole, respectively.

## DISCUSSION

**Comparison with Previous Work.** *n*-Nonane is the only compound of this group that has been studied previously. The "selected" value for *n*-nonane in the API Research Project 44 tables is the value selected by Prosen and Rossini (*16*). Values for the normal alkanes above pentane were obtained by fitting an equation, linear in the number of carbon atoms, to the data of Jessup (*11*) and Prosen and Rossini (*15*). The value of Prosen and Rossini (*15*) for the enthalpy of combustion of *n*-nonane, $\Delta Hc°_{298.15}$, was −1463.89 kcal. per mole. The value of Jessup (*11*), as revised by Prosen and Rossini, was −1463.67. Their selected value was −1463.80 kcal. per mole. The value believed to be the most reliable of the measurements of this laboratory is −1463.96 kcal. per mole, which was derived by using sample mass as the measurement of the amount of reaction. The measurements for the nonanes from this research would be best compared with the API Research Project 44 tables by the subtraction of 0.16 kcal. (1463.96 − 1463.80) from their absolute values. This subtraction has been made in Table VII, and the adjusted values for the heats of combustion are compared to the values predicted by the Rossini-Greenshields (*13*) and the Somayajulu-Zwolinski (*2, 21*) correlations. Except for the values for 2,2-dimethyl-3-ethylpentane and 2,4-dimethylpentane, the agreement of the experimental values of $\Delta Hc°$ with the correlated values is good. Most of the experimental values match the correlated values within allowances for experimental error. The correlations appear to fail for molecules with adjacent methyl and ethyl groups on the alkane chain.

Table IV. Summary of Typical Calorimetric Experiments at 298.15° K.[a]

| | *n*-Nonane | | 2,2-Dimethylheptane | 2,2,3-Trimethylhexane | 2,2,4-Trimethylhexane | 2,2,5-Trimethylhexane | 2,3,3-Trimethylhexane | 2,3,5-Trimethylhexane | 2,4,4-Trimethylhexane | 3,3,4-Trimethylhexane | 2,2-Dimethyl-3-ethylpentane | 2,4-Dimethyl-3-ethylpentane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Series I | Series II | | | | | | | | | | |
| $m'$(compd.), g. | 0.665187 | 0.676467 | 0.673409 | 0.674521 | 0.683356 | 0.669391 | 0.675270 | 0.670069 | 0.663224 | 0.663100 | 0.665974 | 0.661608 |
| $m''$(oil), g. | 0.040102 | 0.028909 | 0.032928 | 0.031305 | 0.022669 | 0.037652 | 0.030063 | 0.036214 | 0.043201 | 0.042456 | 0.040765 | 0.043868 |
| $m'''$(fuse), g. | 0.001048 | 0.001233 | 0.001292 | 0.001240 | 0.001086 | 0.001398 | 0.001146 | 0.001050 | 0.001285 | 0.001149 | 0.001188 | 0.001172 |
| $n^i(H_2O)$, mole | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 |
| $\Delta t_c = t_f - t_i - \Delta t_{cor}$ | 2.00098 | 2.00269 | 2.00078 | 2.00092 | 2.00252 | 2.00084 | 2.00026 | 2.00146 | 2.00264 | 2.00076 | 2.00580 | 2.00293 |
| $\mathcal{E}$(calor.)$(-\Delta t_c)$, cal. | −8013.86 | −8020.30 | −8012.63 | −8013.64 | −8019.62 | −8012.89 | −8010.97 | −8015.38 | −8020.07 | −8013.00 | −8033.16 | −8021.24 |
| $\mathcal{E}$(cont.)$(-\Delta t_c)$,[b] cal. | −10.43 | −10.45 | −10.43 | −10.40 | −10.45 | −10.43 | −10.27 | −10.42 | −10.46 | −10.40 | −10.30 | −10.44 |
| $\Delta E_{ign}$, cal. | 0.39 | 0.47 | 0.55 | 0.34 | 0.73 | 0.51 | 0.34 | 0.59 | 0.75 | 0.49 | 0.65 | 0.69 |
| $\Delta E_{(cor.\ to\ std.\ states)}$,[c] cal. | 1.96 | 1.95 | 1.95 | 1.96 | 1.95 | 1.95 | 2.01 | 1.95 | 1.97 | 1.97 | 1.97 | 1.98 |
| $-m''\Delta Ec°/M$ (oil), cal. | 440.49 | 317.55 | 361.70 | 343.86 | 249.00 | 413.59 | 330.22 | 397.78 | 474.53 | 466.35 | 447.78 | 481.86 |
| $-m'''\Delta Ec°/M$ (fuse), cal. | 4.24 | 4.99 | 5.23 | 5.02 | 4.40 | 5.66 | 4.64 | 4.25 | 5.20 | 4.65 | 4.81 | 4.75 |
| $m'\Delta Ec°/M$(compd.), cal. | −7577.21 | −7705.79 | −7653.63 | −7672.86 | −7773.99 | −7601.61 | −7684.03 | −7621.23 | −7548.08 | −7549.94 | −7588.25 | −7542.40 |
| $\Delta Ec°/M$ (compd.), cal./g. | −11,391.09 | −11,391.21 | −11.365.49 | −11,375.25 | −11,376.18 | −11,356.01 | −11,379.20 | −11,373.78 | −11,380.88 | −11,385.82 | −11,394.20 | −11,400.12 |

[a] Symbols and abbreviations of Hubbard *et al.* (*10*), except as noted. [b] $\mathcal{E}^i(\text{cont.})(t_i - 25) + \mathcal{E}^f(\text{cont.})(25° - t_f + \Delta t_{cor})$. [c] Items 81–85, 87–89, 93 and 94 of computation form of Hubbard *et al.* (*10*).

## Table V. Summary of Experimental Results

Values of $\Delta Ec^{\circ}/M$, in cal. per gram at 298.15° K.

| | *n*-Nonane | | 2,2-Dimethylheptane | 2,2,3-Trimethylhexane | 2,2,4-Trimethylhexane | 2,2,5-Trimethylhexane | 2,3,3-Trimethylhexane | 2,3,5-Trimethylhexane | 2,4,4-Trimethylhexane | 3,3,4-Trimethylhexane | 2,2-Dimethyl-3-ethylpentane | 2,4-Dimethyl-3-ethylpentane |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Series I | Series II | | | | | | | | | | |
| | −11391.22 | −11389.08 | −11365.13 | −11375.85 | −11376.18 | −11356.01 | −11379.20 | −11372.95 | −11380.88 | −11385.81 | −11394.20 | −11400.12 |
| | −11391.67 | −11391.21 | −11365.49 | −11375.53 | −11374.16 | −11356.93 | −11378.47 | −11374.05 | −11379.95 | −11385.26 | −11393.95 | −11399.61 |
| | −11339.73 | −11391.80 | −11365.75 | −11376.59 | −11375.28 | −11355.34 | −11378.17 | −11372.72 | −11380.31 | −11385.22 | −11394.52 | −11400.20 |
| | −11391.10 | −11391.16 | −11365.10 | −11376.63 | −11376.22 | −11354.92 | −11378.62 | −11373.01 | −11380.75 | −11385.39 | −11394.97 | −11400.05 |
| | −11390.53 | −11391.98 | −11367.24 | −11376.15 | −11376.29 | −11356.65 | −11379.67 | −11374.76 | −11381.16 | −11386.22 | −11394.90 | −11400.26 |
| | −11391.09 | −11390.99 | −11366.12 | −11375.25 | −11376.40 | −11357.16 | −11380.06 | −11373.78 | −11381.08 | −11385.82 | −11395.29 | −11400.83 |
| Mean | −11390.89 | −11391.04 | −11365.80 | −11376.00 | −11375.75 | −11356.17 | −11379.03 | −11373.55 | −11380.69 | −11385.62 | −11394.64 | −11400.18 |
| Std. dev. | 0.27 | 0.42 | 0.33 | 0.23 | 0.36 | 0.37 | 0.30 | 0.32 | 0.19 | 0.16 | 0.21 | 0.16 |

## Table VI. Molal Values at 298.15° K., Kcal. per Mole

| | Sample Mass Basis | | | Carbon Dioxide Mass Basis | | |
|---|---|---|---|---|---|---|
| | $\Delta Ec^{\circ}$ | $\Delta Hc^{\circ}$ | $\Delta Hf^{\circ}$ | $\Delta Ec^{\circ}$ | $\Delta Hc^{\circ}$ | $\Delta Hf^{\circ}$ |
| *n*-Nonane (Series I) | −1460.99 ± 0.18 | −1463.96 ± 0.18 | −65.65 ± 0.24 | −1460.96 ± 0.30 | −1463.92 ± 0.30 | −65.69 ± 0.33 |
| *n*-Nonane (Series II) | −1461.01 ± 0.20 | −1463.97 ± 0.20 | −65.64 ± 0.24 | −1461.01 ± 0.22 | −1463.97 ± 0.22 | −65.64 ± 0.26 |
| 2,2-Dimethylheptane | −1457.78 ± 0.20 | −1460.74 ± 0.20 | −68.88 ± 0.24 | −1457.82 ± 0.30 | −1460.78 ± 0.30 | −68.83 ± 0.33 |
| 2,2,3-Trimethylhexane | −1459.08 ± 0.18 | −1462.05 ± 0.18 | −67.57 ± 0.22 | −1459.21 ± 0.18 | −1462.17 ± 0.18 | −67.44 ± 0.23 |
| 2,2,4-Trimethylhexane | −1459.05 ± 0.20 | −1462.01 ± 0.20 | −67.60 ± 0.24 | −1459.04 ± 0.22 | −1462.00 ± 0.22 | −67.61 ± 0.26 |
| 2,2,5-Trimethylhexane | −1456.54 ± 0.20 | −1459.50 ± 0.20 | −70.11 ± 0.24 | −1456.51 ± 0.30 | −1459.47 ± 0.30 | −70.14 ± 0.33 |
| 2,3,3-Trimethylhexane | −1459.47 ± 0.20 | −1462.43 ± 0.20 | −67.18 ± 0.24 | −1459.33 ± 0.25 | −1462.29 ± 0.25 | −67.32 ± 0.29 |
| 2,3,5-Trimethylhexane | −1458.77 ± 0.20 | −1461.73 ± 0.20 | −67.88 ± 0.24 | −1458.81 ± 0.24 | −1461.77 ± 0.24 | −67.84 ± 0.28 |
| 2,4,4-Trimethylhexane | −1459.68 ± 0.18 | −1462.65 ± 0.18 | −66.97 ± 0.22 | −1459.74 ± 0.22 | −1462.70 ± 0.22 | −66.91 ± 0.26 |
| 3,3,4-Trimethylhexane | −1460.32 ± 0.18 | −1463.28 ± 0.18 | −66.33 ± 0.22 | −1460.35 ± 0.26 | −1463.31 ± 0.26 | −66.30 ± 0.30 |
| 2,2-Dimethyl-3-ethylpentane | −1461.47 ± 0.18 | −1464.44 ± 0.18 | −65.18 ± 0.22 | −1461.66 ± 0.23 | −1464.62 ± 0.23 | −64.99 ± 0.27 |
| 2,4-Dimethyl-3-ethylpentane | −1462.18 ± 0.18 | −1465.15 ± 0.18 | −64.47 ± 0.22 | −1462.27 ± 0.25 | −1465.23 ± 0.25 | −64.38 ± 0.29 |

## Table VII. Comparison with Data Correlations of $\Delta Hc^{\circ}_{298.15}$, Kcal. per Mole

| | This Research (Adjusted Values) | Labbauf, Greenshields, and Rossini (*13*) | Somayajulu-Zwolinski (*2, 21*) |
|---|---|---|---|
| *n*-Nonane | −1463.80 | −1463.80 | −1463.80 |
| 2,2-Dimethylheptane | −1460.58 | −1460.53 | −1460.43 |
| 2,2,3-Trimethylhexane | −1461.89 | −1462.02 | −1461.77 |
| 2,2,4-Trimethylhexane | −1461.85 | −1461.78 | −1461.88 |
| 2,2,5-Trimethylhexane | −1459.34 | −1459.20 | −1459.17 |
| 2,3,3-Trimethylhexane | −1462.27 | −1462.51 | −1462.61 |
| 2,3,5-Trimethylhexane | −1461.57 | −1461.56 | −1461.40 |
| 2,4,4-Trimethylhexane | −1462.49 | −1462.27 | −1462.75 |
| 3,3,4-Trimethylhexane | −1463.12 | −1463.12 | −1463.07 |
| 2,2-Dimethyl-3-ethylpentane | −1464.28 | −1462.72 | −1462.19 |
| 2,4-Dimethyl-3-ethylpentane | −1464.99 | −1463.34 | −1462.78 |

The comparison with values from the Rossini-Greenshields correlation is slightly misleading, because the equation given by Rossini and Greenshields (*9*) for the variation of heats of formation with molecular structure will not exactly reproduce the values given by Labbauf, Greenshields, and Rossini (*13*) for the isomeric nonanes.

## NOMENCLATURE

$\partial$ = differential operator
$m$ = mass, grams
$n$ = number of moles
$P$ = pressure, atm.
$T$ = temperature
$\varepsilon$(calor.) = heat equivalent of calorimeter, cal./° K.
$\varepsilon$(cont.) = heat equivalent of contents, cal./° K.
$\Delta E_{\text{dec}}$ = energy of decomposition, cal.
$\Delta E_{\text{ign}}$ = electrical ignition energy, cal.
$\Delta E_{\text{cor. to std. states}}$ = energy for reduction to standard states, cal.
$\Delta Ec^{\circ}/M$ = standard energy of idealized combustion reaction, cal./gram
$\Delta Ec^{\circ}$ = standard energy of idealized combustion reaction, kcal./mole
$\Delta Hc^{\circ}$ = standard enthalpy of combustion, kcal./mole
$\Delta Hf^{\circ}$ = standard enthalpy of formation of liquid, kcal./mole

### Subscripts

$i$ = initial state
$f$ = final state

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# Vapor Pressure of Ketene

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**The boiling point of ketene was measured as –49.8° C. The molar heat of vaporization was calculated as 4880 cal. and the Trouton constant as 21.9.**

THE boiling point of ketene is given in the literature variously between –41° and –56° C. (*2, 4, 5, 6*). In the work reported, another value was obtained, along with the associated thermodynamic constants, by measurements of the vapor pressure of ketene between –49° and –114° C.

## PREPARATION OF KETENE

Ketene was prepared by cracking Analar acetone over a Nichrome filament in a ketene lamp (*7*). The effluent gases were passed through two traps maintained between –40° and –45° C., and a further trap immersed in solid carbon dioxide and acetone. The ketene condensed in the final trap, and after trap-to-trap distillation was shown by mass spectrometric analysis to be approximately 90% pure.

This crude ketene was further purified by distillation on a Podbielniak low-temperature column with a 90-cm. Heligrid packing operated about 20 cm. below atmospheric pressure. The vessel containing the crude ketene was wound with a small electrical heater and surrounded by a tube immersed in solid carbon dioxide and acetone. It was attached directly to the bottom of the column. The top of the column was cooled by a mush of melting methanol (–95° C.) which was maintained by occasional addition of small amounts of liquid nitrogen, accompanied by vigorous stirring.

The column was preflooded, and the heating adjusted to give total reflux. Ketene was taken off slowly from the top of the column to a conventional vacuum system via a needle valve. A first fraction of about 10 ml. boiling below –56° C. was discarded, a middle fraction of about