

The heat of vaporization is 13.8 kcal. per mole. A comparison of the calculated and observed vapor pressure values in Table I shows that a satisfactory straight line is obtained over this temperature range.

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3-Methyl-1,2-butadiene: Enthalpies of Combustion and Formation

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The enthalpy of combustion of liquid 3-methyl-1,2-butadiene was measured in an oxygen-bomb calorimeter. The enthalpy of formation was derived. The following values, in kcal. per mole at 298.15° K., are reported for liquid 3-methyl-1,2-butadiene: $\Delta H_c^\circ = -767.70 \pm 0.10$, $\Delta H_f^\circ = 24.18 \pm 0.12$.

THE ENTHALPIES of combustion of isoprene and five of its isomers, reported by Fraser and Prosen (4), were measured in an electrically calibrated flow calorimeter where the hydrocarbon vapors, carried by helium gas, were burned in a flame at constant pressure. Since 3-methyl-1,2-butadiene was not included in this research, the enthalpy of combustion of this compound was measured as part of a continuing program to provide basic thermodynamic properties of hydrocarbons that occur in or are related to petroleum.

EXPERIMENTAL

Apparatus and Procedures. A detailed description of the calorimetric procedures, the analytical methods, and the calibration procedures for the hydrocarbons was recently reported (7). This procedure was followed in the study of 3-methyl-1,2-butadiene. The rotating-bomb calorimeter BMR II and platinum-lined bomb Pt-3b, internal volume 0.349 liter, have been described (5, 6). Rotation of the bomb was unnecessary. One milliliter of water was added to the bomb, which then was charged to 30 atm. with pure oxygen. A negligible amount of nitric acid was formed in these experiments. Each experiment was initiated at 23° C., and the masses of combustibles were so chosen that the final temperatures were very nearly 25° C.

Materials. The sample of 3-methyl-1,2-butadiene was purchased from the American Petroleum Institute Research Project 58B at Carnegie-Mellon University. The sample impurity was 0.04 ± 0.04 mole %. The sample was dried by means of a vapor pass over a freshly activated molecular sieve before the borosilicate glass ampoules were filled in a vacuum system.

The calorimeter was calibrated with benzoic acid, NBS Sample 39i, which has a heat of combustion of 26.434 ± 0.003 absolute kilojoules per gram under certificate conditions. Conversion to standard conditions (8) gives -6313.02 ± 0.72 cal. per gram for $\Delta E_c^\circ/M$, the energy of the idealized combustion reaction. $\xi(\text{calor.})$ was 4004.62 ± 0.09 cal. per

deg. (mean and standard deviation for six calibration experiments).

The auxiliary oil and cotton thread fuse used to initiate the combustion reactions have been described (5, 6). For the auxiliary oil, the value of $\Delta E_c^\circ/M$ was $-10,984.2 \pm 0.2$ cal. per gram (mean and standard deviation) in a series of experiments chronologically near the 3-methyl-1,2-butadiene experiments.

Units of Measurements and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (2), and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and of the thermochemical calorie; 1 cal. = 4.184 (exactly) abs. joules (3). The laboratory standards of mass and resistance had been calibrated by the National Bureau of Standards.

Several physical properties of 3-methyl-1,2-butadiene were needed for the reduction to standard states (8). The value used for the density at 25° C. was 0.68064 gram per ml. (1). The value of the heat capacity of the liquid at 25° C. (from Bureau research) was 0.53 cal. per deg. per gram. The value of $(\partial E/\partial P)_T$, derived from the temperature dependence of density (1), was -0.0168 cal. per atm. per gram.

Calorimetric Results. Five successful combustion experiments (Table I) were obtained in nine attempts. Three experiments were rejected because unburned carbon was deposited on the bomb walls. In one experiment, the sample detonated and damaged the platinum crucible. Considerable unburned carbon was left, and the experiment was rejected.

The amount of reaction was based on the mass of sample; however, carbon dioxide recoveries from the combustion products, also listed in Table I, correspond closely to the expected stoichiometry. Therefore, if the amount of reaction were based on the carbon dioxide recoveries, the results would barely change. The value of $\Delta E_c^\circ/M$ would increase by 0.004%, and the precision would increase considerably. The values of $\Delta E_c^\circ/M$ for 3-methyl-1,2-butadiene refer to the idealized combustion reaction (1) at 298.15° C.

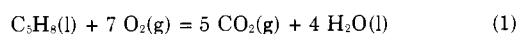


Table I. Summary of Calorimetric Experiments^a

	Experiment				
	1	2	3	4	5
m' (compound), g.	0.670250	0.662986	0.661853	0.642900	0.669105
m'' (oil), g.	0.042690	0.052833	0.051456	0.071100	0.045352
m''' (fuse), g.	0.001198	0.001143	0.001116	0.001084	0.001183
CO ₂ Recovery (%)	99.99 ₃	100.00 ₂	99.99 ₇	99.99 ₃	99.99 ₇
n (H ₂ O), mole	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c = t_f - t_i + \Delta t_{\text{cor.}}$, deg. ⁻¹	1.99974	2.00727	2.00023	2.00063	2.00373
$\xi(\text{calor.})(-\Delta t_c)$, cal.	-8008.21	-8038.35	-8010.18	-8011.79	-8024.17
$\xi(\text{cont.})(-\Delta t_c)$, cal. ^b	-10.44	-10.47	-10.43	-10.44	-10.44
$\Delta E_{\text{ign.}}$, cal.	0.45	0.53	0.61	0.49	0.45
$\Delta E_{\text{cor. to std. states}}$, cal. ^c	2.56	2.57	2.56	2.56	2.57
$-m'' \Delta E_c^\circ/M$ (oil), cal.	468.92	580.34	565.21	780.98	498.16
$-m''' \Delta E_c^\circ/M$ (fuse), cal.	4.85	4.63	4.52	4.39	4.79
$m' \Delta E_d^\circ/M$ (compound), cal.	-7541.87	-7460.75	-7447.71	-7233.81	-7528.64
$\Delta E_c^\circ/M$ (compound), cal./g.	-11,252.32	-11,253.25	-11,252.81	-11,251.84	-11,251.82

^aThe symbols and abbreviations of this table are those of reference (8), except as noted. ^b $\xi'(\text{cont.})(t' - 25) + \xi'(\text{cont.})(25^\circ - t' + \Delta t_{\text{cor.}})$. ^cItems 81-85, 87-89, 93, and 94 of the computation form of reference (8).

Table II. Derived Thermochemical Data at 298.15° K., Kcal./Mole

$\Delta E_c^\circ = -766.51 \pm 0.10$
$\Delta H_c^\circ = -767.70 \pm 0.10$
$\Delta H_f^\circ = 24.18 \pm 0.12$

ΔH_c° = standard enthalpy of combustion, kilocalories per mole

$\Delta H_f^\circ(l)$ = standard enthalpy of formation of liquid, kilocalories per mole

i = superscript indicating initial state

f = superscript indicating final state

The mean value of $\Delta E_c^\circ/M$, with standard deviation, is $-11,252.4_1 \pm 0.2_8$ cal. per gram.

Derived Results. Table II gives the derived results for liquid 3-methyl-1,2-butadiene. The uncertainties expressed are the "uncertainty interval" equal to twice the overall standard deviation of the mean, and they reflect uncertainties in the calibration experiments, in the certification of benzoic acid, and in the combustion experiments with 3-methyl-1,2-butadiene. To calculate values of the standard enthalpy of formation, the following values were used for the enthalpies of formation of gaseous carbon dioxide and liquid water, respectively: -94.051 and -69.315 kcal. per mole (10). The uncertainty in the enthalpy of formation of gaseous carbon dioxide was taken to be 0.0108 kcal. per mole (9), and the uncertainty in the enthalpy of formation of liquid water was taken to be 0.0096 kcal. per mole (11).

NOMENCLATURE

∂	= differential operator
T	= temperature, °K.
m	= mass, grams
n	= number of moles
P	= pressure, atm.
$\xi(\text{calor.})$	= energy equivalent of calorimeter, cal. per deg.
$\xi(\text{cont.})$	= energy equivalent of contents, cal. per deg.
$\Delta E_{\text{dec.}}$	= energy of decomposition, calories
$\Delta E_{\text{ign.}}$	= electrical ignition energy, calories
$\Delta E_{\text{cor. to std. states}}$	= energy for reduction to standard states, calories
$\Delta E_c^\circ/M$	= standard energy of idealized combustion reaction, cal. per gram
ΔE_c°	= standard energy of idealized combustion reaction, kilocalories per mole

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