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

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

30 ml. boiling from approximately −56° to −54° C. was collected, and a small final fraction of about 5 ml. boiling above −54° C. remained and was discarded.

Mass spectrometric analysis showed 0.1 to 0.3% propane, about 0.3% carbon dioxide, and traces of diketene, acetic anhydride, and acetic acid, which probably originated inside the mass spectrometer. The ketene was stored as a solid at liquid nitrogen temperatures to prevent dimerization.

MEASUREMENT OF VAPOR PRESSURE

The vapor pressures were measured by a static technique, the ketene-containing vessel with its thermocouple being attached directly to a U-tube manometer of 0.8-cm. i.d. tubing. The mercury level was observed with a cathetometer and readings were corrected for the height of the meniscus. Silicone greases were used throughout.

Temperatures above −70° C. were maintained by a Townson and Mercer Minus Seventy thermostat bath which controlled the temperature to ±0.05° C. For temperatures below −70° C., the ketene container was placed inside a heavy copper block surrounded by an evacuable air jacket. The system was cooled with liquid nitrogen and the jacket pumped out when the correct temperature was reached. The jacket could be surrounded with solid CO_2 and acetone to warm it up, or liquid nitrogen to cool it down. The rate of cooling or warming with the jacket evacuated was about 0.2° C. per minute, so that a good approximation to equilibrium could be achieved. Readings of vapor pressure were taken with the system being heated and being cooled. The temperatures corresponding to a given vapor pressure in the heating and cooling experiments differed by less than 1.5° C. and an average value was considered acceptable.

Temperatures were measured with a Chromel-Alumel thermocouple, which had been calibrated against an N. P. L.-calibrated Pt-Pt/Rh thermocouple.

RESULTS

The results obtained are shown in the first two columns of Table I. The boiling point of ketene at 760 mm. can be interpolated as −49.8° C.

Attempts to fit the data to the Antoine equation

$$\log_{10} P = A - B/(C + t)$$

showed that wide variations in C had virtually no effect

on the standard deviation. The data were therefore fitted to the simpler equation

$$\log_{10} P = A - B/T$$

by a least squares method, $\log_{10} P$ being taken as the variable parameter. The values of $\log_{10} P$ were weighted according to the magnitude of P, a technique which assumes that the probable error in the measurement of the pressure is independent of its actual magnitude. The resulting equation was

$$\log_{10} P = 7.6607 - 1.0671/T \qquad (1)$$

and the values of vapor pressure predicted by this equation are shown in the third column of Table I. Ignoring the reading at −72.55° C., which appears to be seriously in error, the mean deviation is 1.9 mm.

Values of ΔH_v and ΔS_v were estimated from the gradient of the "least squares" plot.

$$\Delta H_v = 4880 \pm 14 \text{ cal. per mole}$$

$$\Delta S_v = 21.9 \text{ cal. per degree per mole}$$

The value of the Trouton constant is only slightly higher than that of hydrogen sulfide [b.p. = −61° C.; ΔH_v = 4524 cal. per mole, whence ΔS_v = 21.3 cal. per degree per mole (1)] and association may therefore be regarded as negligible.

The boiling point of −49.8° C. is close to Johnson and Strandberg's value of "approximately −50° C." The vapor pressures are much higher than those of Pearson et al. (3).

SAFETY

Ketene is extremely toxic (8). The preparation was carried out in a fume cupboard, and other work in a laboratory which was provided with gas masks and which could be easily and rapidly evacuated.

NOMENCLATURE

P = pressure, mm. Hg
t = temperature, ° C.
T = temperature, ° K.
ΔH_v = molar heat of vaporization
ΔS_v = molar entropy of vaporization (Trouton constant)
A, B, C = empirical constants

Table I. Pressure and Temperature Data

t, ° C.	P (Exptl.)	P (Equation 1)
−49.35	774.3	775.2
−50.15	745.4	745.2
−53.10	646.8	642.8
−55.35	577.0	572.7
−58.05	500.6	496.9
−62.40	393.0	392.4
−63.80	358.9	362.9
−68.50	275.3	277.1
−72.55	207.5	217.4
−87.8	79.5	79.2
−100.9	30.0	28.9
−107.8	13.5	15.9
−113.8	8.1	9.1

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