Vapor Pressure of Methyl-2-cyanoacrylate

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The vapor pressure of methyl-2-cyanoacrylate has been measured over the temperature range −15° to 10° C. by means of a Knudsen effusion cell. The data fit the equation, log p (μ) = 12.9536 − 3018.8/T, and the heat of vaporization is 13.8 kcal. per mole.

METHYL-2-CYANOACRYLATE is very useful in preparing ice crystal replicas in connection with weather modification and ice nucleation studies (*2*). Since the technique involves the deposition of the monomer on the ice crystal by a vapor transport process, it was desirable to determine the vapor pressure and heat of vaporization of this compound over the temperature range 10° to −15° C.

EXPERIMENTAL

The pure monomer must be inhibited for use in these studies because of its rapid rate of polymerization, especially in the presence of moisture. The commercial adhesive, Eastman 910, is used as the source of the acrylate monomer. According to the manufacturer (Tennessee Eastman Co., Kingsport, Tenn.), the adhesive is a mixture consisting of approximately 90% methyl-2-cyanoacrylate and 10% thickening agent, plasticizer, and stabilizer. Mass spectrometric analysis showed that the vapor above the adhesive consisted of only the monomer. The adhesive was used as received in 1-ounce polyethylene bottles; material from two bottles (Lots 842 and 843) was used for the vapor pressure measurements.

The vapor pressure was measured by means of a Knudsen effusion cell. The effusion cell was a brass cylinder with inside dimensions of 1.58 cm. in diameter by 2.22 cm. in depth. It was fitted with a screw cap with a Teflon gasket. The cap had a 5-mm. hole in the center, over which a piece of 1-mil aluminum foil was cemented with epoxy cement. The orifice had been drilled in the center of the aluminum foil with a high-speed drill. The diameter of the orifice was measured with a microscope and was 0.780 mm. To break up the foam which formed when the cell was evacuated, a piece of platinum screen was inserted about half way into the cell. Reproducible results were unobtainable at the higher temperatures because of polymerization of the monomer; however, with the screen in place, the surface area of the vaporizing monomer was increased sufficiently to give consistent results. Above 10° C. the polymerization became too rapid, even with the screen present.

The holder for the effusion cell consisted of a section of 40-mm. i.d. glass tubing, one end of which was a standard taper 50/50 ground joint to connect with the vacuum line and the other end of which was plugged by a brass block made vacuum-tight by two neoprene O rings. The effusion cell was placed in a closely fitting hole in the brass block, which was immersed in a constant-temperature bath. The bath contained a water-propanol mixture and was controlled at each temperature to ±0.01° C. A cold finger, cooled with a dry ice–acetone mixture, was placed approximately 9 cm. above the cell. A pressure of 4×10^{-6} torr could be obtained with the apparatus when no monomer was present.

The Knudsen cell was loaded with the Eastman 910 monomer under dry nitrogen in a disposable dry box, weighed, and put into the cell holder as rapidly as possible. The constant-temperature bath was raised around the cell holder. After 15 minutes, temperature equilibrium was attained, and the apparatus was evacuated. After the desired time had elapsed, atmospheric pressure was restored; the cell was removed, allowed to reach room temperature in a desiccator, and then reweighed.

Table I. Vapor Pressure Data for Methyl-2-cyanoacrylate

Temp., °C.	Observed Pressure, μ Hg		Calcd. Pressure, μ Hg	% Difference
	Measured	Average		
10	198.8 190.7 193.2 191.4	193.5	196.2	−1.40
5	127.6 127.0	127.3	126.2	+0.87
0	80.8 77.8 81.9	80.2	79.9	+0.37
−5	49.8 50.8	50.3	49.7	+1.19
−10	31.1 29.3	30.2	30.4	−0.66
−15	18.1 18.1	18.1	18.2	−0.55

RESULTS

The vapor pressures were calculated from the equation

$$p = 17143.5 \frac{G}{AtK} (T/M)^{1/2} \qquad (1)$$

in which p is the pressure in microns of Hg, G is the number of grams of material lost by effusion in t seconds, A is the area of the orifice in sq. cm., K is the Clausing factor, the magnitude of which depends upon the geometry of the orifice, T is the absolute temperature, and M is the molecular weight of the effusing species (*1, 3*). For the orifice used in these experiments, the ratio of the thickness to the area is 0.053, and a Clausing factor of 0.97 was obtained by interpolation from the table given by Dushman (*1*).

The results of the measurements are given in Table I. Each of the observed vapor pressures is the average of two to four determinations. A least squares analysis of the log p *vs.* $1/T$ data, using the average vapor pressures at each temperature, gives the constants in the equation

$$\log p = 12.9536 - 3018.8/T \qquad (2)$$

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.

LITERATURE CITED

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RECEIVED for review January 21, 1969. Accepted May 9, 1969.

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: $\Delta Hc^\circ = -767.70 \pm 0.10$, $\Delta Hf^\circ = 24.18 \pm 0.12$.

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_4 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 39*i*, 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 $\Delta Ec^\circ/M$, the energy of the idealized combustion reaction. $\mathcal{E}$(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 $\Delta Ec^\circ/M$ was −10,984.2 ± 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 $\Delta Ec^\circ/M$ would increase by 0.004%, and the precision would increase considerably. The values of $\Delta Ec^\circ/M$ for 3-methyl-1,2-butadiene refer to the idealized combustion reaction (1) at 298.15° C.

$$C_5H_8(l) + 7\,O_2(g) = 5\,CO_2(g) + 4\,H_2O(l) \qquad (1)$$