than H_2O over the entire temperature range; however, at the higher temperatures the viscosities of D_2O and H_2O appear to approach each other. For example, at 5° the difference between the viscosity of D_2O and H_2O is 0.4628 cP while at 70° the difference is only 0.0693 cP. One might attribute the decrease in the difference between the η of D_2O and H_2O to the formation of similar structure for D_2O and H_2O at high temperatures (*i.e.*, if the larger η of D_2O is due to greater structure). The effect of temperature on the differences between the compressibilities of D_2O and H_2O also agree with this suggestion (*3, 4, 12*).

In future work, we plan to investigate the temperature dependence of other pure solvents and hopefully use these results to obtain a better understanding of the structural properties of water by comparison.

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Heats of Combustion, Heats of Formation and Vapor Pressures of Some Organic Carbonates

Estimation of Carbonate Group Contribution to Heat of Formation

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Heats of combustion were measured, using oxygen bomb calorimetry, for some organic carbonates—*i.e.*, ethylene carbonate, diethyl carbonate, propylene carbonate, vinylene carbonate, di-(*p*-phenylbenzyl)carbonate. Sublimation pressure of low vapor pressure compounds—*i.e.*, ethylene carbonate—were measured by the Knudsen effusion method. High vapor pressure compounds—*i.e.*, propylene carbonate, diethyl carbonate, and vinylene carbonate—were measured using a modified manometric apparatus. The gaseous phase heats of formation were used to estimate the carbonate group contribution to the heat of formation. A value of −133 ± 1 kcal/mole was obtained.

Simple methods of calculating thermodynamic properties of organic compounds readily and with a minimum of data have been developed by a number of workers, and have been reviewed critically by Reid and Sherwood (*11*), Janz (*6*) and Benson (*1*). From the various possibilities, the additive-atomic group method was selected to calculate the organic carbonate group contribution to the heat of formation in the gaseous state. An additive-atomic group contribution method for heats of formation (gas) has been developed by Franklin (*4*) for hydrocarbons and other organic compounds such as simple free radicals. The method of Franklin is based on the extension of the relations and principles developed by Pitzer (*10*) for the long-chain paraffins.

EXPERIMENTAL

Vapor Pressure Measurements. The Knudsen effusion method (*7, 12*) was employed to measure the sublimation pressure of low vapor pressure compounds, whereas a modified manometric method was employed for high vapor pressure compounds.

Knudsen Effusion Method. The measurement of weight loss in a known period of time at a known constant temperature allows the calculation of the vapor pressure, using the effusion formula, and assuming that the pressure in the vacuum above the effusion hole is negligibly small compared to the vapor pressure of compounds to be measured. A high vacuum system is required when using this method; details of this system are available elsewhere (*3*).

The following Knudsen effusion formula was used to calculate the sublimation pressure after insertion of proper values for the constants:

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$$P_{\mathrm{mm\ Hg}} = 17143.5\ (G/A \cdot t)(T/M)^{1/2} \qquad (1)$$

where P is the pressure of the saturated vapor inside the Knudsen cell, G is the weight in grams lost by effusion, A is the orifice area of Knudsen cell in cm^2, t is the time in seconds for loss of G grams, T is the absolute temperature in ° K, and M is the molecular weight of sample.

Modified Manometric Method. It was necessary to devise a different method and apparatus for the measurement of vapor pressures of compounds which have high vapor pressure at room temperature. The modified manometric method was employed for this purpose, and a schematic diagram of the apparatus employed is shown in Figure 1. In this diagram, R_t and R_b represent the reaction chamber, top and bottom, respectively. R_{in} is the water inlet to R_t; R_{out} is the water outlet to the bath. B_{out} is the water outlet of the bath connected to R_{in}. I_s is the sample inlet to R_b; F_r is a frit covered with mercury; P_f is a clamp holding R_t and R_b together.

The over-all height of the reaction chamber is 160 cm and the inside diameter of the chamber is 5 cm. The closed-end U-type mercury manometer is fastened to the top of the reaction chamber, R_t. An accurate, mercury-filled thermometer (the range of accuracy ±0.05° C) is attached to the manometer. A fine frit, covered with mercury, forms the closed end of the manometer. This allows the lower pressure arm of the manometer to be evacuated without difficulty. Such a frit is also employed for the sample inlet, I_s. The reaction chamber consists of two parts, top part, R_t, and the bottom part, R_b. These two parts are joined together with an O-ring held by clamp P_f. This design provides many advantages with regard to such items as handling and filling.

After the reaction chamber as shown in Figure 1 is assembled, the entire system was evacuated and the bottom part was immersed in the constant-temperature bath (Haake Gebroede, Berlin-Steglitz, West Germany). R_{in} was connected to B_{out}, and water was allowed to circulate around the top part of the reaction chamber. Since the constant-temperature water bath employed is equipped with a strong water pump as a component part, the rate of water circulation was rapid enough that the temperature difference between the inside and the outside of the bath was less than ±0.1° C, the range of accuracy of temperature measurement. The temperature can be changed very easily and quickly by using the adjustable thermoregulator.

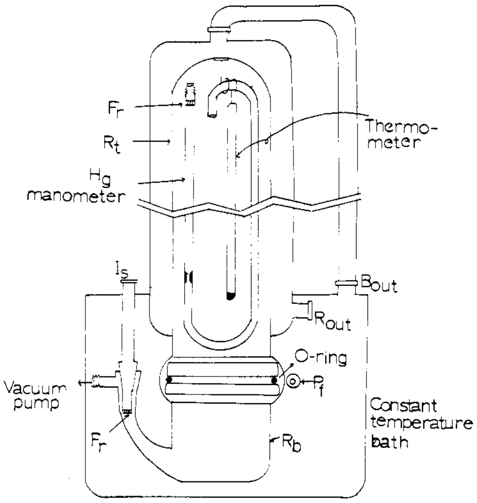


Figure 1. Schematic diagram of the modified vapor pressure measurement apparatus for liquid compounds

R_t and R_b	Reaction chamber top and bottom, respectively
R_{in}	Water inlet to R_t
R_{out}	Water outlet to the bath
B_{out}	Water outlet of the bath connected to R_{in}
I_s	Sample inlet to R_b
F_r	Frit covered with mercury
P_f	Clamp holding R_t and R_b together

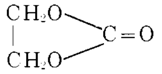
The reaction chamber was evacuated to a pressure of less than 0.1 micron Hg by using a mechanical pump and a one-stage glass oil-diffusion pump. The system was tested by a vacuum maintained for more than 12 hr when isolated from the pumping. After the system was evacuated, the sample was introduced through the sample inlet, I_s, at the end of which a frit is attached. After thermal equilibrium was established, the vapor pressure was measured. The vapor pressure was simply the difference in height between the two mercury columns as measured by a cathetometer (Griffin & George Ltd., London, England).

When a constant pressure was obtained at one temperature, the temperature was changed and the same procedure was repeated at the new temperature. Before one compound was changed to the next, the whole system was evacuated as completely as possible. The entire system was then cleaned thoroughly to remove any contamination of the mercury manometer by sample and also to prevent the contamination of one sample by another.

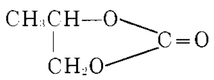
Measurement of Heat of Combustion. An adiabatic oxygen bomb calorimeter (Parr Instrument Co. Inc., Moline, Ill.) was employed for measuring heats of combustion of organic carbonates. The internal volume of this double-valved oxygen bomb, whose cylinder and head are made of Durimet 20, was 360 ml. The initial oxygen pressure was 30 atm. Temperature rise was measured by Dymec model 2801 A quartz thermometer (Dymec, A Division of Howlett-Packard Co., Palo Alto, Calif.). The calorimetric system was calibrated with National Bureau of Standards benzoic acid which had a heat of combustion of 6317.8 defined thermochemical calories per gram.

Seven experiments gave a calorimetric equivalent of −2538.2 ± 0.8 cal/° C. The correction for the formation of nitric acid which was titrated with standard solution of Na_2CO_3 (0.0725*N*) never exceeded more than 0.5 cal and was based on a value of −14.0 kcal/mole for the heat of formation of nitric acid from nitrogen, oxygen, and water. The ice point was taken as 273.15° K. Whenever the combustion was carried out, the inside of the bomb was carefully examined for soot due to the incomplete combustion. The $\Delta n\ Rt$ terms were applied for obtaining ΔH_c°.

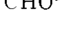
Materials. The zone refining method (*9*) using commercial zone refiner (Material Research Co., Orangeburg, N. Y.) was employed for purification of ethylene carbonate



(mol wt 88.06, mp 39–42° C, Aldrich Chemical Co. Inc., Milwaukee, Wis.). The solid sample was usually dried under high vacuum to remove volatile impurities and moisture. Purity of liquid samples was checked using a Bausch & Lomb refractometer. Agreement with values given by manufacturers was quite good—for example, propylene carbonate



(mol wt 102.09, bp 241.7° C, Jefferson Chemical Co., Inc., Houston, Tex.), $n_D^{25} = 1.4201$ ($n_D^{20} = 1.4209$); vinylene carbonate



(mol wt 86.05, Aldrich Chemical Co. Inc., Milwaukee, Wis.), $n_D^{25} = 1.4225$ ($n_D^{20} = 1.4228$); diethyl carbonate, $(CH_3CH_2)_2CO_3$, (mol wt 118.13, bp 126.8° C, FMC Co., New York, N. Y.), $n_D^{25} = 1.3882$ ($n_D^{20} = 1.3852$). Values in parenthesis are given by manufacturers.

RESULTS AND DISCUSSION

Heats of combustion, formation, vaporization, or sublimation are given in Table I. Heats of formation (solid or liquid) were obtained according to the relationship between heats of formation (solid or liquid) and heats of combustion

$$\Delta H^\circ_{f(\text{s or l})} = a\Delta H^\circ_{f(CO_2,\ 298\ K)} + b/2\Delta H^\circ_{f(H_2O,\ 298\ K)} - \Delta H^\circ_c \quad (2)$$

for the general organic compound, $C_aH_bN_cO_d$, where $\Delta H^\circ_{f(CO_2,\ 298\ K)} = -94.051$ kcal per mole, and $\Delta H^\circ_{f(H_2O,\ 298\ K)} = -68.315$ kcal per mole were employed (*13*).

The heat of formation (gas), $\Delta H^\circ_{f(g)}$, has the following relation to the heat of formation (solid or liquid) and with the heat of sublimation or vaporization.

$$\Delta H^\circ_{f(g)} = \Delta H^\circ_{f(\text{s or l})} + \Delta H_{\text{vap or sub}} \quad (3)$$

The Clausius-Clapeyron equation was employed for calculation of the heat of sublimation or vaporization from vapor pressure data—*i.e.*

$$d \ln P = -(\Delta H/R)\, d\,(1/T) \quad (4)$$

ln P was plotted as a function of $1/T$. The slope of the straight line obtained is $-\Delta H/R$, where ΔH is the heat of vaporization or sublimation. The graph for such a plot is shown in Figure 2. The vapor pressure data are given in Table II. No ideal gas correction was performed because of lack of data (*2*). The Knudsen effusion method was employed to measure the vapor pressure for low vapor pressure compounds whereas the modified manometric method was employed for the high vapor pressure compounds.

The group contribution of the carbonate group to the heat of formation (gas) was calculated by using the Franklin's method (*4*, *5*). The heat of formation in the gaseous state of ethylene carbonate consists of the group contribution of two methylene groups and a carbonate group. According to the Franklin's method, the group contribution to the heat of formation in the gaseous state of the methylene group, CH_2, is −4.93 kcal/mole at 298° K. Therefore, the following equation is readily obtained:

$$\Delta H^\circ_{f(g)} = 2\,\Delta H^\circ_{CH_2} + (1)\,\Delta H^\circ_{CO_3} \quad (4)$$

Therefore

$$\Delta H^\circ_{CO_3} = \Delta H^\circ_{f(g)} - 2\,\Delta H^\circ_{CH_2} = -144.43 - 2\,(-4.93) = -134.58 \text{ kcal/mole}$$

Table I. Heats of Combustion (ΔH°_c), Heats of Formation (ΔH°_f), Heats of Vaporization or Sublimation ($\Delta H_{\text{vap or sub}}$)

Unit: kcal/mole

Compounds	$\Delta H^{\circ a}_c$	$\Delta H^\circ_{f(s,\ l)}$	$\Delta H_{\text{vap, sub}}$	$\Delta H^\circ_{f(g)}$
Ethylene carbonate	−255.58	−163.20	18.77	−144.43
Propylene carbonate	−430.14	−151.01	7.33	−143.68
Diethyl carbonate	−638.75	−173.08	9.35	−163.53
Vinylene carbonate	−240.56	−109.91	9.86	−100.55
Di-(*p*-phenylbenzyl) carbonate	−3214.15	−76.69	26.7[b]	−50.0[b]

[a] Heats of combustion data are the average values more than four experiments. [b] The estimated values (for further details, refer to Discussion section).

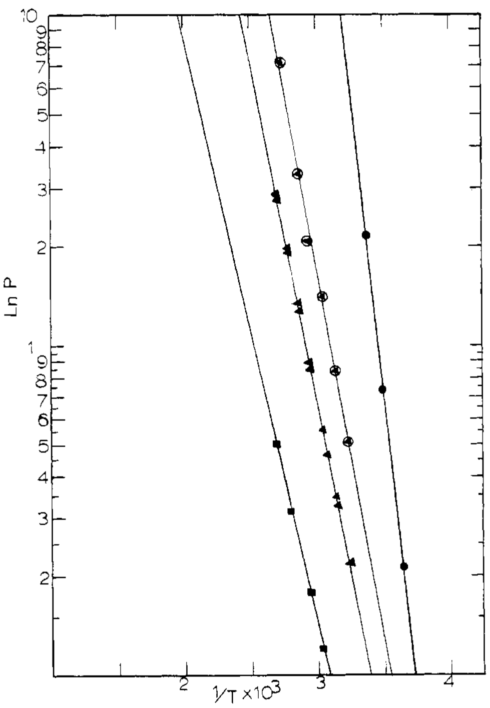


Figure 2. Plot ln *P* vs 1/*T*

■ Propylene carbonate (pressure in mm Hg)
▲ Diethyl carbonate (mm Hg × 10^{-1})
⊕ Vinylene corbonate (mm Hg)
● Ethylene carbonate (mm Hg × 10^{3})

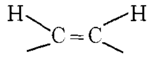
where $\Delta H^\circ_{CO_3}$ and $\Delta H^\circ_{CH_2}$ are the group contribution to the heat of formation (gas) from the carbonate and methylene groups, respectively. According to the same procedure, carbonate group contribution from propylene carbonate, diethyl carbonate and vinylene carbonate were estimated to be −130.9, −133.4, and −118.9 kcal/mole, respectively.

The average carbonate contribution to the heat of formation (gas) was estimated to be −133 ± 1 kcal/mole. However, this is not the case for the carbonate group

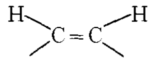
Table II. Vapor Pressures of Organic Carbonates

Compounds	Temp, ° K	Av, mm Hg
Ethylene carbonate	273.9	2.15×10^{-3}
	286.1	7.39×10^{-3}
	296.6	21.72×10^{-3}
Propylene carbonate	328.2	1.20
	338.6	1.78
	358.6	3.14
	369.6	5.07
Vinylene carbonate	308.2	5.12
	318.7	8.42
	328.0	14.07
	338.2	20.84
	348.2	33.06
	399.8	73.31
Diethyl carbonate	308.3	21.97
	317.3	32.68
	318.4	34.45
	324.9	46.98
	328.4	55.61
	338.1	86.23
	339.2	89.68
	348.0	130.82
	348.9	135.26
	358.2	195.75
	358.5	197.98
	367.8	280.18
	368.4	286.22

for vinylene carbonate unless suitable corrections are employed. The carbonate group contribution for vinylene carbonate calculated according to the Franklin's method turned out to be −118.9 kcal/mole without using any correction factor when the



was assumed to have the cis- configuration. It was a well-known fact that the calculations for monoolefins are complicated by hyperconjugation (*8*) and cis-trans isomerism and proved not to be strictly additive. If it is assumed that there is resonance between the double bond in



group then the resonance correction factor, 12.04 kcal/mole, must be added (*4*, *5*). This correction leads to a revised value for the carbonate contribution of vinylene carbonate to be −130.9 kcal/mole. This corrected value is in good agreement with the calculated value.

The heat of formation (solid) of di-(*p*-phenylbenzyl)-carbonate was calculated to be −76.69 kcal/mole from the heat of combustion according to Equation 2. The vapor pressure of this compound could not be measured because of lack of sample compound. Therefore, the heat of sublimation and the heat of formation (gas) could not be obtained. By utilizing our estimated value for carbonate group contribution to the heat of formation (gas), the heat of formation (gas) of this carbonate compound might be estimated to be −50.0 kcal/mole, if the heat of formation (gas) was assumed to consist of contributions from 18 $\rightleftarrows$CH groups, six $\rightleftarrows$C— groups and two CH_2 groups, and a carbonate group, where contributions from a $\rightleftarrows$CH and a $\rightleftarrows$C— and a CH_2 were +3.30, +5.57, and −4.926 kcal/mole, respectively, and a $\rightleftarrows$CH and a $\rightleftarrows$C— indicate a resonating structure—*e.g.*, one of the CH groups in benzene according to the Franklin's method (*4*, *5*). The heat of sublimation of this compound was estimated to be +26.7 kcal/mole from the heat of formation (solid) and the estimated heat of formation (gas) according to Equation 3.

The Knudsen effusion system and the modified manometric apparatus were calibrated using mercury and water, respectively, whose vapor pressures were well-known and in good agreement with the literature value (*14*) within the experimental error.

NOMENCLATURE

A = orifice area of the Knudsen cell in cm^2
B_{out} = water outlet of the bath connected to R_{in}
bp = boiling point, °C
F_r = frit covered with mercury
G = weight lost by effusion, grams
ΔH_c° = heat of combustion, kcal/mole
$\Delta H_{f(g,\,l,\,s)}^\circ$ = heat of formation (gas, liquid, or solid), kcal/mole
$\Delta H_{\text{vap or sub}}$ = heat of vaporization or sublimation, kcal/mole
$\Delta H_{CO_3,\ CH_2,\ etc}^\circ$ = group contribution to the heat of formation (gas) from the carbonate group, CH_2, etc., respectively, kcal/mole
I_s = sample inlet to the reaction chamber
ml = mililiter
mp = the melting point
n = the refractive index
P = pressure, mm Hg
P_l = clamp which holds R_t and R_b together
R = universal gas constant
R_t, R_b = the reaction chamber, top and bottom, respectively
R_{in}, R_{out} = water inlet to R_t and the water outlet to the bath, respectively
t = time, sec
T = abs temp, °K

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