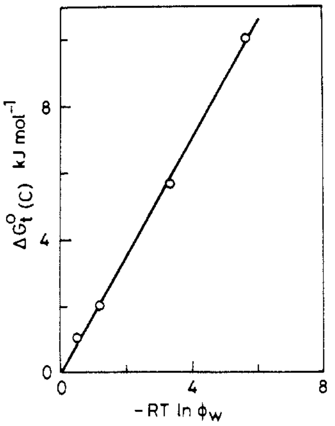

Figure 3. Plot of $\Delta G_t{}^\circ{}_c$ against $-RT \ln \phi_w$ at 25 °C.

the values of $\Delta H_t{}^\circ{}_{\text{nonel}}$ change from positive to negative at about 20% and decrease further negatively thereafter, indicating the predominantly structure-making ion–solvent interactions at higher compositions of propylene glycol. Feakins et al (*14*) have suggested a different approach to account for the variation ΔG_t° with solvent composition in terms of, ϕ_w, the volume fraction of water. A plot of the standard molar free energy of transfer, $\Delta G_t{}^\circ{}_c$, against solvent composition in terms of volume fraction of water in these media (Figure 3) according to the relation

$$\Delta G_t{}^\circ{}_c = -nRT \ln \phi_w \qquad (16)$$

is linear with $n = 1.8$. This value represents the number of water molecules coordinated to HBr and is less than the values obtained in other media as reported elsewhere (*15*).

Registry No. Ag, 7440-22-4; AgBr, 7785-23-1; HBr, 10035-10-6; propylene glycol, 57-55-6.

Literature Cited

(1) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1974**, *19*, 201.
(2) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1979**, *24*, 255.
(3) Kalidas, C.; Sivaprasad, P. *Adv. Chem. Ser.* **1979**, *No. 177*, 345–54.
(4) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1976**, *21*, 314.
(5) Kundu, K. K.; Jana, D.; Das, M. N. *J. Phys. Chem.* **1970**, *74*, 2625.
(6) Feakins, D.; Watson, P. *J. Chem. Soc.* **1963**, 4686.
(7) Kundu, K. K.; Banerjee, S. K.; Das, M. N. *J. Chem. Soc. A* **1967**, 161.
(8) Hills, G. J.; Ives, D. J. G. "Reference Electrodes"; Ives, D. J. G., Janz, G. J., Eds.; Academic Press: New York, 1961; p 190.
(9) Feakins, D.; Voice, P. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1390.
(10) Kalidas, C.; Srinivas Rao, V.; Subramanyam, R. S., SAEST, India, Proceedings of the 13th Seminar, 1972.
(11) Kalidas, C.; Sivaprasad, P.; Venkatram, U. V. *Z. Naturforsch. A* **1977**, *32*, 791.
(12) Franks, F.; Ives, D. J. G. *Q. Rev. Chem. Soc.* **1966**, *20*, 1.
(13) Feakins, D.; Thakur, L.; Smith, B. C. *J. Chem. Soc.* **1966**, 714.
(14) Feakins, D.; French, C. M. *J. Chem. Soc.* **1957**, 2581.
(15) Mussini, T.; Formara, C. M.; Andrigs, P. *J. Electroanal. Chem.* **1971**, *33*, 189.
(16) Popovych, O. *Crit. Rev. Anal. Chem.* **1970**, *1*, 73.
(17) Kundu, K. K.; Jana, D.; Das, M. N. *J. Phys. Chem.* **1970**, *74*, 2629.
(18) Kundu, K.; De, A. L.; Das, M. N. *J. Chem. Soc., Dalton Trans.* **1972**, 373.
(19) Sastry, V. V.; Kalidas, C. *J. Chem. Eng. Data* **1983**, *28*, 5.

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Enthalpies of Combustion and Formation of Ethylene Carbonate

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Combustion calorimetry was used to determine a value for the standard enthalpy of combustion of ethylene carbonate (crystal) from which the standard enthalpy of formation was calculated; the results were $\Delta H_c^\circ(298.15\ \text{K}) = -1165.87 \pm 3.74$ kJ/mol = -278.65 ± 0.89 kcal/mol and $\Delta H_f^\circ(298.15\ \text{K}) = -586.30 \pm 3.76$ kJ/mol = -140.13 ± 0.90 kcal/mol. The results were obtained by burning a sample of known purity in an oxygen bomb calorimeter and correcting for trace amounts of combustibles. This compound affords a striking example of the effect of empirical formula on the standard-states correction.

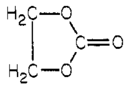
This investigation was undertaken to establish the enthalpy of formation of solid ethylene carbonate for use in reaction enthalpy-change calculations. Discordant heat-of-combustion values had appeared in the literature (*1*, *2*) which led to significantly altered results for any process designs involving the formation and subsequent reactions of this compound, and both of those studies seemed to represent conscientious work.

Reported here are the results obtained at this laboratory for measurements carefully performed of the heat of combustion of a highly purified sample of solid ethylene carbonate and a value for the enthalpy of formation derived from it.

Table I. Impurities in Ethylene Carbonate Used and Their ΔE_c° Values for Corrections

	concn, ppm	ΔE_c°, kJ/mol
benzene	215	−3263.85
n-hexane	198	−4154.63
water	6 (max)	0

Ethylene carbonate has the structural formula



Experimental Section

Apparatus and Procedure. A Parr 1241 automatic adiabatic oxygen bomb calorimeter (Parr Instrument Co., Moline, IL) was employed for the heat-of-combustion measurements. The 1108 double-valve oxygen bomb used has an internal volume of 0.342 dm^3. The fuse wire used was Parr 45C10 nickel alloy wire. Exactly 1 cm^3 (approximately 1 g) of distilled water was

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Table II. Summary of Calorimetric Determinations on Ethylene Carbonate

	run no.				
	1	2	3	4	5
ϵ(as used), J/K	9993.53	9993.53	9993.58	9993.56	9993.57
ΔT, K	2.196	2.195	2.243	2.243	2.234
$-Q$(total), J	−21945.79	−21935.80	−22415.60	−22415.56	−22325.64
q(fuse), J	61.03	62.94	62.94	66.76	72.48
$q(HNO_3)$, J	27.91	32.56	32.56	32.56	32.56
q(im), J	30.52	30.42	31.22	31.01	31.01
ΔE(cor to 28 °C), J	0.58	0.26	0.66	0.66	0.35
ΔE(cor, WC), J	27.68	27.67	28.37	28.16	28.18
sample wt, vac,[a] g	1.6456	1.6438	1.6865	1.6741	1.6744
$\Delta E_c°$(28 °C), J/g	−13251.91	−13256.62	−13204.33	−13300.11	−13240.76
$\Delta E_c°$(28 °C), kJ/mol	−1167.00	−1167.42	−1162.81	−1171.25	−1166.02

[a] To be corrected for impurities in Table I.

Table III. Derivation of the Enthalpy of Formation of Ethylene Carbonate, $C_3H_4O_3$[a]

$\Delta E_c°$(mean, 28 °C), kJ/mol	−1166.90 ± 3.74[b]
$\Delta n_g RT$, 28 °C, kJ/mol	+1.25
$\Delta H_c°$(28 °C), kJ/mol	−1165.65 ± 3.74
$\Delta(nC_p°)(25 - 28)$, kJ/mol	−0.22
$\Delta H_c°$(25 °C), kJ/mol	−1165.87 ± 3.74
$\Delta H_c°$(25 °C),[c] kcal/mol	−278.65 ± 0.89
$\Delta H_f°$(c, 25 °C), kcal/mol	−140.13 ± 0.90

[a] Gram formula weight = 88.063. [b] Standard deviation of the mean = 1.35 for combustion determinations only. Overall precision given includes calibration uncertainty propagated by eq 43 of Olofsson (7). [c] 1 cal = 4.184 J.

pipetted into the bomb before closing, both for the calibration runs with benzoic acid and for the ethylene carbonate determinations. The bomb was filled to a gauge pressure of 30 atm with oxygen of ultrahigh-purity grade to carry out the combustions. The temperature rise of the water in which the bomb was immersed was measured with a calibrated calorimetric glass thermometer supplied with the calorimeter and equipped with a reading lens to enhance the precision of the readings. Nitric acid formed in the combustion process was measured by titrating the bomb liquid to the methyl orange end point with a solution of Na_2CO_3 made up to a concentration of 2.032 g/dm^3 (0.038 34 N) to simplify the preliminary calculations. The amount of sample burned in each benzoic acid calibration and each combustion experiment was determined from the mass of sample corrected to "in vacuo" values. The ethylene carbonate was made into pellets of appropriate weight to give the desired temperature rise when burned. No trace of soot was found in the bomb following any of the calibration or sample combustions.

The energy equivalent (ϵ) of the calorimeter was determined by using pellets of standardized calorific grade benzoic acid obtained from Parr Instrument Co., Moline, IL, having a certified heat of combustion of 11 373 Btu/lb (26.454 kJ/g) when weighed against brass weights in air. An equivalent value including corrections for weights in vacuo and departure from certification conditions was employed in deriving the energy equivalent from a series of six calibration experiments performed at a mean calorimetric temperature approximately equal to that of the ethylene carbonate combustions. The procedure suggested by Jessup (*3*) was followed in computing ϵ_s of the standard calorimeter (ϵ_s = 9990.94 ± 10.99 J/K) and the value of ϵ of the calorimeter "as used" for each ethylene carbonate determination. Corrections were applied to the total energy released to the calorimeter, Q(total), for the heat of combustion of the fuse wire consumed, for the heat released by forming nitric acid from oxygen, nitrogen, and liquid water, and for the heats of combustion of known small quantities of impurities in the ethylene carbonate. The reduction of values of ΔE_c to standard states and to a common temperature followed the Washburn procedure (*4*), with the approximate form of the standard-states correction being used.

***Materials*.** The ethylene carbonate used was taken from a lot especially synthesized and purified by Union Carbide chemists for use in process research studies. As received, the sample had been purified by recrystallization from benzene upon hexane addition and had been dried by having air pulled through it overnight on a diaphragm-covered Büchner funnel. Nevertheless, a faintly perceptible solvent odor persisted upon first opening the tightly capped sample; and since heating such a low-melting material was inadvisable, it was subjected to the "deadhead" vacuum of a vacuum pump for about 30 min at room temperature to effect further solvent removal. This procedure virtually eliminated the residual odor, but an analysis of the sample was obtained by mass spectrometry to characterize any remaining volatiles. The analysis reported for impurities in the sample as combusted is shown in Table I. The sample melting point lay in the temperature range of 35–36.5 °C.

Results and Discussion

The results of the combustion experiments are summarized in Table II. The symbols are defined in the Glossary section. In Table III is given the derivation of the enthalpy of formation from the mean value of the standard energy of combustion.

The result for the standard enthalpy of formation of ethylene carbonate is closely in accord with that which may be derived from the combustion measurements of Silvestro and Lenchitz (*1*), viz., −138.83 ± 0.31 kcal/mol (*5*), although not quite overlapping within the quoted uncertainty limits. (This literature value was subsequently smoothed to −139.0 ± 0.2 kcal/mol (*6*).) However, the goal of this investigation was accomplished in that it has been shown that a value in this range is to be preferred for practical applications over the value for $\Delta H_f°$(c, 25 °C) = −163.20 kcal/mol reported by Choi and Joncich (*2*).

This compound provides a rather striking example of the effect of empirical formula upon the percentage magnitude of the "Washburn" or standard-states correction. The percentage correction to $-\Delta E_b$ is from 2 to 3 times that usually found. While this may have been anticipated after a close reading of Washburn's original paper (*4*), it is a point that is rarely brought out elsewhere.

Acknowledgment

The required operation of the Parr calorimeter was performed by W. F. Williams. The mass-spectrometric analysis of the sample was performed by R. T. Drake. B. C. Ream provided the ethylene carbonate.

Glossary

ϵ_s average energy equivalent of the standard calorimeter system including the bomb, interior parts, 1 cm^3 of water, and 30 atm abs of oxygen pres-

	sure, but no sample, at the mean temperature of the experiments, J/K
ϵ(as used)	energy equivalent of the standard calorimeter with additions for the heat capacity of the sample of ethylene carbonate and the heat capacity of the oxygen in excess of 30 atm abs at the referral temperature of the reaction (t_f), J/K
t_f	final temperature of the calorimeter for a given run, °C
ΔT	observed adiabatic temperature rise of the calorimeter system after ignition of the sample, K
Q(total)	total heat evolved to the calorimeter system (=ϵ(as used)ΔT), J
q(fuse)	correction for heat of combustion of fuse wire, J
q(HNO_3)	correction for heat released by forming nitric acid from nitrogen, oxygen, and liquid water, J
q(im)	correction for heats of combustion of impurities in sample, J
ΔE(cor to 28 °C)	correction to adjust observed heat of the bomb process from actual final temperature of each experiment (t_f) to common temperature of 28 °C, J
ΔE(cor, WC)	total "Washburn correction" (*4*) to reduce the observed heat of the bomb process to standard conditions having reactants and products in their thermodynamic standard states at 1-atm pressure and the common (isothermal) temperature selected, J
$\Delta E_c°$	change in energy due to idealized combustion reaction under standard-state conditions, J/g or kJ/mol as noted
ΔE_b	change in energy due to combustion of the sample itself under bomb conditions, i.e., after other thermal corrections to $-Q$(total), J/(gram formula weight)
Δn_g	change in number of moles of gas across the idealized combustion reaction
$\Delta H_c°$	isothermal enthalpy change for combustion of the compound with the reactants and products in standard states ("standard enthalpy of combustion") for a specified temperature, kJ/mol or kcal/mol as noted
n	number of moles of each product or reactant in the idealized combustion reaction used in correcting $\Delta H_c°$ from the selected final reaction temperature to 25 °C
$C_p°$	mean molar heat capacity at constant pressure, 25-28 °C, of a product or reactant in its thermodynamic standard state, kJ/(mol K)
$\Delta H_f°$(c)	standard enthalpy of formation of the crystalline compound for the reference temperature of 25 °C, kJ/mol or kcal/mol as noted

Registry No. Ethylene carbonate, 96-49-1.

Literature Cited

(1) Silvestro, G.; Lenchitz, C. *J. Phys. Chem.* **1961**, *65*, 694.
(2) Choi, J. K.; Joncich, M. J. *J. Chem. Eng. Data* **1971**, *16*, 87.
(3) Jessup, R. S. "Precise Measurement of Heat of Combustion with a Bomb Calorimeter"; National Bureau of Standards: Washington, DC, Feb 26, 1960; *NBS Monogr.* (*U.S.*), No. 7.
(4) Washburn, E. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1933**, *10*, 525.
(5) Cox, J. D.; Pilcher, G. "Thermodynamics of Organic and Organometallic Compounds"; Academic Press: New York, 1970.
(6) Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex: Brighton, United Kingdom, 1977 (soft cover); units converted.
(7) Olofsson, G. In "Combustion Calorimetry"; Sunner, S., Månsson, M., Eds.; Pergamon Press Ltd. for International Union of Pure and Applied Chemistry: Oxford, United Kingdom, 1979; Chapter 6.

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Solid-Liquid Phase Behavior of Nonadecylcyclohexane and Nonadecylbenzene

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The melting points of nonadecylcyclohexane (NDC) and nonadecylbenzene (NDB) have been determined to be 42.59 and 29.50 °C, and their freezing points, 29.97 and 24.94 °C, respectively. It is suggested that, analogous to the normal paraffins, these compounds form "rigid" (β) and "rotator" (α) phases in the solid state. In the present cases, however, the α phases are metastable and are formed directly from the melt as the result of kinetic factors. When the compounds stand for a sufficient length of time, the transitions to the more stable β phases are complete. The enthalpies of fusion of both phases for each substance have been estimated by using simple calorimetry and differential scanning calorimetry (DSC).

Introduction

Before initiating studies using NDC and NDB as liquid phases in gas-liquid chromatography, we decided to estimate their purities by using the cooling-curve method described by Rossini (*1*). It was soon discovered that each solid melts at a temperature considerably above that at which it freezes. Apparently there are (at least) two solid crystalline phases for these compounds, the less stable of which forms more readily from the melt. Upon standing, the crystal transforms into the more stable phase, which, when heated, melts at a higher temperature than that at which the liquid had solidified.

Because the enthalpy of fusion of the crystalline phase which is in equilibrium with the melt is required for purity estimation from the cooling curve, and because of the curious nature of these transitions, a study of the liquid-solid behavior of NDC and NDB was initiated.

Experimental Section

Cooling curves were obtained by using a MINCO platinum resistance thermometer (PRT), wrapped in copper screen, immersed in an insulated Pyrex tube containing the sample under study. A Rubicon potentiometer was used to oppose the emf drop across the PRT, and the imbalance was displayed on a

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