The absolute accuracy of the calculated derived properties depends primarily on the accuracy of the partial derivatives that were generated through the isobaric and isothermal equations. Although there is no direct statistical method for obtaining a reasonable bound on the possible error in the partial derivatives, a more stringent test of the accuracy of the derived properties would be the examination of the thermodynamic consistency of the calculated properties. For this purpose, the basic thermodynamic relation

$$\left(\frac{\partial p}{\partial T}\right)_\rho = -\rho^2\left(\frac{\partial S}{\partial \rho}\right)_T \qquad (7)$$

was employed. The two sides of eq 7 were found to be well within 2% of each other for several states which were selected at random (*1*).

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Supplementary Material Available: Table IV, thermodynamic properties of SF_6 (11 pages). Ordering information is given on any current masthead page.

The Enthalpies of Combustion and Formation of 2-Methyl-2-oxazoline and 2-Ethyl-2-oxazoline

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The enthalpies of combustion of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline were determined by precision oxygen-bomb combustion calorimetry. The following values, based on the mass of sample burned, are reported for the standard enthalpy of combustion $\Delta H_c°$ (298.15 K) $kcal_{th}$ mol^{-1} of these compounds in the liquid state: 2-methyl-2-oxazoline, −574.79 ± 0.20 kcal mol^{-1}; 2-ethyl-2-oxazoline, −731.51 ± 0.25 kcal mol^{-1}. (Throughout this paper cal_{th} = 4.184 J, atm = 101.325 kPa.) Enthalpies of formation in the condensed and in the gaseous state are derived.

In continuation of a study of the thermodynamic properties of oxazole, isoxazole, and related compounds, we have measured the enthalpy of combustion of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline. These values have not been previously reported in the literature.

Experimental Section

Apparatus and Procedures. The apparatus and experimental procedures have been described previously (*2*). The temperature rise was measured by quartz thermometry. The internal volume of the bomb was 0.342 dm^3. For every experiment approximately 1 g of water was added to the bomb, and the bomb was flushed and charged to 30 atm with pure oxygen. Fragile flexible ampoules of borosilicate glass confined the liquid samples. The samples were weighed to an accuracy of 0.01 mg, and corrections for air buoyance were applied. Ignition was accomplished by fusing a 10 cm length of no. 44 s.w.g. platinum wire in contact with a small piece (≃4 mg) of Whatman No. 1 filter paper. The value of $\Delta E_c°/M$ for the filter paper was taken as −4118 ± 10 cal g^{-1} (*7*). The extent of combustion was based on the mass of sample. All calculations, including conversion of time and temperature measurements to initial and final temperature, correction for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer (*8*). The computer program followed the procedure of Hubbard et al. (*3*).

Materials. 2-Methyl-2-oxazoline and 2-ethyl-2-oxazoline were obtained from Aldrich Chemical Co., Inc., and had a claimed purity of 99+%. Both compounds were further purified by distillation through a molecular sieve directly into glass ampoules. Samples of the two compounds purified by the above method were tested on a gas chromatograph, and 2-ethyl-2-oxazoline was additionally tested via ir; no impurities were found.

The calorimeter was calibrated with benzoic acid, NBS sample 39i, which had a heat of combustion of 26.434 ± 0.0003 absolute kJ g^{-1} under certificate conditions.

The auxiliary oil had empirical formula $CH_{1.96}$. The value of $\Delta E_c°/M$ for the oil was determined by us and found to be −11 018.75 ± 1.05 cal g^{-1} (mean and standard deviation).

Results

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*1*) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale. For reducing weights in air to weights in vacuo and correcting to standard states, the values summarized in Table I, all for 298.15 K, were used for density, ρ, specific heat, C_p, and $(\partial E/\partial P)_T$ for the substances. Values of density were measured in a Weld type pycnometer. Specific heat values were measured with a Perkin-Elmer DSC-1B differential scanning calorimeter (*5*). Values of $(\partial E/\partial P)_T$ were derived from the ap-

Table I. Physical Properties at 298.15 K

	ρ, g ml^{-1}	C_p, cal deg^{-1} g^{-1}	$(\partial E/\partial P)_T$, cal atm^{-1} g^{-1}
2-Methyl-2-oxazoline	0.997	0.492	−0.001 06
2-Ethyl-2-oxazoline	0.974	0.417	−0.005 19
Benzoic acid	1.320	0.289	−0.002 78
Auxiliary oil	0.870	0.530	(−0.006)
Fuse	1.50	0.400	(−0.002 8)

Table II. Summary of Combustion Experiments[a] for 2-Methyl-2-oxazoline

m'(compd), g	0.863 62	0.809 89	0.828 55	1.210 33	0.785 71	0.813 09
m''(oil), g	0.040 30	0.044 31	0.046 33	0.038 48	0.035 19	0.039 09
m'''(fuse), g	0.003 85	0.003 78	0.003 92	0.004 06	0.004 00	0.003 85
Δt_c, deg	2.632 90	2.498 85	2.560 67	3.602 72	2.388 17	2.484 33
$n^i(H_2O)$, mol	0.059 84	0.060 67	0.056 62	0.056 29	0.057 84	0.059 17
ϵ(calor)($-\Delta t_c$), cal	−6295.63	−5975.10	−6122.92	−8614.61	−5710.45	−5940.38
ϵ(cont)($-\Delta t_c$), cal[b]	−12.74	−12.06	−12.40	−17.94	−11.32	−11.89
ΔE, corr to std states, cal	3.31	3.11	3.19	4.79	2.96	3.09
ΔE^fdec(HNO_3), cal	15.35	14.18	14.69	19.94	12.91	13.71
$-m''\Delta E_c^\circ/M$(oil), cal	444.06	488.24	510.50	424.00	387.75	430.72
$-m'''\Delta E_c^\circ/M$(fuse), cal	15.85	15.57	16.14	16.72	16.47	15.85
ΔE_{ign}, cal	0.21	0.21	0.21	0.21	0.21	0.21
$\Delta E_c^\circ/M$(compd), cal g^{-1}	−6750.17	−6748.88	−6747.44	−6747.66	−6747.36	−6750.41

Mean value and std dev of the mean −6748.65 ± 0.57

Derived results at 298.15 K, kcal mol^{-1}

$\Delta E_c^\circ = -574.35 \pm 0.20$ $\Delta H_c^\circ = -574.79 \pm 0.20$ $\Delta H_{vap} = 9.34 \pm 0.08$

$\Delta H_f^\circ(l) = -40.52 \pm 0.21$ $\Delta H_f^\circ(g) = -31.18 \pm 0.22$

The uncertainty interval is taken as twice the final overall standard deviation (*6*).

[a] Reaction temperature is 298.15 K. Symbols and terminology are those of ref 3. [b] $\epsilon^i(\text{cont})(t_i - 25^\circ) + \epsilon^f(\text{cont})(25^\circ - t_f + \Delta t_{corr})$.

Table III. Summary of Combustion Experiments[a] for 2-Ethyl-2-oxazoline

m'(compd), g	1.010 33	1.019 93	0.797 45	0.960 54	0.911 16
m''(oil), g	0.038 20	0.055 71	0.052 10	0.041 11	0.059 18
m'''(fuse), g	0.003 85	0.003 80	0.003 91	0.004 13	0.004 14
Δt_c, deg	3.298 44	3.410 06	2.705 47	3.158 99	3.089 71
$n^i(H_2O)$, mol	0.057 78	0.055 18	0.056 01	0.062 95	0.057 17
ϵ(calor)($-\Delta t_c$), cal	−7887.03	−8153.93	−6469.16	−7553.59	−7387.93
ϵ(cont)($-\Delta t_c$), cal[b]	−16.28	−16.70	−12.93	−15.82	−15.14
ΔE, corr to std states, cal	3.79	3.89	2.96	3.64	3.46
ΔE^fdec(HNO_3), cal	15.47	16.98	11.64	14.81	12.72
$-m''\Delta E_c^\circ/M$(oil), cal	420.92	613.85	574.08	452.98	652.09
$-m'''\Delta E_c^\circ/M$(fuse), cal	15.85	15.65	16.10	17.01	17.05
ΔE_{ign}, cal	0.21	0.21	0.21	0.21	0.21
$\Delta E_c^\circ/M$(compd), cal g^{-1}	−7370.93	−7373.10	−7369.87	−7371.65	−7372.51

Mean value and std dev of the mean −7371.61 ± 0.57

Derived results at 298.15 K, kcal mol^{-1}

$\Delta E_c^\circ = -730.77 \pm 0.25$ $\Delta H_c^\circ = -731.51 \pm 0.25$ $\Delta H_{vap} = 10.57 \pm 0.10$

$\Delta H_f^\circ(l) = -46.16 \pm 0.26$ $\Delta H_f^\circ(g) = -35.59 \pm 0.28$

The uncertainty interval is taken as twice the final overall standard deviation (*6*).

[a] Reaction temperature is 298.15 K. Symbols and terminology are those of ref 3. [b] $\epsilon^i(\text{cont})(t_i - 25^\circ) + \epsilon^f(\text{cont})(25^\circ - t_f + \Delta t_{corr})$.

proximation $(\partial E/\partial P)_T \simeq -T(\partial V/\partial T)_P$. Values in parentheses are estimated.

Calorimetric Results. The apparent energy equivalent of the calorimeter, ϵ(calor), was determined from nine calibration runs. The average value was 2391.14 ± 0.22 cal deg^{-1} where the uncertainty is expressed as the standard deviation of the mean. Six satisfactory combustion experiments were obtained for 2-methyl-2-oxazoline and five for 2-ethyl-2-oxazoline.

Data for the combustion experiments are summarized in Tables II and III. The values of $\Delta E_c^\circ/M$ at 298.15 K for the compounds in these tables refer to the equations:

2-methyl-2-oxazoline

$$C_4H_7ON_{(l)} + {}^{21}\!/\!_4 O_{2(g)} \rightarrow 4CO_{2(g)} + {}^{7}\!/\!_2 H_2O_{(l)} + {}^{1}\!/\!_2 N_{2(g)}$$

2-ethyl-2-oxazoline

$$C_5H_9ON_{(l)} + {}^{27}\!/\!_4 O_{2(g)} \rightarrow 5CO_{2(g)} + {}^{9}\!/\!_2 H_2O_{(l)} + {}^{1}\!/\!_2 N_{2(g)}$$

Derived Results. Values of the enthalpies of combustion derived from mass of sample and current best values (*4*) of the enthalpies of formation of gaseous carbon dioxide and liquid water were combined to derive values of the enthalpy of formation in the condensed state. These are listed in Tables II and III. Measurement of the enthalpy of vaporization at 298.15 K was made in this laboratory with a LKB8721-3 calorimeter. Three determinations were made on each compound. The values of the mean and standard deviation of the mean of ΔH_{vap} for each compound are listed in Tables II and III.

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