

molecule which can hydrogen bond with water molecules.

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Received for review October 27, 1977. Accepted February 17, 1978. The authors wish to acknowledge the support of the Office of Naval Research (N00014-75-C-0173) and the Oceanographic Section of the National Science Foundation (OCE73-00351-A01) for this study.

Enthalpies of Combustion and Formation of 3-Methylisoxazole and 5-Methylisoxazole

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The enthalpies of combustion of 3-methylisoxazole and 5-methylisoxazole were measured by precision oxygen-bomb calorimetry. The following values, based on the mass of sample burned, are reported for the standard enthalpy of combustion, $\Delta H_c^\circ(298.15\text{ K})/\text{kcal mol}^{-1}$, of these compounds in the liquid state: 3-methylisoxazole, -546.00 ± 0.14 ; and 5-methylisoxazole, -545.65 ± 0.17 . Enthalpies of vaporization, determined calorimetrically, are 3-methylisoxazole, $9.51 \pm 0.05\text{ kcal mol}^{-1}$, and 5-methylisoxazole, $9.48 \pm 0.04\text{ kcal mol}^{-1}$. These data were used to calculate standard enthalpies of formation for the gaseous compounds, $\Delta H_f^\circ(\text{g})$, which are: 3-methylisoxazole, $8.52 \pm 0.16\text{ kcal mol}^{-1}$, and 5-methylisoxazole, $8.14 \pm 0.18\text{ kcal mol}^{-1}$. Throughout this paper $\text{cal}_{\text{th}} = 4.184\text{ J}$ and $\text{atm} = 101.325\text{ kPa}$.

Introduction

The enthalpies of combustion of liquid 3-methylisoxazole and 5-methylisoxazole were measured as part of a continuing study of the thermodynamic properties of nitrogen compounds. This paper presents basic experimental data for the enthalpy-of-combustion measurements of two methylisoxazoles. Values of the enthalpy of combustion were used to derive values of the enthalpy of formation in the liquid state. Enthalpies of vaporization of the two compounds were determined by direct calorimetric measurements. Values of the enthalpy of formation in the gaseous state were derived.

Experimental Section

Apparatus and Procedures. The apparatus and experimental procedures have been described (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 ampules of borosilicate glass confined the liquid samples. The samples were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied. Ignition was accomplished by discharging a large capacitor through a 10-cm length of no. 44 Brown and Sharpe gauge platinum wire in contact with a small piece ($\approx 4\text{ mg}$) of Whatman No. 1 filter paper. The electrical ignition energy was calculated by noting the charge on the capacitor before and after discharge. The value of $\Delta E_c^\circ/M$ for the filter paper was taken as $-(4118 \pm 10)\text{ cal g}^{-1}$ (8). 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 (11). The computer program followed the procedure of Hubbard et al. (3).

Materials. 3-Methylisoxazole was obtained from Aldrich Chemical Co., Inc., and had a claimed purity of 98%. 5-Methylisoxazole was obtained from Roche Chemical Division, Hoffmann-La Roche, Inc. Both compounds were further purified by drying over calcium hydride and distilling under reduced

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
3-Methylisoxazole	1.032	0.379	-0.006 78
5-Methylisoxazole	1.017	0.375	-0.006 98
Benzoic acid	1.320	0.289	-0.002 78
Auxilliary oil	0.870	0.530	(-0.006)
Fuse	1.50	0.400	(-0.002 8)

pressure. The final distillation was carried out so that the vapor passed through a column packed with molecular sieve and was condensed in a receiver containing the ampules under reduced pressure. Samples of the two compounds purified by the above method were examined on a gas chromatograph and by infrared spectrography. No impurities were found including water, which shows in trace quantities in the infrared spectra of both compounds at ca. 2.8 nm.

The calorimeter was calibrated with benzoic acid, NBS sample 39I, which had an energy of combustion of 26.434 ± 0.0003 absolute kJ g⁻¹ under certificate conditions. The auxiliary oil had an empirical formula of CH_{1.96}. The value of $\Delta E_c^\circ/M$ for the oil was determined by us and found to be $-10\,983.99 \pm 0.54$ cal g⁻¹ (mean and standard deviation of the mean).

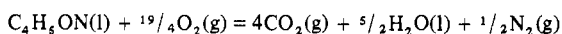
Results

Units of Measure and Auxilliary 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 masses 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 taken from the literature (7). 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 approximation $(\partial E/\partial P)_T \approx -T(\partial V/\partial T)_P$. 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 2390.19 ± 0.12 cal deg⁻¹ where the uncertainty is expressed as the standard deviation of the mean. Five satisfactory combustion experiments were obtained for each compound.

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



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 an LKB 8721-3 calorimeter (10). Six or more determinations were made on each compound. The value of the mean and standard deviation of the

Table II. Summary of Combustion Experiments^a for 3-Methylisoxazole

m' (compd), g	0.86514	0.92860	0.93518	0.84704	0.91210
m'' (oil), g	0.04672	0.05053	0.04661	0.04877	0.04835
m''' (fuse), g	0.00408	0.00423	0.00404	0.00398	0.00426
Δt_c , deg	2.60190	2.79346	2.79296	2.56025	2.73762
n^i (H ₂ O), mol	0.05501	0.05506	0.05573	0.05584	0.05562
ϵ (calor)($-\Delta t_c$), cal	-6219.04	-6676.90	-6675.71	-6119.48	-6547.51 ^c
ϵ (cont)($-\Delta t_c$), ^b cal	-11.34	-12.24	-12.16	-11.09	-11.88
ΔE_c° cor to std states, cal	3.23	3.49	3.51	3.15	3.43
ΔE_c° dec (HNO ₃), cal	12.81	13.08	13.42	11.85	13.37
$-m'' \Delta E_c^\circ/M$ (oil), cal	513.17	555.02	511.96	535.69	531.08
$-m''' \Delta E_c^\circ/M$ (fuse), cal	16.80	17.42	16.64	16.39	17.54
ΔE_{ign} , cal	0.12	0.13	0.13	0.08	0.10
$\Delta E_c^\circ/M$ (compd), cal g ⁻¹	-6570.32	-6569.03	-6567.94	-6568.06	-6571.51

Mean value and std dev of the mean -6569.37 ± 0.68

Derived results at 298.15 K, kcal mol⁻¹

$$\Delta E_c^\circ = -545.85 \pm 0.14$$

$$\Delta H_c^\circ = -546.00 \pm 0.14$$

$$\Delta H_f^\circ(l) = -0.99 \pm 0.15$$

$$\Delta H_{vap} = 9.51 \pm 0.05$$

$$\Delta H_f^\circ(g) = 8.52 \pm 0.16$$

The uncertainty interval is taken as twice the final overall standard deviation (δ)

^a Reaction temperature is 298.15 K. Symbols and terminology are those of ref 3. ^b $\epsilon^i(\text{cont})(t_i - 25^\circ\text{C}) + \epsilon^f(\text{cont})(25^\circ\text{C} - t_f + \Delta t_{\text{cor}})$. ^c ϵ (calor) was 2391.68 ± 0.14 for this experiment.

Table III. Summary of Combustion Experiments^a for 5-Methylisoxazole

m' (compd), g	0.96459	0.98185	1.05869	1.01113	0.97670
m'' (oil), g	0.04150	0.03956	0.05103	0.04618	0.05005
m''' (fuse), g	0.00420	0.00405	0.00390	0.00425	0.00425
Δt_c , deg	2.84742	2.88763	3.14958	2.99820	2.92203
n^i (H ₂ O), mol	0.05495	0.05551	0.05540	0.05523	0.06056
ϵ (calor)($-\Delta t_c$), cal	-6810.12 ^c	-6906.29 ^c	-7532.79 ^c	-7166.27	-6984.62
ϵ (cont)($-\Delta t_c$), ^b cal	-12.29	-12.50	-13.81	-13.05	-12.95
ΔE_c° cor to std states, cal	3.59	3.66	4.02	3.78	3.70
ΔE_c° dec (HNO ₃), cal	14.10	15.70	16.25	13.09	13.68
$-m'' \Delta E_c^\circ/M$ (oil), cal	455.84	434.53	560.51	507.24	549.75
$-m''' \Delta E_c^\circ/M$ (fuse), cal	17.30	16.68	16.06	17.50	17.50
ΔE_{ign} , cal	0.31	0.10	0.13	0.14	0.10
$\Delta E_c^\circ/M$ (compd), cal g ⁻¹	-6563.69	-6567.32	-6564.37	-6564.51	-6565.82

Mean value and std dev of the mean -6565.14 ± 0.64

Derived results at 298.15 K, kcal mol⁻¹

$$\Delta E_c^\circ = -545.50 \pm 0.17$$

$$\Delta H_c^\circ = -545.65 \pm 0.17$$

$$\Delta H_f^\circ(l) = -1.34 \pm 0.18$$

$$\Delta H_{vap} = 9.48 \pm 0.04$$

$$\Delta H_f^\circ(g) = 8.14 \pm 0.18$$

The uncertainty interval is taken as twice the final overall standard deviation (δ)

^a Reaction temperature is 298.15 K. Symbols and terminology are those of ref 3. ^b $\epsilon^i(\text{cont})(t_i - 25^\circ\text{C}) + \epsilon^f(\text{cont})(25^\circ\text{C} - t_f + \Delta t_{\text{cor}})$. ^c ϵ (calor) was 2391.68 ± 0.14 for these experiments.

mean of ΔH_{vap} for each compound are listed in Tables II and III.

Discussion

The previously reported values for the enthalpies of combustion of 3-methylisoxazole and 5-methylisoxazole, -541.96 and -540.57 kcal mol $^{-1}$ (9), respectively, differ by nearly 1% from the values reported here. We observed in the course of this investigation that the value of $\Delta E_c^0/M$ for both these compounds is sensitive to atmospheric moisture.

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Received for review November 7, 1977. Accepted February 17, 1978. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Phase Equilibria Behavior of the Ternary Systems Carbon Dioxide-*trans*-Decalin-*n*-Eicosane and Carbon Dioxide-*trans*-Decalin-2-Methylnaphthalene

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The phase equilibria behavior of the two ternary systems carbon dioxide-*trans*-decalin-2-methylnaphthalene and carbon dioxide-*trans*-decalin-*n*-eicosane was investigated in both the liquid-vapor (L-V) and liquid-liquid-vapor (L₁-L₂-V) regions. Three mixtures of approximately 25, 50, and 75 CO₂-free mol % *trans*-decalin were studied for each ternary system. Pressure, liquid-phase composition, and liquid-phase molar volume data were measured at several temperatures for all mixtures of both ternary vapor-liquid systems. Pressure, liquid-phase compositions, and molar volumes of the two coexisting liquid phases are presented as a function of temperature for the same ternary systems along their liquid 1-liquid 2-vapor loci. The termination of these loci are located and characterized. CO₂-free selectivities between the liquid phases in the L₁-L₂-V region are presented, in view of the possible use of CO₂ as a selective solvent in separation processes.

Introduction

CO₂ can be used as a selective solvent for the separation of a mixture of hydrocarbons by taking advantage of the formation of two liquid phases upon pressurization of the mixture with CO₂. Furthermore, there is growing interest in CO₂-hydrocarbon phase equilibria behavior as pertains to enhanced oil recovery processes.

The authors have for some time been engaged in studying the phase equilibria behavior of CO₂-hydrocarbon systems, with a view to providing data which would be useful for the design of separational processes, using CO₂ as a selective solvent, and could as well be relevant to the understanding of enhanced oil recovery processes. Huie and co-workers (1) studied the ternary system CO₂-*n*-decane-*n*-eicosane and showed that the CO₂-rich phase (L₂) selectively extracts the lower alkane from the higher alkane. Kulkarni et al. (2) studied the ternary system

CO₂-*n*-decane-2-methylnaphthalene (where 2-methylnaphthalene and *n*-eicosane have similar melting points) and found that the L₂ phase once again selectively extracts the *n*-decane. Zarah et al. (6) studied the ternary system CO₂-*n*-butylbenzene-*n*-eicosane and Yang et al. (5) studied the ternary system CO₂-*n*-butylbenzene-2-methylnaphthalene. Both found that the L₂ phase selectively extracts the lighter aromatic *n*-butylbenzene from both the *n*-eicosane and the 2-methylnaphthalene.

Studies have been performed previously on the CO₂-hydrocarbon binary systems which serve as limits to the CO₂-hydrocarbon ternary system results to be reported herein. Kulkarni (2) studied the CO₂-2-methylnaphthalene system, Huie et al. (1) studied the CO₂-*n*-eicosane system, and Tiffin et al. (4) studied the CO₂-*trans*-decalin system. The binary system studies focused on L-V and L₁-L₂-V phase behavior.

This present investigation of the phase equilibria behavior and separability of these two CO₂-hydrocarbon systems will complement the aforementioned studies and help elucidate the phase behavior of CO₂-hydrocarbon studies in general. The systems were chosen to provide information on a typical naphthenic hydrocarbon, such as *trans*-decalin in the presence of other hydrocarbon types.

Experimental Section

A detailed description of the experimental equipment and procedure is given elsewhere (1, 3). Briefly, for the L-V isotherms, a known amount of the desired hydrocarbon was placed in a 10-mL glass equilibrium cell. During the experimental runs, measured amounts of pure CO₂ gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. By a mass balance, the moles of CO₂ added to the liquid phase were then determined.

In the case of the L₁-L₂-V runs, the moles of CO₂ in an individual liquid phase were determined by making a run in which