

changes in their chemical reactivity. This view is consistent with the observation that cells exposed to 2,2'-bipyridine, 1,10-phenanthroline, and their LDH-inducing derivatives obtain a pink coloration, assumedly due to complex-bound ferrous ions. The formation of complexes with intracellular ferrous ions could possibly bring about conditions to some extent resembling hypoxia, a condition known to stimulate LDH synthesis in Chang cells.^{5,6}

However, if the formation of complexes with intracellular ferrous ions would be the only mechanism causing the increased LDH synthesis, it could be expected that the addition of ferrous ions, similar to cobaltous ions,² would abolish the action of the chelating agents on LDH synthesis analogously to the abolishment of the fungistatic action of 2,2'-bipyridine and 1,10-phenanthroline by the addition of various metal ions.⁷ Since this is not the case, it appears probable that the chelating agents may also act by some other mechanism. It is known that chelates of metal ions often show catalytic properties in reactions involving oxygen. Ferrous complexes of 1,10-phenanthroline and some of its substituted derivatives have been reported to possess a certain catalase activity.⁸ Thus it also appears possible that the complexes of 2,2'-bipyridine, 1,10-phenanthroline and some of their substituted derivatives interfere with some reaction of importance to the synthesis of LDH.

Acknowledgements. The excellent technical assistance of Miss Cecilia Granström and Mrs. Eva Thedenskög is gratefully acknowledged. This work was supported by a grant from the Swedish National Science Research Council.

1. Goodfriend, T. L., Sokol, D. M. and Kaplan, N. O. *J. Mol. Biol.* **15** (1966) 18.
2. Johansson, G. *Acta Chem. Scand.* **22** (1968) 1677.
3. Stambaugh, R. and Post, D. *Anal. Biochem.* **15** (1966) 470.
4. Smith, G. F. and McCurdy, W. H., Jr. *Anal. Chem.* **24** (1952) 371.
5. Johansson, G. *Exptl. Cell Res.* **43** (1966) 95.
6. Johansson, G. *Acta Chem. Scand.* **21** (1967) 953.
7. Zsolnai, T. *Biochem. Pharmacol.* **7** (1961) 195.
8. Langenbeck, W. and Kasper, F. *Chem. Ber.* **89** (1956) 2460.

Received October 1, 1968.

Acta Chem. Scand. **22** (1968) No. 8

Heats of Combustion Diethyl Ether and 1,1-Diethoxyethane

KALEVI PIHLAJA and JUSSI HEIKKILÄ

*Department of Chemistry, University of
Turku, Turku, Finland*

Because the heats of combustion, $\Delta H_c^\circ(g)$, of diethyl ether and 1,1-diethoxyethane were required for a recent derivation of a bond-bond interaction scheme for aliphatic alcohols, ethers, and acetals,¹ this paper reports the measurement of these quantities.

1,1-Diethoxyethane was prepared from acetaldehyde and ethanol by allowing the mixture to stand overnight over anhydrous calcium chloride in a stoppered flask. The water layer was discarded and the excess alcohol distilled off. After several redistillations from sodium to remove the remaining alcohol and water, a 99.95% pure sample was obtained. B.p. 102–104°C, n_D^{20} 1.3811, d_4^{20} 0.8218.

Diethyl ether was commercial product of E. Merck AG (guaranteed reagent), which was purified carefully and distilled several times from sodium. B.p. 36.0°C, n_D^{20} 1.3523, d_4^{20} 0.7077. Purity $\geq 99.99\%$ by gas chromatographic analysis.

Samples of these compounds were sealed in thin soda glass ampoules and burned in oxygen in an adiabatic bomb calorimeter No. 1221 manufactured by Parr Instruments Co., Illinois, USA, as described earlier.^{2–4} The energy equivalent of the standard calorimeter system, $e^\circ(\text{calor})$, was $1359.13 \pm 0.33 \text{ cal}^\circ\text{F}$. The experimental results are presented in Table 1.

The heat of vaporization of 1,1-diethoxyethane, $7.82 \text{ kcal}\cdot\text{mole}^{-1}$ (*Intern. Crit. Tables*), at the boiling point was corrected to refer to 25°C ($9.04 \text{ kcal}\cdot\text{mole}^{-1}$) employing the equation proposed by Watson.⁵ The heat of vaporization of diethyl ether, $6.36 \text{ kcal}\cdot\text{mole}^{-1}$, was that reported by Pilcher *et al.*⁶

The value, $-657.96 \pm 0.44 \text{ kcal}\cdot\text{mole}^{-1}$, obtained for the heat of combustion of gaseous diethyl ether is in close agreement with the value, $-657.52 \pm 0.19 \text{ kcal}\cdot\text{mole}^{-1}$, reported by Pilcher *et al.*⁶ and with the value, $-658.1 \text{ kcal}\cdot\text{mole}^{-1}$, reported by Stohmann as corrected by Pilcher *et al.*⁶ No reliable data have been reported for 1,1-diethoxyethane.

Table 1. Combustion data for diethyl ether and 1,1-diethoxyethane. $t_h = t_i = 25.00^\circ\text{C}$. e° (calor) = 1359.13 ± 0.33 cal/ $^\circ\text{F}$.

m g	Δt $^\circ\text{F}$	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3)$ cal	ΔE_{Σ} cal	$e^f(\text{cont})$ cal/ $^\circ\text{F}$	$-\Delta E_c^\circ/\text{M}$ cal·g $^{-1}$
Diethyl ether				$M = 74.124$		
0.34453	2.239	16.94	8.22	0.59	2.19	8772.08
0.45952	2.985	18.90	9.50	0.89	2.26	8779.72
0.41384	2.682	11.06	8.77	0.67	2.23	8772.90
0.40614	2.626	2.10	8.50	0.65	2.23	8774.27
$-\Delta E_c^\circ/\text{M} = 8774.74 \pm 1.72^a$ cal·g $^{-1}$ $-\Delta E_c^\circ = 650.42 \pm 0.22^b$ kcal·mole $^{-1}$ $-\Delta H_c^\circ(\text{liq.}) = 651.60 \pm 0.43^c$ kcal·mole $^{-1}$ $\Delta H_{\text{vap}}(25^\circ) = 6.36$ kcal·mole $^{-1}$ $-\Delta H_c^\circ(\text{g}) = 657.96 \pm 0.44$ kcal·mole $^{-1}$ $-\Delta H_f^\circ(\text{g}) = 59.82 \pm 0.44$ kcal·mole $^{-1}$						
1,1-Diethoxyethane				$M = 118.177$		
0.58667	3.389	10.64	16.22	1.77	2.30	7815.73
0.58627	3.385	13.58	10.72	1.77	2.30	7815.14
0.47242	2.730	13.72	8.90	1.36	2.24	7816.27
0.73367	4.237	14.14	18.50	2.30	2.38	7815.20
0.58938	3.413	25.48	11.85	1.78	2.30	7817.45
0.51137	2.957	18.62	11.09	1.50	2.26	7811.21
$-\Delta E_c^\circ/\text{M} = 7815.33 \pm 0.88^a$ cal·g $^{-1}$ $-\Delta E_c^\circ = 923.59 \pm 0.27^b$ kcal·mole $^{-1}$ $-\Delta H_c^\circ(\text{liq.}) = 925.07 \pm 0.54^c$ kcal·mole $^{-1}$ $\Delta H_{\text{vap}}(25^\circ) = 9.04 \pm 0.20$ kcal·mole $^{-1}$ $-\Delta H_c^\circ(\text{g}) = 934.11 \pm 0.74$ kcal·mole $^{-1}$ $-\Delta H_f^\circ(\text{g}) = 108.41 \pm 0.74$ kcal·mole $^{-1}$						

^a Standard deviation of the mean, ^b Over-all standard deviation, ^c Twice the over-all standard deviation.

Pihlaja and Kankare¹ have used the heats of formation determined in this work together with data for other oxygen compounds to derive a bond-bond interaction scheme for gaseous aliphatic alcohols, ethers, and acetals. The derived parameters show that the mean of the above values for diethyl ether fits into the scheme and also our value for 1,1-diethoxyethane seems to be reliable.

A more detailed discussion will be given in connection with the publication of the above-mentioned bond-bond interaction scheme.¹

Acknowledgements. The authors wish to thank the National Research Council for Sciences for financial support. We also wish to

express our gratitude to Professor Pentti Salomaa, Ph.D., who induced us to make the calorimetric measurements.

1. Pihlaja, K. and Kankare, J. *To be published.*
2. Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **21** (1967) 2390.
3. Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **21** (1967) 2430.
4. Pihlaja, K. and Luoma, S. *Acta Chem. Scand.* **22** (1968) 2401.
5. Watson, K. *Ind. Eng. Chem.* **23** (1931) 362.
6. Pilcher, G., Skinner, H. A., Pell, A. S. and Pope, A. E. *Trans. Faraday Soc.* **59** (1963) 316.

Received September 17, 1968.