

Short Communications

Enthalpies of Formation of Cyclic Acetals. 1,3-Dioxolane, 2-Methyl-1,3-Dioxolane, and 2,4-Dimethyl-1,3-Dioxolanes

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The heats of formation, $\Delta H_f^\circ(l)$, of 1,3-dioxolane and its derivatives were determined recently in our laboratory.¹ For continuation of the study of cyclic acetals this paper reports the measurement of the heats of formation of 1,3-dioxolane and its derivatives by combustion calorimetry.

1,3-Dioxolane was synthesized by boiling 93.0 g of 1,2-ethanediol (BDH), 51.0 g of paraformaldehyde (E. Merck AG.), and 2.0 g of *p*-toluenesulfonic acid in 150 ml of toluene in a water entrainment unit.² After the reaction had proceeded to completion, the mixture was neutralized with potassium carbonate and the 1,3-dioxolane was separated from the organic layer by distillation. The water layer was saturated with potassium carbonate and the 1,3-dioxolane that separated was combined with the main fraction. To remove unchanged aldehyde, the crude product was left to stand over a saturated solution of sodium bisulfite for 20–30 h before a second distillation. This was repeated twice. The 1,3-dioxolane was purified by several distillations on sodium. The final yield of pure 1,3-dioxolane (≥ 99.98 mole-%, GLC) was 86.5 g (78 %). B.p. 74.2–74.7°C, n_D^{20}

1.3992, d_4^{20} 1.0545, $(R_D)_{obs}$. 17.00 (calc. 16.97).³

2-Methyl-1,3-dioxolane and a mixture containing 67.1 % of *cis*- and 32.9 % of *trans*-2,4-dimethyl-1,3-dioxolane were kindly donated by Dr. A. Kankaanperä. Physical constants:³ See below.

The purities (≥ 99.98 mole-%, GLC) were checked with a Shandon Universal gas chromatograph fitted with a 6-foot-long copper tube containing Silocel C 22 as solid support and didecyl phthalate as stationary phase and a flame ionization detector. The carrier gas was composed of 75 % nitrogen and 25 % hydrogen and its flow rate was about 100 ml/min. The column temperature was about 62°C.

The water content was minimized by a distillation on calcium hydride and by several distillations on sodium. Immediately after the last fractionation on sodium, the samples (6–8 samples of each compound) were sealed in thin soda glass ampoules and burned in oxygen in an adiabatic bomb calorimeter No. 1221 manufactured by Parr Instruments Co., Illinois, U.S.A., as described earlier.¹ The energy equivalent of the standard calorimeter system, e° (calor), was determined by burning Parr standard benzoic acid.¹ Recalibrations were carried out after any change in the calorimeter system.

Heats of combustion, $-\Delta H_c^\circ(l)$, were calculated on an IBM 1130 computer at the Computer Center, University of Turku, Turku.⁴ The heat of vaporization of 1,3-dioxolane, 8.5 ± 0.2 kcal·mole⁻¹, was taken from the paper of Fletcher *et al.*⁵ and the heats of vaporization of the other dioxolanes were calculated using the equation proposed by Klages⁶ as improved by Wadsö.⁷ The results are shown in Table 1.

Derivative	B.p.	n_D^{20}	d_4^{20}	$(R_D)_{obs}$.	$(R_D)_{calc}$.
2-Me	81.2–81.8	1.3971	0.9814	21.62	21.59
<i>cis</i> -2,4-diMe	90.3–90.5	1.3940	0.9280	26.33	26.22
<i>trans</i> "	93.2–93.3	1.3956	0.9322	26.31	26.22

Table 1. Results of combustion experiments.

<i>m</i> g	Δt °F	$t_h = t_i = 25.00^\circ\text{C}$				
		ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3)$ cal	ΔE_{Σ} cal	$e^f(\text{cont})$ cal/°F	$-\Delta U_c^\circ/M$ cal/g
1,3-Dioxolane M = 74.080 $^{aa}e^\circ(\text{calor}) = 1360.31 \pm 0.23 \text{ cal/}^\circ\text{F}$ $^{bb}e^\circ(\text{calor}) = 1358.78 \pm 0.28 \text{ }^\circ$						
0.80820	3.275	7.98	15.14	2.38	2.30	5490.08 ^{aa}
0.74585	3.021	11.62	16.21	2.18	2.27	5478.82 ^{aa}
0.74084	3.003	8.68	14.99	2.16	2.29	5482.24 ^{bb}
0.72573	2.946	14.14	15.56	2.11	2.26	5481.12 ^{bb}
0.70110	2.846	11.06	15.24	2.03	2.25	5484.47 ^{bb}
$-\Delta U_c^\circ/M = 5483.35 \pm 1.83^a \text{ cal}\cdot\text{g}^{-1}$ $-\Delta U_c^\circ(l) = 406.21 \pm 0.16^b \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_c^\circ(l) = 406.50 \pm 0.33^c \text{ }^\circ$ $-\Delta H_f^\circ(l) = 80.60 \pm 0.33^c \text{ }^\circ$ $\Delta H_{\text{vap}}^{25} = 8.50 \pm 0.20^b \text{ }^\circ$ $-\Delta H_f^\circ(g) = 72.10 \pm 0.53 \text{ }^\circ$						
2-Methyl-1,3-dioxolane M = 88.107 $e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/}^\circ\text{F}$						
0.81487	3.805	13.58	12.06	2.36	2.34	6319.19
1.03422	4.830	14.84	20.36	3.13	2.44	6317.92
0.66442	3.104	7.28	13.83	1.80	2.27	6321.83
0.97545	4.549	9.94	19.95	2.90	2.41	6312.12
0.71367	3.332	13.02	11.08	2.00	2.30	6315.90
0.80898	3.768	6.44	12.12	2.34	2.34	6311.73
0.91779	4.273	9.10	14.06	2.73	2.39	6306.90
$-\Delta U_c^\circ/M = 6315.08 \pm 1.94^a \text{ cal}\cdot\text{g}^{-1}$ $-\Delta U_c^\circ(l) = 556.40 \pm 0.22^b \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_c^\circ(l) = 556.99 \pm 0.44^c \text{ }^\circ$ $-\Delta H_f^\circ(l) = 92.48 \pm 0.44^c \text{ }^\circ$ $\Delta H_{\text{vap}}^{25} = 8.34 \pm 0.30^7 \text{ }^\circ$ $-\Delta H_f^\circ(g) = 84.14 \pm 0.74 \text{ }^\circ$						
2,4-Dimethyl-1,3-dioxolanes M = 102.13 $e^\circ(\text{calor}) = 1360.77 \pm 0.27 \text{ cal/}^\circ\text{F}$						
0.75707	3.893	19.32	16.17	2.15	2.33	6959.61
0.66797	3.429	17.50	11.94	1.86	2.29	6950.38
0.63903	3.284	16.38	9.31	1.77	2.28	6961.79
0.69160	3.544	10.08	12.04	1.94	2.30	6950.07
0.77920	3.993	11.62	10.80	2.28	2.35	6953.59
0.75837	3.888	15.96	10.97	2.20	2.34	6949.96
0.61730	3.171	13.02	8.86	1.70	2.27	6963.58
$-\Delta U_c^\circ/M = 6955.57 \pm 2.25^a \text{ cal}\cdot\text{g}^{-1}$ $-\Delta U_c^\circ(l) = 710.37 \pm 0.28^b \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_c^\circ(l) = 711.26 \pm 0.56^c \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_f^\circ(l) = 100.58 \pm 0.56^c \text{ }^\circ$						
$-\Delta H_f^\circ(\text{cis}, l) = 100.70 \pm 0.58 \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_f^\circ(\text{trans}, l) = 100.34 \pm 0.58 \text{ kcal}\cdot\text{mole}^{-1}$ $\Delta H_{\text{vap}}^{25}(\text{cis}) = 9.25 \pm 0.30^7 \text{ }^\circ$ $\Delta H_{\text{vap}}^{25}(\text{trans}) = 9.38 \pm 0.30^7 \text{ }^\circ$ $-\Delta H_f^\circ(\text{cis}, g) = 91.45 \pm 0.88 \text{ }^\circ$ $-\Delta H_f^\circ(\text{trans}, g) = 90.96 \pm 0.88 \text{ }^\circ$						

^a Standard deviation of the mean. ^b Over-all standard deviation.^{1,12} ^c Twice the over-all standard deviation.

The value, -406.50 ± 0.33 kcal·mole⁻¹, for the heat of combustion of liquid 1,3-dioxolane is in close agreement with the value, -406.4 ± 0.9 kcal·mole⁻¹, reported by Fletcher *et al.*⁵ Skuratov *et al.*⁸ have reported the value -407.6 kcal·mole⁻¹.

Kankaanperä measured the free energy difference between the liquid 2,4-dimethyl-1,3-dioxolanes³ and assuming that $\Delta S = 0$ for these isomers, we can estimate that $\Delta H^\circ = \Delta G^\circ = -0.36$ kcal·mole⁻¹, the *cis* form being the more stable. Now it is possible to evaluate the heats of formation of both liquid isomers since the experimental result can be expressed as follows:

$$-100.58 = 0.671 \cdot \Delta H_f^\circ(l, \textit{cis}) + 0.329[\Delta H_f^\circ(l, \textit{cis}) + 0.36]$$

Thus $-\Delta H_f^\circ(l, \textit{cis}) = 100.70$ and $-\Delta H_f^\circ(l, \textit{trans}) = 100.34$ kcal·mole⁻¹.

Using a previously proposed bond-bond interaction scheme for aliphatic oxygen compounds,⁹ we can write:

$$\begin{aligned} \text{1,3-Dioxolane: } \Delta H_f^\circ(g) &= 3\Delta H_a^\circ(\text{C}, g) \\ &+ 6\Delta H_a^\circ(\text{H}, g) + 2\Delta H_a^\circ(\text{O}, g) - \sum E_b - \\ &2\Gamma_{\text{COC}} - \Delta_{\text{OCO}} + [S] \end{aligned}$$

$$\begin{aligned} \text{2-Me-1,3-d.: } \Delta H_f^\circ(g) &= 4\Delta H_a^\circ(\text{C}, g) + 8\Delta H_a^\circ(\text{H}, g) \\ &+ 2\Delta H_a^\circ(\text{O}, g) - \sum E_b - 4\Gamma_{\text{CCO}} - 2\Gamma_{\text{CCO}} \\ &- \Gamma_{\text{OCO}} - \Delta_{\text{OCO}} + [S] \end{aligned}$$

$$\begin{aligned} \textit{cis}\text{-2,4-diMe: } \Delta H_f^\circ(g) &= 5\Delta H_a^\circ(\text{C}, g) + \\ &10\Delta H_a^\circ(\text{H}, g) + 2\Delta H_a^\circ(\text{O}, g) - \sum E_b - 5\Gamma_{\text{CCO}} \\ &- 2\Gamma_{\text{COC}} - \Gamma_{\text{OCO}} - \Gamma_{\text{CCO}} - \Delta_{\text{OCO}} - \Delta_{\text{CCO}} - \\ &S_{\text{is}}^{\text{HH}} + [S] \end{aligned}$$

By substituting the experimental heats of formation and the heats of atomization of the elements, the bond energies (E_b) and the values of the group increments given in Ref. 9 in the above equations, the values 6.67, 5.46 and 6.72 kcal·mole⁻¹ are obtained for the apparent strain $[S]$ ¹⁰ of the 1,3-dioxolane ring in these compounds, respectively. On average $[S] = 6.3$ kcal·mole⁻¹.

These and other data for "oxanes" will be discussed in detail in a paper which deals with bond-bond interactions of "oxanes".¹¹

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Mesomorphous Phases in Systems of Water-Nonionic Emulsifier-Hydrocarbon

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Our work on the influence of mesomorphous phases on the stability of emulsions showed the existence of a large region with a mesomorphous phase possessing a lamellar structure in the system water-nonionic emulsifier-*p*-xylene and gave also convincing evidence of the stabilizing action on the emulsion by the presence of this phase.¹ Since these results appeared to make a contribution to the understanding of hitherto unexplained behaviour of emulsions, we found further investigations along these lines to be of general value. The results of these investigations have confirmed the hypothesis of stabilizing influence of the mesomorphous phases.²

The investigations have included phase equilibria in three component systems: water-nonylphenol nona-ethylene glycol ether-*p*-xylene (Fig. 1 A), water-nonyl-