

Heats of Combustion of 1,3-Dioxane and Its Methyl Derivatives

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The standard heats of formation of 1,3-dioxane and several of its methyl derivatives were evaluated from the heats of combustion at 25°C measured in a bomb calorimeter. The group contributions of methyl substituents at various positions on the 1,3-dioxane ring to the standard heats of formation of the compounds were estimated. Also the contributions of the ether oxygen atoms and the interaction increments due to the oxygen atoms are discussed.

1,3-Dioxane and its methyl derivatives represent interesting problems for calorimetric investigation. The ring in these compounds closely resembles the ring in cyclohexane, but it has its own special character owing to the two oxygen atoms.¹ On the basis of the standard heats of formation of 1,3-dioxane and its methyl derivatives we can evaluate not only the group contributions of the methyl groups but also the interaction enthalpies in different conformations of methyl-substituted 1,3-dioxanes. Moreover, it is possible to solve structural problems by this method. This study forms a basis for a more extensive investigation of the group increments and interactions due to the methyl groups at different positions in the 1,3-dioxane ring.

EXPERIMENTAL

Preparation of 1,3-dioxane and its methyl derivatives. 1,3-Dioxane and its methyl derivatives were synthesized by the method of Rondestvedt² from paraldehyde or paraformaldehyde and 1,3-propanediol or its methyl derivatives employing *p*-toluenesulfonic acid as catalyst. The reaction products were carefully fractionated in an efficient Hempel column and the isolated products were distilled several times from sodium metal. All the isolated compounds were found pure on analysis in a Perkin-Elmer F-11 gas chromatograph equipped with a 6-foot-long glass column filled with Chromosorb P containing 10% Apiezon L. 2,*cis*-4,*trans*-6-Trimethyl-1,3-dioxane was prepared from paraldehyde and DL-2,4-pentanediol as described elsewhere.¹

The physical constants and purities of the synthesized samples of the compounds are given in Table 1.

Calorimetric measurements. The cyclic acetals were burned in oxygen in an adiabatic bomb calorimeter No. 1221 manufactured by Parr Instruments Co., Illinois, U.S.A.

Table 1. Physical constants and purities of the studied compounds.

Compound	Boiling point °C/torr	n_D^{20}	d_4^{20}	$(R)_D$		Purity %
				Obs.	Calc.	
1,3-Dioxane	104–106/760	1.4173	1.0301	21.52	21.65	≥99.99
4-Methyl-1,3-dioxane	113–115/760	1.4161	0.9716	26.38	26.28	≥99.99
2-Methyl-1,3-dioxane	110–111/760	1.4129	0.9702	26.24	26.28	≥99.99
<i>cis</i> -2,4-Dimethyl-1,3-dioxane	118–119/760	1.4131	0.9337	31.03	30.90	≥99.99
4,5-Dimethyl-1,3-dioxane	135.5/760	1.4232	0.9654	30.65	30.90	≥99.9
5,5-Dimethyl-1,3-dioxane	126.6/747	1.4208	0.9555	30.82	30.90	≥99.99
2, <i>cis</i> -4, <i>trans</i> -6-Tri-methyl-1,3-dioxane	138.3–138.8/758	1.4201	0.9256	35.60	35.53	≥99.99

The temperature changes were measured in Fahrenheit degrees with a Parr standard thermometer. The energy equivalent, W (cal/°F), of the calorimeter was determined by burning Parr standard benzoic acid pellets. After each combustion the water used to rinse the bomb was analyzed for nitric acid produced from traces of nitrogen in the oxygen and the loss in weight of the igniting wire coil was determined. Only those combustions after which no carbon deposits were seen in the bomb were accepted as yielding reliable results. The water contents of the reagents were considered negligible because the compounds had been repeatedly distilled from sodium, the last distillation having taken place immediately before the combustion.

The samples of 1,3-dioxane and its methyl derivatives were sealed in thin soda glass ampoules and burnt in oxygen at a pressure of 30 atm at 25°C in the bomb calorimeter. The samples were ignited by an electric current passing through Parr stainless steel wire.

Calculations. To obtain the weights *in vacuo* the weights of the samples in air were multiplied by the following factors based on the densities of the compounds at 20°C:

Compound	Correction factor
1,3-Dioxane	1.00110
4-Methyl-1,3-dioxane	1.00117
2-Methyl-1,3-dioxane	1.00118
<i>cis</i> -2,4-Dimethyl-1,3-dioxane	1.00123
4,5-Dimethyl-1,3-dioxane	1.00118
5,5-Dimethyl-1,3-dioxane	1.00120
2, <i>cis</i> -4, <i>trans</i> -6-Trimethyl-1,3-dioxane	1.00124

The gross heat of combustion, ΔH_g (cal/g), of a compound was computed from eqn. (1).

$$\Delta H_g = \frac{W \Delta t - q_i - q_t}{m} \quad (1)$$

where Δt is the change in temperature (°F), q_t the correction due to the formation of nitric acid (cal), q_i the correction due to the burnt ignition wire (cal) and m the mass of the sample *in vacuo*.

The heats of combustion of liquid 1,3-dioxane and its methyl derivatives were calculated from eqn. (2)

$$\Delta H_c^\circ(\text{liq.}) = M\Delta H_g + \Delta nRT \quad (2)$$

where M is the molecular weight of the compound in question and Δn the difference in the numbers of moles of gaseous products before and after the combustion.

The heats of formation of the gaseous compounds were calculated from the heats of combustion, $\Delta H_c^\circ(\text{liq.})$, employing the values $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -94.052$ kcal/mole and $\Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) = -68.317$ kcal/mole recommended by the National Bureau of Standards and reported heats of vaporization. Snelson and Skinner³ have reported the value

Table 2. Calibration of the calorimeter.

 $\Delta H_f^\circ(\text{solid, benzoic acid}) = 6318 \text{ cal/g.}$

m (g)	Δt ($^\circ\text{F}$)	$q_i(\text{cal})$	$q_t(\text{cal})$	$W(\text{cal}/^\circ\text{F})$
1.0239	4.781	17.92	10.15	1358.9
1.1025	5.140	13.16	10.82	1359.8
1.1417	5.324	14.56	11.10	1359.7
1.1366	5.303	17.36	11.02	1359.5
1.1150	5.205	16.80	11.00	1358.8
1.1010	5.132	16.24	10.75	1360.7

 $W_1 = 1359.6 \pm 0.3 \text{ cal}/^\circ\text{F.}$

The calibration was repeated when necessary.

 $W_2 = 1360.4 \pm 0.4 \text{ cal}/^\circ\text{F.}$ $W_3 = 1361.6 \pm 0.2 \text{ cal}/^\circ\text{F.}$

Table 3. 1,3-Dioxane.

m (g)	Δt ($^\circ\text{F}$)	$q_i(\text{cal})$	$q_t(\text{cal})$	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.83292	3.888	14.28	17.92	556.57	557.16
0.85114	3.968	6.16	11.96	557.39	557.98
0.75533	3.521	5.60	19.74	556.25	556.84
0.77665	3.623	12.60	10.53	556.99	557.58
0.72940	3.404	9.80	14.08	556.96	557.55
0.70477	3.293	16.38	16.87	556.36	556.95

 $-\Delta nRT = 0.59 \text{ kcal/mole}$ $-\Delta H_c^\circ(\text{liq.}) = 557.34 \pm 0.20 \text{ kcal/mole}$ $-\Delta H_f^\circ(\text{liq.}) = 92.13 \pm 0.3 \text{ kcal/mole}$ $\Delta H_{\text{vap}}^{25^\circ\text{C}} = 8.50 \pm 0.2 \text{ kcal/mole}$ Energy equivalent used W_3 .

Table 4. 4-Methyl-1,3-dioxane.

m	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.75759	3.899	15.68	14.05	711.07	711.96
0.76860	3.955	14.20	16.55	710.87	711.76
0.78071	4.020	11.62	19.92	711.31	712.20
0.77190	3.976	14.00	18.95	711.32	712.21
0.80274	4.124	7.84	13.22	711.12	712.01

 $-\Delta nRT = 0.89 \text{ kcal/mole}$ $-\Delta H_c^\circ(\text{liq.}) = 712.03 \pm 0.08 \text{ kcal/mole}$ $-\Delta H_f^\circ(\text{liq.}) = 99.81 \pm 0.15 \text{ kcal/mole}$ $\Delta H_{\text{vap}}^{25^\circ\text{C}} = 9.36 \pm 0.3 \text{ kcal/mole}$ Energy equivalent used W_2 .

Table 5. 2-Methyl-1,3-dioxane.

<i>m</i>	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.67189	3.441	13.58	14.96	707.23	708.12
0.66508	3.406	20.02	9.17	707.06	707.95
0.72145	3.689	21.84	10.53	705.87	706.76
0.67690	3.461	15.82	9.47	706.60	707.49
0.72515	3.706	10.92	18.35	705.96	706.85
0.68791	3.512	10.64	10.27	706.24	707.13
0.66829	3.413	17.36	9.92	705.42	706.31

$-\Delta nRT = 0.89$ kcal/mole
 $-\Delta H_c^\circ(\text{liq.}) = 707.23 \pm 0.25$ kcal/mole
 $-\Delta H_f^\circ(\text{liq.}) = 104.61 \pm 0.4$ kcal/mole
 $\Delta H_{\text{vap}}^{25^\circ\text{C}} = 9.23 \pm 0.3$ kcal/mole
 Energy equivalent used W_2 .

Table 6. *cis*-2,4-Dimethyl-1,3-dioxane.

<i>m</i>	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.73560	4.023	9.52	10.77	861.03	862.21
0.85255	4.667	6.58	20.96	861.30	862.48
0.60004	3.295	18.06	13.78	860.05	861.23
0.61385	3.372	14.00	18.12	861.98	863.16
0.64730	3.551	7.28	21.20	861.79	862.97

$-\Delta nRT = 1.18$ kcal/mole
 $-\Delta H_c^\circ(\text{liq.}) = 862.41 \pm 0.34$ kcal/mole
 $-\Delta H_f^\circ(\text{liq.}) = 111.79 \pm 0.5$ kcal/mole
 $\Delta H_{\text{vap}}^{25^\circ\text{C}} = 9.53 \pm 0.3$ kcal/mole
 Energy equivalent used W_2 .

Table 7. 4,5-Dimethyl-1,3-dioxane.

<i>m</i>	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.59911	3.296	10.50	9.28	865.02	866.20
0.71204	3.918	16.52	10.97	864.53	865.71
0.53233	2.933	16.80	8.85	864.56	865.74
0.88614	4.875	8.26	22.17	864.85	866.03
0.45854	2.530	17.08	9.93	864.54	865.72

$-\Delta nRT = 1.18$ kcal/mole
 $-\Delta H_c^\circ(\text{liq.}) = 865.88 \pm 0.14$ kcal/mole
 $-\Delta H_f^\circ(\text{liq.}) = 108.32 \pm 0.3$ kcal/mole
 $\Delta H_{\text{vap}}^{25^\circ\text{C}} = 10.16 \pm 0.3$ kcal/mole
 Energy equivalent used W_1 .

Table 8. 5,5-Dimethyl-1,3-dioxane.

<i>m</i>	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.72847	3.998	10.50	18.42	862.15	863.33
0.79996	4.398	20.16	15.20	863.14	864.31
0.64227	3.529	11.90	18.53	862.26	863.44
0.74009	4.061	12.88	13.95	862.38	863.56
0.71516	3.933	12.88	18.90	863.38	864.56
0.63126	3.466	18.76	9.61	861.92	863.10
0.62535	3.435	8.96	19.42	862.23	863.41

$-\Delta nRT = 1.18$ kcal/mole

$-\Delta H_c^\circ(\text{liq.}) = 863.67 \pm 0.21$ kcal/mole

$-\Delta H_f^\circ(\text{liq.}) = 110.53 \pm 0.35$ kcal/mole

$\Delta H_{\text{vap}}^{36^\circ\text{C}} = 9.86 \pm 0.3$ kcal/mole

Energy equivalent used W_1 .

Table 9. 2,cis-4,trans-6-Trimethyl-1,3-dioxane.

<i>m</i>	Δt	q_i	q_t	$-\Delta H_g$ kcal/mole	$-\Delta H_c^\circ(\text{liq.})$
0.70267	4.060	13.58	17.27	1017.62	1019.10
0.50603	2.921	0.14	15.23	1018.43	1019.91
0.42042	2.433	14.98	7.67	1017.94	1019.42

$-\Delta nRT = 1.48$ kcal/mole

$-\Delta H_c^\circ(\text{liq.}) = 1019.48 \pm 0.24$ kcal/mole

$-\Delta H_f^\circ(\text{liq.}) = 117.09 \pm 0.5$ kcal/mole

$\Delta H_{\text{vap}}^{36^\circ\text{C}} = 10.32 \pm 0.3$ kcal/mole

Energy equivalent used W_2 .

8.50 ± 0.20 kcal/mole for the heat of vaporization of 1,3-dioxane. The heats of vaporization of the methyl-substituted 1,3-dioxanes at their boiling points were estimated with the aid of eqn. (3) derived by Kistiakowsky⁴

$$\Delta H_{\text{vap}}/T_b = 8.75 + 4.571 \log T_b \quad (3)$$

The estimated values were then corrected to refer to 298.2°K (25°C) employing eqn. (4) derived by Watson.⁵

$$\frac{\Delta H_{\text{vap}}^1}{\Delta H_{\text{vap}}^2} = \left(\frac{1 - T_{r1}}{1 - T_{r2}} \right)^{0.38} \quad (4)$$

where T_{r1} and T_{r2} are the reduced temperatures corresponding to T_b and 298.2°K, respectively. The required critical temperatures, T_c , were estimated from eqn. (5) proposed by Meissner and Redding.⁶

$$T_c = 1.027 T_b + 159 \quad (5)$$

The computed heats of vaporization are not very accurate, but still sufficiently accurate for the calculation of group contributions to the heats of formation, $\Delta H_f^\circ(\text{g})$, of closely related compounds, such as 1,3-dioxane and its methyl derivatives.

RESULTS AND DISCUSSION

The value, -557.34 ± 0.18 kcal/mole, obtained for the heat of combustion of liquid 1,3-dioxane is in excellent agreement with the value, -557.4 kcal/mole, at 20°C reported by Skuratov *et al.*⁸ The value reported by Fletcher, Mortimer and Springall⁷ is -555.0 ± 1.3 kcal/mole and that reported by Snelson and Skinner³ -559.47 ± 0.14 kcal/mole. Fletcher, Mortimer and Springall reported data from four experiments, the results of which exhibited a large scatter, and Snelson and Skinner reported that they did not succeed in isolating 1,3-dioxane in the pure state.

The heat of combustion, -709.8 kcal/mole, reported by Skuratov and Kozina⁹ for liquid 4-methyl-1,3-dioxane is more than 2 kcal/mole higher than the value, -712.03 ± 0.08 kcal/mole, found in this work. These authors give only a few details of the experimental work and do not report any probable error limits. The experimental data of the present work are presented in Tables 2-9 and the heats of formation of the gaseous compounds are collected in Table 10.

The heat of formation, -29.5 kcal/mole, of gaseous cyclohexane and the heats of formation of tetrahydropyrene and 1,4-dioxane given in the paper of Snelson and Skinner³ can be used to estimate the increment to $\Delta H_f^\circ(\text{g})$ resulting from the replacement of a methylene group in cyclohexane by an oxygen atom. This increment is found to be -23.2 ± 0.8 kcal/mole (Tables 10 and 11). The heat of formation of 1,3-dioxane determined in this work and that of 1,4-dioxane give for the heat of isomerization associated with the reaction 1,4-dioxane (g) \rightarrow 1,3-dioxane (g) the value -7.6 ± 0.8 kcal/mole. The greater stability of the 1,3-dioxane compared with that of 1,4-dioxane is noteworthy and the difference is even larger than estimated by Snelson and Skinner.³ According to the bond-bond interaction scheme presented by Skinner¹⁰ this greater stability is due to the strong interaction of the adjoining carbon-oxygen bonds in 1,3-dioxane. The presented increments lead to the value -121.9 ± 2.4 kcal/mole for the heat of formation of sym-trioxane; this value is in agreement with the experimentally determined value -120.8 ± 1.5 kcal/mole reported by Walker and Carlisle.¹¹

Table 10. The standard heats of formation measured in this work or adopted by other investigators.

Compound	$-\Delta H_f^\circ(\text{g})$, kcal/mole
1,3-Dioxane	$83.6_3 \pm 0.5$
4-Methyl-1,3-dioxane	90.45 ± 0.45
2-Methyl-1,3-dioxane	$95.3_3 \pm 0.7$
<i>cis</i> -2,4-Dimethyl-1,3-dioxane	$102.2_6 \pm 0.8$
4,5-Dimethyl-1,3-dioxane	$98.1_6 \pm 0.6$
5,5-Dimethyl-1,3-dioxane	$100.6_7 \pm 0.65$
2, <i>cis</i> -4, <i>trans</i> -6-Trimethyl-1,3-dioxane	$106.7_7 \pm 0.8$
Tetrahydropyrene ³	52.6 ± 0.6
1,4-Dioxane ³	76.0 ± 0.4
<i>sym</i> -Trioxane ¹¹	120.8 ± 1.5

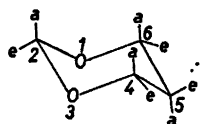


Fig. 1. Chair conformation of the 1,3-dioxane ring.

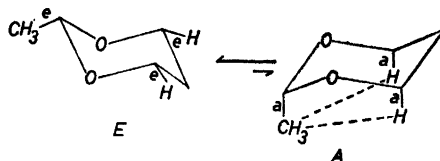


Fig. 2. Equatorial (E) and axial (A) conformer of 2-methyl-1,3-dioxane.

It should be remembered, when methyl substituents are introduced into the 1,3-dioxane ring, that the latter compound mainly occurs in the chair form^{1,12,13} (Fig. 1). Consequently the substituents may be either equatorially (*e*) or axially (*a*) oriented. An axial methyl group at position 2, 4, or 6 interacts with two axial hydrogen atoms at the other two positions. An axial methyl group at position 5 interacts only with the "axial" electron pairs of the oxygen atoms and hence the difference in the contributions of 5*e* and 5*a* methyl groups to the heat of formation is definitely smaller than the difference in the contributions of equatorial and axial methyl groups at other positions.

4-Methyl-1,3-dioxane and 2-methyl-1,3-dioxane can exist as either the equatorial or axial conformer (Fig. 2). The equatorial conformer is, however, so much more stable than the axial conformer^{1,14} that the increments of the 4*e* and 2*e* methyl groups can be deduced with fair accuracy from the heats of formation of 1,3-dioxane, 4-methyl-1,3-dioxane, and 2-methyl-1,3-dioxane. The value, $\Delta H_f^\circ(g) = -102.20 \pm 1.30$ kcal/mole, calculated for the heat of formation of *cis*-2,4-dimethyl-1,3-dioxane with the aid of these increments (Table 11) and the heat of formation of 1,3-dioxane is in good agreement with the experimentally found value -102.26 ± 0.8 kcal/mole.

The group contribution of a 4*a* or 6*a* methyl group is equal to the difference, -4.51 ± 0.8 kcal/mole, between the heats of formation of *cis*-2,4-dimethyl-1,3-dioxane and 2,*cis*-4,*trans*-6-trimethyl-1,3-dioxane (Fig. 3).

Table 11. The group contributions to $\Delta H_f^\circ(g)$ of 1,3-dioxane and its methyl derivatives.

Group	Contribution, $-\Delta H_f^{298^\circ\text{K}}$ kcal/mole
	23.2 ± 0.8
	7.6 ± 0.5
CH ₃ : 4 <i>e</i> or 6 <i>e</i>	$6.8_2 \pm 0.5$
2 <i>e</i>	11.75 ± 0.6
4 <i>a</i> or 6 <i>a</i>	$4.5_1 \pm 0.8$
5 <i>e</i>	$8.9_1 \pm 0.7$
5 <i>a</i>	8.07 ± 0.7
4 <i>e</i> and 5 <i>e</i> } or 4 <i>e</i> and 5 <i>a</i> } or 4 <i>a</i> and 5 <i>e</i> }	$H^{1e,e} = H^{1e,a}$ -1.26 ± 0.6

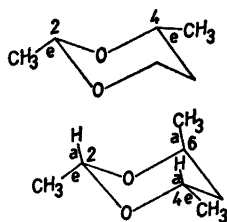


Fig. 3. The stable conformations of *cis*-2,4-dimethyl-1,3-dioxane and 2,*cis*-4,*trans*-6-trimethyl-1,3-dioxane.

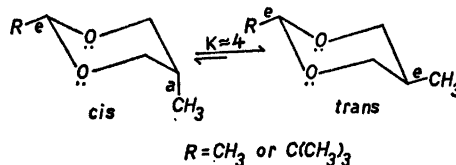


Fig. 4. The equilibrium between liquid *cis*- and *trans*-2-alkyl-5-methyl-1,3-dioxanes at 25°C.

Pihlaja¹ has found the standard free energy difference between the *cis* and *trans* forms of 2,5-dimethyl-1,3-dioxane to be 0.81 kcal/mole by adding *p*-toluenesulfonic acid to the pure liquid *trans* form and analyzing the equilibrium mixture which follows. Eliel and Knoeber¹⁴ found the free energy difference between the *cis* and *trans* configurations of 2-*t*-butyl-5-methyl-1,3-dioxane at 25°C to be 0.80 kcal/mole by a similar method. The interaction enthalpy of an axial methyl group at position 5 may be taken equal to this value because the entropies of the isomers can be assumed to be approximately equal (Fig. 4). *cis*-2,5-Dimethyl-1,3-dioxane (*e,a*-form) boils at a temperature that is about three degrees higher than the boiling point of *trans*-2,5-dimethyl-1,3-dioxane and hence the heat of vaporization of the former isomer is about 0.1 kcal/mole higher than that of the latter isomer, which means that the standard free energy difference between the two isomers in the gas phase at 25°C is higher by this amount and hence about 0.90 kcal/mole.

The group contribution of a 5*a*-methyl group is thus about 0.9 kcal/mole less in absolute value than that of a 5*e*-methyl group or $\Delta H_{5e} = \Delta H_{5a} - 0.9$ kcal/mole in the gas phase. The contributions of the 5*e*- and 5*a*-methyl groups may now be estimated from the heats of formation of 5,5-dimethyl-1,3-dioxane and 1,3-dioxane, for

$$\Delta H_f^\circ(\text{g}, 5,5\text{-dimethyl-1,3-dioxane}) - \Delta H_f^\circ(\text{g}, 1,3\text{-dioxane}) =$$

$\Delta H_{5e} + \Delta H_{5a} = 2\Delta H_{5e} + 0.9 \cong -100.67 - (-83.63) = -17.04$ kcal/mole, and hence $\Delta H_{5e} = -8.97$ kcal/mole and $\Delta H_{5a} = -8.07$ kcal/mole.

4,5-Dimethyl-1,3-dioxane may exist in both the *cis* and *trans* configuration (Fig. 5). The predominating conformation of *cis*-4,5-dimethyl-1,3-dioxane is the *e,a*-form and that of *trans*-4,5-dimethyl-1,3-dioxane the *e,e*-form.^{1,14} The heats of formation of these *cis* and *trans* forms may now be estimated from the heat of formation of 1,3-dioxane and the contributions of the methyl groups:

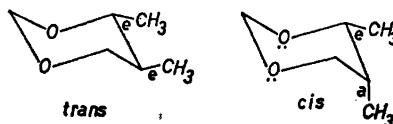


Fig. 5. The predominating conformations of *cis*- and *trans*-4,5-dimethyl-1,3-dioxane.

$$\begin{aligned} \Delta H_f^\circ(\text{g, cis-4,5-dimethyl-1,3-dioxane}) &= -83.63 - 6.82 - 8.07 \\ &= -98.52 \text{ kcal/mole} \\ \Delta H_f^\circ(\text{g, trans-4,5-dimethyl-1,3-dioxane}) &= -83.63 - 6.82 - 8.97 \\ &= -99.42 \text{ kcal/mole} \end{aligned}$$

In these calculations the interactions of the methyl groups on adjoining carbon atoms have not been taken into account. Such an interaction exists if either or both of the methyl groups are equatorial. The interaction energy of the two methyl groups in 1,2-dimethylcyclohexanes in the gaseous state at 25°C is 1.14 kcal/mole.¹⁵ This interaction energy in 4,5-dimethyl-substituted 1,3-dioxanes may be assumed to be approximately equal.

The sample of 4,5-dimethyl-1,3-dioxane which was used in the calorimetric measurements consisted of only one isomer according to gas chromatographic analysis. Its heat of formation was found to be -98.16 ± 0.6 kcal/mole. When the heats of formation calculated above are subtracted from this value, the enthalpies of interaction of the adjoining methyl groups are found to be

$$\begin{aligned} 1. \quad & -98.16 - (-98.52) = 0.36 \text{ kcal/mole} = H_{e,e}^i = H_{e,a}^i \\ 2. \quad & -98.16 - (-99.42) = 1.26 \text{ kcal/mole} = H_{e,e}^i = H_{e,a}^i \end{aligned}$$

The latter value is in agreement with the value 1.14 kcal/mole for the cyclohexane derivatives and consequently the isomer of 4,5-dimethyl-1,3-dioxane employed in the calorimetric measurements had the *trans* configuration. On the basis of kinetic data, Pihlaja¹ has also concluded that the 4,5-dimethyl-1,3-dioxane sample consisted of the *trans* configuration.

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