

Bond-bond Interactions in Organic Oxygen Compounds

Part V. Enthalpies of Formation of Methyl and Ethyl Orthoformates and the Contributory Group Increments. The Magnitude of the So-called Rabbit-ear Effect in Acyclic Oxygen Compounds

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The heats of combustion of methyl (I) and ethyl (II) orthoformates have been determined by combustion calorimetry. The values derived for the enthalpies of formation in the liquid and gaseous states are, respectively, (-137.51 ± 0.47) and (-128.41 ± 0.67) kcal/mol for I, and (-162.84 ± 0.70) and (-151.84 ± 0.90) kcal/mol for II.

By using the bond-bond interaction scheme for organic oxygen compounds, the value -5.46 kcal/mol was computed for the destabilization effect due to an oxygen trio attached to the same carbon atom. The most stable rotamers of I and II include two rabbit-ear effects, the magnitude of which in the gaseous state was shown to be about 1.0 kcal/mol on the basis of the enthalpies of formation of the gaseous esters.

Bond-bond interactions in aliphatic alcohols, ethers, and acetals have been discussed in a number of earlier papers.¹⁻⁴ These data, however, did not allow the evaluation of the magnitude of the so-called rabbit-ear effect in these compounds. The most stable rotamers of methyl (I) and ethyl (II) orthoformates both include two rabbit-ear effects [RE] (Fig. 1). The enthalpies

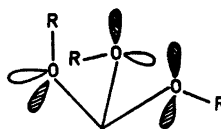


Fig. 1. The most stable rotamer of methyl and ethyl orthoformates.

of formation of gaseous orthoformates may be evaluated from the equation

$$\begin{aligned}
 -\Delta H_f^0(\text{g}) = & \sum E_b + 3(n\Gamma_{\text{CCO}} + \Gamma_{\text{COC}} + \Gamma_{\text{OCO}}) + 4S_{15}^{\text{HO:}} \\
 & + \Delta_{\text{OOO}} + 2[\text{RE}] - \Delta H_a^0(\text{g, atoms})
 \end{aligned}
 \quad (1)$$

where n is 1 for ethyl and 0 for methyl orthoformate, $\sum E_b$ the sum of bond energies,^{1,4} and Γ_{CCO} , Γ_{COC} , and Γ_{OCO} are the stabilization increments due to next-nearest-neighbor carbon and oxygen atoms attached to the same carbon atom, next-nearest-neighbor carbon atoms attached to the same oxygen atom, and next-nearest-neighbor oxygen atoms attached to the same carbon atom, respectively (Table 1).^{1,4} S_{15}^{HO} is the contribution of the non-

Table 1. Values of the group increments contributing to the enthalpies of formation of gaseous methyl and ethyl orthoformates (eqn. 1).

Group increment	Contributory energy to $-\Delta H_f^0(\text{g})$, kcal mol ⁻¹	Reference
Γ_{CCO}	5.53	1, 4
Γ_{COC}	5.90	1, 4
Γ_{OCO}	13.365	1, 4
S_{15}^{HO}	-0.15	1, 4
Δ_{OOO}	-5.46	This work
[RE]	-0.98	This work

bonded interaction between fifth-neighbor hydrogen atoms and the lone pair orbital of an oxygen atom, Δ_{OOO} the destabilization effect due to an oxygen trio attached to the same carbon atom, [RE] the interaction energy of a rabbit-ear effect, and $\Delta H_a^0(\text{g, atoms})$ the heat of atomization of the gaseous atoms. By measuring the enthalpies of formation of methyl (I) and ethyl (II) orthoformates, the magnitude of [RE] may be evaluated from the equation

$$2[\text{RE}] + \Delta_{\text{OOO}} = \Delta H_f^0(\text{g, obs.}) - (\Delta H_f^0(\text{g, calc.}) - \Delta_{\text{OOO}} - 2[\text{RE}]) \quad (2)$$

where the last term in parentheses is estimated from eqn. (1).

EXPERIMENTAL

Materials. Methyl and ethyl orthoformates were obtained from Fluka AG. They were purified by several distillations from metallic sodium at reduced pressure. The purities were checked on a Perkin-Elmer F 11 gas chromatograph, equipped with a column containing 10 % potassium hydroxide on Apiezon L grease.^{3,3} Physical constants were

	B.p. °C/torr	n_D^{20}	d_4^{20}
$\text{CH}(\text{OCH}_3)_3$	99.5/755	1.3795	0.9691
$\text{CH}(\text{OEt})_3$	146/760	1.3916	0.8927
	32.7-33.0/9		

Combustion experiments. The samples were sealed in thin gelatin capsules and burned in oxygen in an adiabatic bomb calorimeter No. 1221, manufactured by Parr Instruments Co., Ill. U.S.A., as described earlier.^{3,3,5-8} The energy equivalent of the standard calorimeter system, e^0 (calor), was determined by burning Parr standard benzoic acid.⁵ The calibration and combustion experiments were carried out at an initial oxygen pressure of 35 atm. to avoid incomplete burning of the orthoformates, and hence the quantity of

Table 2. Energies of combustion of methyl and ethyl orthoformates at 298.15°K. m is the mass of the sample *in vacuo*, m' the mass of the gelatin capsule, Δt the observed rise of temperature, q_1 the correction due to the burned ignition wire, $q(\text{HNO}_3)$ and $q(\text{H}_2\text{SO}_4)$ the corrections due to the formation of nitric and sulfuric acids, q_w the Washburn correction, and $e^{\text{f}}(\text{cont})$ the contribution of the contents of the bomb to the energy equivalent at the end of the combustion.

$$e^{\text{f}}(\text{calor}) = (1360.69 \pm 0.23) \text{ cal/}^\circ\text{F}; -\Delta u_c^{\text{c}}(\text{gel}) = (4562.39 \pm 4.93) \text{ cal/g}; T_i = T_f = 298.15^\circ\text{K}; p_1 = 35 \text{ atm.}$$

m/g	m'/g	$\Delta t/^\circ\text{F}$	q_1/cal	$q(\text{HNO}_3)/\text{cal}$	$q(\text{H}_2\text{SO}_4)/\text{cal}$	q_w/cal	$e^{\text{f}}(\text{cont})/\text{cal}^\circ\text{F}^{-1}$	$-\Delta U_c^{\text{c}}/\text{cal g}^{-1}$
0.77655	0.1233	3.535	2.38	11.01	0.97	3.14	2.60	5459.01
0.78947	0.1260	3.601	13.72	11.27	0.99	3.19	2.60	5453.26
0.78126	0.1242	3.566	12.46	10.585	0.98	3.16	2.60	5462.49
0.76884	0.1215	3.512	19.60	10.52	0.955	3.11	2.60	5461.93
0.78056	0.1277	3.578	16.52	10.71	1.00	3.18	2.60	5462.49
0.78266	0.1227	3.572	15.54	10.54	0.96	3.16	2.60	5468.15
0.78506	0.1168	3.562	15.12	10.41	0.92	3.15	2.60	5469.09
0.75733	0.1287	3.489	17.22	10.11	1.01	3.10	2.59	5463.72
Methyl orthoformate								
M = 106.12								
0.73098	0.1273	4.209	14.98	11.705	1.00	3.19	2.62	7013.16
0.70164	0.1159	4.024	16.24	11.79	0.91	3.04	2.60	7020.78
0.70195	0.1249	4.052	11.34	10.45	0.98	3.08	2.60	7020.98
0.68723	0.1252	3.982	19.04	9.41	0.98	3.04	2.60	7020.85
0.71256	0.1253	4.110	10.22	10.515	0.985	3.12	2.61	7026.31
0.71336	0.1337	4.137	12.60	9.24	1.05	3.17	2.61	7014.57
0.72037	0.1251	4.155	17.78	10.995	0.98	3.15	2.61	7025.37
0.72207	0.1133	4.120	13.16	10.505	0.89	3.11	2.62	7024.56
Ethyl orthoformate								
M = 148.21								
Standard deviation of the mean = 1.77								
Standard deviation of the mean = 1.71								

Table 3. Energies and enthalpies of combustion and formation at 298.15°K. All values in kcal mol⁻¹ (1 cal = 4.1840 J).

Orthoformate	$-\Delta U_c^{\text{c}}(\text{l})$	$-\Delta H_c^{\text{c}}(\text{l})$	$-\Delta H_f^{\text{c}}(\text{l})$	ΔH_{vap}	$-\Delta H_f^{\text{c}}(\text{g})$
Methyl	579.68 ± 0.24^a	580.27 ± 0.47^b	137.51 ± 0.47	9.10 ± 0.20	128.41 ± 0.67
Ethyl	1040.56 ± 0.35^a	1042.04 ± 0.70^b	162.84 ± 0.70	11.00 ± 0.20	151.84 ± 0.90

^a Overall standard deviation. ^b Twice the overall standard deviation.

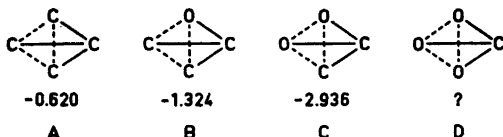
heat evolved by combustion of Parr standard benzoic acid⁵ was multiplied by the factor 1.00010.⁹

The average energy of combustion of the gelatin capsules (4562.4 ± 4.9 cal/g) has been determined earlier.³ The other corrections are stated in Ref. 5. The combustion data for methyl (I) and ethyl (II) orthoformates are shown in Tables 2 and 3.

RESULTS

The heats of vaporization were calculated from the expression reported by Wadsö.¹⁰ Using the data collected in Table 1, eqn. (1) yields the value $+135.75$ kcal/mol for the last term of eqn. (2) in the case of I, and the value $+159.33$ kcal/mol in the case of II. By substituting these values and the experimental values of the enthalpies of formation in the gaseous state into eqn. (2), the values -7.34 and -7.49 kcal/mol were derived for the sum of Δ_{ooo} and $2[\text{RE}]$, respectively.

The destabilization effect of an oxygen trio attached to the same carbon atom may be estimated in the following way:



The destabilization effect per carbon pair in a carbon trio attached to the same carbon atom is -0.21 kcal/mol (A). Using this value and the group increment of an O,C,C-trio attached to the same carbon atom (B), the value -1.12 kcal/mol is obtained for the destabilization energy of a carbon-oxygen pair. Similarly, the value -1.82 kcal/mol is derived for the destabilization, due to an oxygen pair in the oxygen trio attached to the same carbon atom (C and D). Thus, the magnitude of the group increment due to an oxygen trio attached to the same carbon atom is three times -1.82 or -5.46 kcal/mol.

It is shown above that the experimental results gave the value -7.42 kcal/mol for the sum of Δ_{ooo} and two rabbit-ear effects. Consequently, the contribution of the rabbit-ear effects is $-7.42 - (-5.46)$ or -1.96 kcal/mol, *i.e.* about -1.0 kcal/mol per rabbit-ear effect.

DISCUSSION

It has been estimated earlier that the magnitude of a rabbit-ear effect in cyclic oxanes is around 1.7 kcal/mol.^{3,11} Taking into account that *gauche* type interactions are frequently somewhat weaker in acyclic systems than in cyclic systems, the value -1.0 kcal/mol derived for the rabbit-ear effect in orthoformates seems to be reasonable. For instance, the CH_3/CH_3 *gauche* interaction is 0.6 kcal/mol¹² and the interaction energy of an axial CH_3 in cyclohexane 1.7 kcal/mole¹³ (two CH_3/CH_3 *gauche* interactions). If a similar difference prevails in the case of rabbit-ear effects its magnitude in acyclic systems

should be 1.2 kcal/mol. Similarly, the *gauche* interaction between CH₂ and O (S₁₅^{HO:}) is 0.15 kcal/mol,⁴ whereas the value 0.26 kcal/mol¹³ is obtained by dividing by two the value for axial OH in cyclohexanol. On the basis of these values, the magnitude of a rabbit-ear effect in acyclic systems should be about 0.95 kcal/mol. Both of the above approximations are in satisfactory agreement with the experimentally obtained value 1.0 kcal/mol.

For justification of the method used in the estimation of the group increment due to an oxygen trio attached to the same carbon atom, it is worth mentioning that the Δ_{OCO} increment does not include rabbit-ear effects, since dimethoxymethane and its homologs have been shown to attain the *gauche* conformation to avoid the rabbit-ear effects.¹³

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Received June 9, 1970.