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TR 75

AD 468273

NAVORD REPORT NO. 5491

DETERMINATION OF THE C-O BOND ENERGY FROM THE HEATS OF COMBUSTION OF FOUR ALIPHATIC ETHERS

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12 APRIL 1957

DOCUMENT RELEASE STATUS
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AD NUMBER (To be inserted by DDC) TC-75

CLASSIFICATION: Unclassified

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ORIGINATING AGENCY: NAVol Powder Factory

ENCLOSURE (REPORT TITLE): Determination of the C-O Bond Energy From The Heats of Combustion of Four Aliphatic Ethers

REPORT SERIES AND NUMBER: NAVORD 5491

REPORT DATE: 2 April 1957

COG. BUWEPS CODE (For use in BUWEPS only): DLI 30X

CONTRACT/PROJECT/WEPTASK NUMBER: Task Assignment RFF-RE2d-02-1-53

SECURITY CLASSIFICATION	UNCLAS	CONFI.	SECRET
REPORT	✓		
TITLE OR SUBJECT	✓		
ABSTRACT OR SUMMARY	✓		

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CLASSIFICATION: Unclassified

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D 6540

(5) Naval Ordnance Plant,
Indian Head, Md.

NavOrd Report No. 5491
Technical Report No. 75

U. S. NAVAL POWDER FACTORY
RESEARCH AND DEVELOPMENT DEPARTMENT
INDIAN HEAD, MARYLAND

(6) DETERMINATION OF THE C-O BOND ENERGY FROM THE HEATS OF COMBUSTION OF FOUR ALIPHATIC ETHERS.

(1) Tech. rept.,

(10) By

J. W. Murrin and
S. Goldhagen.

(14) Rept. no. TR-75

(17) Task NPF-Re2d02/1/53

Ldc

FOREWORD

This report is part of a series in which the various chemical groupings and bond energies present and propellant ingredients are being examined. From these data the thermodynamic quantities of theoretical compounds may be calculated on the basis of structure without recourse to chemical synthesis.

The work reported herein was performed under Bureau of Ordnance Task Assignment NPF-Re2d-02-1-53, "Physical-Chemical investigation of Gun Propellants," and was reviewed for technical accuracy by E. D. Margolin and E. F. Hare. The data are as of 27 January 1957.

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ABSTRACT

The heats of combustion at 25° C of four simple aliphatic ethers of homologous series (diethyl ether, di-n-propyl ether, di-n-butyl ether, and di-n-amyl ether) were determined by means of a Dickinson-type precision calorimeter. The heats of formation in the liquid and gaseous states were then calculated. By means of K. J. Laidler's empirical method of estimating heats of formation of organic compounds, a mean value of 87.6 kcal for the C-O bond energy is obtained.

LIST OF SYMBOLS

ΔR_c = the temperature rise of the system, in ohms, as measured by a platinum resistance thermometer in conjunction with a Leeds and Northrup type G-2 Mueller bridge, corrected for radiation and stirring

Δr_i = the temperature correction in ohms for ignition energy from the fuze wire in the calorimeter

Δr_n = the temperature correction in ohms for energy released in formation of nitric acid

Δr_{std} = the small temperature correction in ohms for variation in the mean temperature of an experiment from the "standard" value of 28.5° C

Δr = the temperature correction in ohms for energy released from benzoic acid igniter

ΔR_f = the increase in temperature corrected for Δr_i, Δr_n, Δr_{std}, and Δr, in absolute ohms per gram of sample, as measured by the platinum resistance thermometer in the calorimeter

$-\Delta U^0_{30° C}$ = the heat of combustion at 30° C at constant volume after the Washburn corrections[8] modified such that gases are corrected to zero pressure, have been applied for products and reactants in their standard states

$-\Delta H^0_{30° C}$ = the heat of combustion at 30° C at constant pressure

$-\Delta H^0_{25° C}$ = the heat of combustion at 25° C at constant pressure

$-\Delta H^{0}_{f_{25^\circ C}}$ = the heat of formation at 25° C from the elements

$\Delta H_{vap_{25^\circ C}}$ = the heat of vaporization at 25° C

$-\Delta H_{A_{25^\circ C}}$ = the heat of atomization at 25° C

DETERMINATION OF THE C-O BOND ENERGY FROM THE HEATS OF COMBUSTION OF FOUR ALIPHATIC ETHERS

In a continuation of the program of determining bond and group energies,[1] the C-O linkage in four ether compounds has been chosen for investigation.

According to Kharasch's investigations,[2] heats of combustion of several ether compounds have been studied as early as 1852 by Favre and Silbermann, 1887 by Stohmann, and 1905 by Thomsen. Since the reliability of these early data is questionable, the values leading to the calculation of the C-O bond energy were redetermined; the heats of combustion of additional ethers were also measured.

The compounds included in this study were di-ethyl ether, di-n-propyl ether, di-n-butyl ether, and di-n-amyl ether. The data obtained in these determinations have been used to calculate the heat of formation in the liquid and gaseous states.

The method used for calculating the C-O bond energy was that of K. J. Laidler.[3] It is based on empirically obtained C-C and C-H bond energies.

UNIT OF ENERGY, MOLECULAR WEIGHTS, AND UNCERTAINTIES

The unit of energy used here is the absolute joule. The conversion to the defined calorie is 1 calorie = 0.0041840 absolute kilojoules. The molecular weights are based on the 1947 Revision of the Atomic Weights.[4]

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method described by F. D. Rossini and co-workers.[5]

MATERIALS

The simple aliphatic ether compounds, which were supplied by the Eastman Kodak Company, were purified by drying with calcium chloride and distilling from metallic sodium. In addition, a portion of the diethyl ether was also distilled from methyl magnesium bromide. As can be seen in Appendix A, this additional distillation had no effect on the calorimetric value (ΔR_f) for the heat of combustion.

The procedure used for sealing these volatile compounds in glass ampoules, purifying the oxygen, and igniting the compounds has been previously described.[1, 6] Carbon formation in the ignition of diethyl ether and di-n-propyl ether prompted the use of 0.15-gram benzoic acid pellets as an auxiliary fuel.

METHOD AND APPARATUS

Essentially the same method and apparatuses were used in the present investigation as in the investigation of the nitrate group.[1] They are described more fully in that report.

The heats of combustion were determined with a Dickinson-type precision calorimeter. The isothermal jacket was maintained at 30.000° ± .001° C. The temperature rise in the calorimeter was measured with a platinum resistance thermometer in conjunction with a Leeds and Northrup type G-2 Mueller bridge. Calorimetric data are shown in Appendix A.

The following formulas define the heats of combustion and formation:

$$-\Delta U^0_{30^\circ\,C}:\ C_aH_bO_cN_{d(liq)} + \left(a + \frac{b}{4} - \frac{c}{2}\right) O_{2(gas)} \longrightarrow$$

$$a\,CO_{2(gas)} + \frac{b}{2}\,H_2O_{(liq)} + \frac{d}{2}\,N_{2(gas)}$$

$$-\Delta H^0_{f_{25^\circ\,C}}:\ a\,C_{(graphite)} + \frac{b}{2}\,H_{2(gas)} + \frac{c}{2}\,O_{2(gas)} +$$

$$\frac{d}{2}\,N_{2(gas)} \longrightarrow C_aH_bO_cN_{d(liq)}$$

CALIBRATION OF THE CALORIMETER

National Bureau of Standards Benzoic Acid Sample Number 39 G was used to obtain the calorimeter constants. The results obtained are shown in Appendix B.

The No. 1002 Parr bomb was calibrated yielding a value of 143752.0 abs j/ohm, obtained from experiments 1 through 8. This value was used in the determinations of diethyl ether and di-n-propyl ether. A No. 1002 Parr bomb, which had a new type snap-on intake valve, was used in the determinations of di-n-butyl ether and di-n-amyl ether. From the data listed for experiments 9 through 16, a calibration constant of 143961.7 abs j/ohm was obtained.

DISCUSSION OF RESULTS

Table I gives the values for the heats of combustion and formation of each compound corrected to standard-state conditions by means of the Washburn corrections,[7] modified to refer all gases to zero pressure. The result obtained for diethyl ether ($-\Delta H^0_{25^\circ\,C}$ = 652.99 kcal/mole) agrees closely with the value obtained by Stohmann,[2] after his value for the heat of combustion is corrected to 25° C and the 1947[4] atomic weights of carbon and hydrogen

Table I

HEATS OF COMBUSTION AND FORMATION OF THE ETHER COMPOUNDS

Compound	$-\Delta U^0_{30^\circ C}$ abs j/gram	$-\Delta H^0_{30^\circ C}$ abs j/gram	$-\Delta H^0_{25^\circ C}$ abs j/gram	$-\Delta H^0_{25^\circ C}$ cal/gram	$-\Delta H^0_{25^\circ C}$ kcal/mole	$-\Delta H^0_{f_{25^\circ C}}$ kcal/mole
Diethyl ether	36780.6	36848.6	36860.7	8809.91	652.99 ± 0.45	64.81
Di-n-propyl ether	39340.8	39414.8	39432.3	9424.55	962.92 ± 0.49	79.61
Di-n-butyl ether	40938.9	41016.3	41029.9	9806.38	1277.03 ± 0.66	90.24
Di-n-amyl ether	41881.0	41960.7	41978.4	10033.08	1588.00 ± 0.71	104.02

are used ($-\Delta H_{25^\circ C}$ = 651.92 kcal/mole). However, the value for di-n-amyl ether ($\Delta H^0_{25^\circ C}$ = 1588.0 kcal/mole) differs greatly from that obtained by Favre and Silbermann[2] ($-\Delta H_{25^\circ C}$ = 1608.7 kcal/mole). Kharasch[2] calculated a value of 1582.0 kcal/mole at 18° C using his method of predicting the heats of combustion of organic compounds. It is therefore believed that Favre and Silbermann's value is in error. Values for the heat of combustion of di-n-propyl ether and di-n-butyl ether are not available in the literature.

Table II shows the C-O bond energies obtained. The values were calculated by subtracting the sum of the bond energies from the heats of atomization at 25° C not including the C-O bond. The heat of atomization of each compound in turn is the sum of the heats of atomization of the individual atoms plus the heat of formation in the gaseous state. The values obtained for the C-O bond in each of the simple ethers agree to within 0.8% of the mean. It is believed that the deviations observed are largely due to inaccuracies in the values used for the respective heats of vaporization rather than deviations in the energy of the bond. Another possible reason for the observed deviations is the assumption that the substitution of atoms other than carbon or hydrogen does not affect the energies of the C-C and C-H bonds.[3]

Table II

HEATS OF VAPORIZATION, FORMATION, AND ATOMIZATION AND ENERGY OF THE C-O BOND

Compounds	$\Delta H_{vap_{25^\circ C}}$ [1] (kcal/mole)	$-\Delta H^0_{f_{gas_{25^\circ C}}}$ (kcal/mole)	$-\Delta H_{A_{25^\circ C}}$ [2] (kcal/mole)	Energy C-O bond [3] (kcal)
Diethyl ether	6.4 [8]	58.4	1325.4	87.3
Di-n-propyl ether	8.2 [9]	71.4	1890.1	88.3
Di-n-butyl ether	10.3 [10]	79.8	2480.3	87.2
Di-n-amyl ether	11.9 [10]	93.1	3014.2	87.8
Mean				87.6

[1] Calculated from vapor pressure data in the indicated sources.

[2] Based on the following values (in kcal) for heat of atomization of individual atoms: C(gaseous), -171.7; H, -52.09; 0, -59.16; These values are from reference 3.

[3] Based on the following values (in kcal) for bond energy of individual bonds: C-C, 86.75; C-H(primary), 98.025; C-H(secondary), 97.275; C-H(tertiary), 96.725. All values are from reference 3.

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APPENDIX A

CALORIMETRIC DATA ON FOUR ALIPHATIC ETHERS

Experiment number	Mass[1] (gram)	ΔR_c ohm	Δr_i ohm	Δr_n ohm	Δr_{std} ohm	Benzoic acid Mass (gram)	Benzoic acid Δr (ohm)	ΔR_f[2] (ohm/gram)
				Diethyl ether				
1	0.90008	0.26100	0.00066	0.00005	0.00000	0.16310	0.02998	0.25588
2[3]	0.49403	0.16201	0.00071	0.00009	0.00001	0.18937	0.03481	0.25583
3[3]	0.84865	0.24763	0.00047	0.00011	0.00000	0.16188	0.02976	0.25604
Mean								0.25592
Standard deviation								0.00006

[1]/Corrected to in vacuo conditions.

[2]/Corrected to 28.5° C.

[3]/Samples distilled from methyl magnesium bromide.

APPENDIX A (cont'd)

Experiment number	Mass[1] (gram)	ΔR_c ohm	Δr_i ohm	Δr_n ohm	Δr_{std} ohm	Benzoic acid Mass (gram)	Benzoic acid Δr (ohm)	ΔR_f[2] (ohm/gram)
				Di-n-propyl ether				
1	0.67779	0.229195	0.000506	0.000117	-0.000004	0.23406	0.043030	0.273739
2	0.56253	0.188011	0.000415	0.000091	-0.000011	0.18229	0.033513	0.273729
3	0.61807	0.207699	0.000686	0.000015	-0.000007	0.20560	0.037798	0.273746
4	0.81048	0.222417	0.000543	0.000017	0.000000	0.00000	0.000000	0.273736
Mean								0.273737
Standard deviation								0.000003

[1]/Corrected to in vacuo conditions.

[2]/Corrected to 28.5° C.

Experiment number	Mass[1] (gram)	ΔR_c (ohm)	Δr_l (ohm)	Δr_n (ohm)	Δr_{std} (ohm)	ΔR_f[2] (ohm/gram)
			Di-n-butyl ether			
1	0.96157	0.274131	0.000653	0.000031	+0.000012	0.284388
2	1.12297	0.320050	0.000614	0.000028	0.000000	0.284431
3	1.16348	0.331644	0.000518	0.000038	-0.000014	0.284561
4	1.08970	0.310554	0.000554	0.000038	-0.000019	0.284430
Mean						0.284452
Standard deviation						0.000037

[1] Corrected to in vacuo conditions.

[2] Corrected to 28.5° C.

APPENDIX A (cont'd)

Experiment number	Mass[1]/ (gram)	ΔR_c (ohm)	Δr_i (ohm)	Δr_n (ohm)	Δr_{std} (ohm)	ΔR_f[2]/ (ohm/gram)
			Di-n-amyl ether			
1	1.11445	0.324915	0.000572	0.000042	-0.000014	0.290984
2	1.12211	0.327109	0.000503	0.000026	-0.000021	0.291022
3	1.11529	0.325254	0.000664	0.000033	-0.000017	0.290992
Mean						0.290999
Standard deviation						0.000011

[1]/Corrected to in vacuo conditions.

[2]/Corrected to 28.5° C.

APPENDIX B

RESULTS OF CALIBRATION EXPERIMENTS

Experiment number	Mass (gram)	ΔR_c (ohm)	Δr_i (ohm)	Δr_m (ohm)	Δr_{std} (ohm)	ΔR_f (ohm/gram)
1	1.00811	0.185617	0.000500	0.000000	-0.000016	0.183612
2	1.04268	0.192433	0.000591	0.000016	-0.000005	0.183969
3	1.05848	0.195134	0.000533	0.000013	+0.000003	0.183839
4	1.00068	0.184591	0.000577	0.000013	0.000000	0.183876
5	1.08355	0.199869	0.000528	0.000027	+0.000002	0.183946
6	1.98178	0.180961	0.000453	0.000027	-0.000003	0.183827
7	0.98653	0.182273	0.000584	0.000330	0.000000	0.183834
8	0.99578	0.183800	0.000698	0.000010	+0.000001	0.183870
Mean						0.183846
Standard deviation						0.000040
Calibration constant						143752.0 abs j/ohm

APPENDIX B (cont'd)

Experiment number	Mass (gram)	ΔR_c (ohm)	Δr_i (ohm)	Δr_m (ohm)	Δr_{std} (ohm)	ΔR_f (ohm/gram)
9	0.99845	0.183864	0.000436	0.000025	+0.000003	0.183690
10	1.04198	0.191838	0.000530	0.000029	-0.000006	0.183567
11	1.01303	0.186445	0.000527	0.000019	0.000000	0.183508
12	1.00842	0.185569	0.000503	0.000009	+0.000006	0.183518
13	.98999	0.182368	0.000572	0.000021	+0.000003	0.183615
14	1.01526	0.186811	0.000516	0.000022	-0.000005	0.183468
15	0.98328	0.181203	0.000480	0.000020	+0.000002	0.183776
16	1.03613	0.190656	0.000571	0.000034	+0.000005	0.183429
Mean						183571
Standard deviation						0.000038
Calibration constant						143961.7 abs j/ohm