Heats of Combustion and Formation of 4-Phenyl-1,2,3-selenadiazole and Dibenzyl Diselenide

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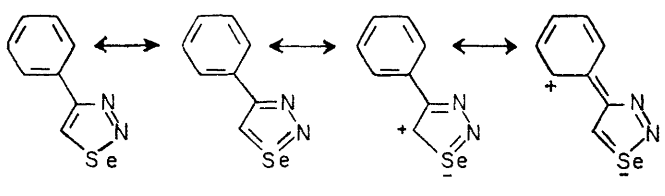
By means of a conventional adiabatic bomb calorimeter, the heats of combustion of crystalline 4-phenyl-1,2,3-selenadiazole and dibenzyl diselenide have been determined to be 1097 and 1942·7 kcal mol^{-1} respectively. Also, by means of transpiration and mass spectrometric methods, the heats of sublimation were determined. The values obtained are 22·5 kcal mol^{-1} for 4-phenyl-1,2,3-selenadiazole and 31·2 kcal mol^{-1} for dibenzyl diselenide. From these values for dibenzyl diselenide and available thermochemical data, the carbon–selenium bond energy has been calculated to be 57 kcal mol^{-1}.

ORGANOSELENIUM compounds have attracted much attention in recent years.[1-5] Work [6-8] here and at the University of Tehran, has resulted in new methods for synthesis of heterocyclic compounds containing selenium. However, the lack of thermochemical and kinetic data for these compounds has been a matter of concern and hindered progress in this field to some extent. In order to remedy this situation we decided to make a systematic thermochemical study of these compounds to compare them with their sulphur analogues.

The first two compounds to be investigated were dibenzyl diselenide and 4-phenyl-1,2,3-selenadiazole. A study of dibenzyl diselenide can provide a value for the carbon–selenium single bond energy which is required in most thermochemical studies of organoselenium compounds. The second compound 4-phenyl-1,2,3-selenadiazole, has a number of different resonance structures (1) suggesting relatively high stability.



(1)

EXPERIMENTAL

Materials.—Benzyl diselenide was provided by Professor Lalezari, Faculty of Pharmacy, University of Tehran. 4-Phenyl-1,2,3-selenadiazole was synthesised by Dr. Yalpany,[8] this department.

Benzyl diselenide was recrystallised from ethanol and 4-phenyl-1,2,3-selenadiazole from ethanol–water several times and dried in vacuum oven, prior to combustion. M.p. and t.l.c. analyses proved that both compounds were free from impurities.

Calorimeter.—This was an adiabatic B.T.L. standard bomb calorimeter equipped with a Beckman thermometer capable of reading to 0·001 °C. The sample, in pellet form was burned in a platinum crucible in oxygen at 37 atm. initial pressure and fired at 25 °C using a cotton fuse. After combustion the bomb contents were analysed for nitrogen and selenium acids.

Selenium acid analysis was performed by two different methods: (1) the determination of the quantity of selenium present in the solution as selenious acid by oxidizing selenions to selenic acid using standard potassium permanganate solution; [9] and (2) the determination of the total acidity of the bomb solution by potentiometric titration with

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standard sodium hydroxide solution. The acids present in the solution were HNO_3, H_2SeO_3, and possibly H_2SeO_4. Both selenium acids being dibasic, the amount of HNO_3 could be determined by the difference between the first and the second equivalence points. The amount of H_2SeO_3 found in the first method was equal to the amount of total selenium acids found in the second method, indicating that all the selenium in the solution was present as selenious acid.

However, 4-phenyl-1,2,3-selenadiazole, gave a small deposit of red selenium on the inside walls of the combustion chamber. The exact quantity of this deposit was determined by the difference in the original amount of selenium present in the sample and that found in the bomb solution, and the appropriate correction was made in the final results.

The heat equivalent of the calorimeter was determined by burning pure benzoic acid obtained from Baird and Tatlock, London, with a heat of combustion of 6318·16 cal g^{-1}. This value was corrected for the non-standard conditions prevailing in the combustion chamber. Corrections for nitric acid formation were based on 14·3 kcal mol^{-1} for the heat of formation of 0·1N-nitric acid from N_2,O_2, and water and the correction for the heat of combustion of cotton fuse was 3·88 kcal mol^{-1}.[10] The Washburn corrections were made using the method of Hubbard *et al.*[11]

Measurement of Heats of Sublimation.—The vapour pressures of 4-phenyl-1,2,3-selenadiazole, in the range 54·0—71·5 °C were measured by transpiration method.[12] From the plot of these values *versus* the reciprocal of temperature the heat of sublimation was obtained. The heat of sublimation of dibenzyl diselenide was obtained using a modification of the method of Grimley.[13] Details of this modification and its application to other organic compounds will be described elsewhere.[14]

RESULTS AND DISCUSSION

The results of the combustion of 4-phenyl-1,2,3-selenadiazole and dibenzyl diselenide are reported in Tables 1 and 2 respectively.

TABLE 1

Results of combustion experiments of 4-phenyl-1,2,3-selenadiazole

			Se converted to H_2SeO_3 (%)					
Expt. no.	m/g [a]	Δt/°C [b]	KMnO$_4$ Method	NaOH Method	q_{HNO_3}/ cal [c]	$q_{w.c.}$/ cal [d]	$-q_{Se}$/ cal g^{-1} [e]	$-\Delta U_c$/ cal g^{-1} [f]
1	0·8716	1·894	97·81	98·00	12·14	29·1	5·2	5246
2	0·9543	2·060	98·5	99·4	11·73	29·3	2·6	5238
3	1·0504	2·270	98·15	97·79	13·5	29·7	5·2	5244
4	0·8321	1·804	95·54	95·19	11·04	29·1	11·7	5250
5	1·2655	2·732	94·17	94·34	15·2	30·4	15·1	5248

$\Delta U_{Ave} = -5246 \pm 6$ cal g^{-1}.

[a] Weight of sample. [b] Change in calorimeter temperature due to combustion. [c] Correction for formation of aqueous HNO_3. [d] Sum of Washburn correction and correction for heat gained by combustion of cotton fuse. [e] Correction for incomplete conversion of Se to H_2SeO_2. [f] Energy of combustion.

TABLE 2

Results of combustion experiments of dibenzyl diselenide [a]

			Se converted to H_2SeO_3 (%)				
Expt. no.	m/g	Δt/°C	KMnO$_4$ Method	NaOH Method	q_{HNO_3}/cal	$q_{w.c.}$/cal	$-\Delta U_c$/cal g^{-1}
1	0·5049	1·178	99·90	99·85	2·07	27·86	5706
2	0·4960	1·157	100	99·95	1·93	27·82	5704
3	0·5949	1·386	100	100	2·21	28·18	5702
4	0·5446	1·270	100	100	2·10	28·00	5703

$\Delta U_{Ave} = -5704 \pm 2$ cal g^{-1}.

[a] For symbols see Table 1.

The heats of combustion of the compounds ΔH_c, corresponding to reactions (1) and (2), were calculated

$$C_8H_6N_2Se(C) + \frac{21}{2}\,O_2(g) = 8\,CO_2(g) + 2\,H_2O\,(liq) + H_2SeO_3(aq) + N_2(g) \qquad (1)$$

$$C_{14}H_{14}Se_2(C) + \frac{37}{2}\,O_2(g) = 14\,CO_2(g) + 5\,H_2O\,(liq) + 2\,H_2SeO_3(aq) \qquad (2)$$

from the ΔU_c values of the respective experiments and are expressed in kcal mol^{-1} (1 cal = 4·1840 J). Using the standard values for the heats of formation of gaseous CO_2, liquid H_2O, and aqueous H_2SeO_3, −94·05, −68·31, and −122·4 kcal mol^{-1} respectively,[15] the corresponding heats of formation of the compounds in the crystalline and gaseous states were calculated. These values, and the heats of sublimation, are in Table 3.

The result of the vapour pressure measurements on 4-phenyl-1,2,3-selenadiazole is expressed by relationship (3) where P is in mmHg and T is in K.

$$\log_{10} P = 12{\cdot}3449 - 4735{\cdot}6/T \qquad (3)$$

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[14] M. R. Arshadi, unpublished data.

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The heat of formation of gaseous dibenzyl diselenide can be used to evaluate the carbon–selenium single bond energy. To do this, however, one has to find a value for the selenium–selenium bond energy. The enthalpies of formation given in ref. 16 for $SeCl_{2(g)}$, $Se_2Cl_{2(g)}$, $SeBr_{2(g)}$, $Se_2Br_{2(g)}$, and $Se_{(g)}$ yield an average value of 42·5 kcal mol^{-1} for this quantity. Using this value, the bond energy terms, the enthalpies of formation of $C_{(g)}$, and $H_{(g)}$ given by Cox and Pilcher,[17] the C–Se energy is 57·2 kcal mol^{-1}. This can be compared with the value of 61·6 kcal mol^{-1} which is obtained from the heat of formation of diethyl selenide.[17] The difference of approximately 4 kcal mol^{-1} can be attributed partly to the stabilization effect due to the replacement of CH_3 in the CH_3–CH_2–Se radical by a phenyl group. The same effect, but to a lesser extent (1·4 kcal mol^{-1}), can be observed for the sulphur analogue, as calculated from the enthalpies of formation of dibenzyl sulphide and benzyl ethyl sulphide.[17]

From the heat of formation of 4-phenyl-1,2,3-selenadiazole, the C–N and N–N energy terms, calculated from the enthalpies of formation of pyrazine and pyridazine respectively,[17] and the other thermochemical data outlined above, one calculates a value of 137 kcal mol^{-1} for the sum of the D(C–Se) and D(N–Se) energies. Unfortunately lack of information does not permit the accurate determination of the individual dissociation energies of these two bonds. However, approximate values can be obtained by the following argument. The average dissociation energies for the C–S bond in 2-methylthiophen and 2-methylthiazole, calculated from the heats of formation of these compounds[17] is 1·25 times the normal C–S single bond energy (87·3 *versus* 70 kcal mol^{-1}).[17] If one takes the value obtained above for the C–Se single bond energy and assumes that the factor 1·25 also applies to the 1,2,3-selenadiazole ring, one obtains values of 71 and 66 kcal mol^{-1} for D(Se–C) and D(Se–N) respectively.

TABLE 3

Thermochemical data at 25 °C (kcal mol^{-1})

Compound	ΔH^0_c [a]	ΔH^0_f (c)	ΔH^0(sublimation)	ΔH^0_f(gas)
4-Phenyl-1,2,3-selenadiazole	1097·0 ± 2	85·6 ± 2	22·5 ± 0·2	108·1 ± 2
Dibenzyl diselenide	1942·7 ± 0·8	40·8 ± 0·8	31·2 ± 0·2	72·0 ± 1

[a] The given uncertainties are twice the final overall standard deviation.

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[16] Selected Values of Chemical Thermodynamic Properties,' Circular 270—273, National Bureau of Standards, Washington.

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