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Abstract

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THERMOCHEMICAL DETERMINATION OF THE STABILIZATION ENERGY OF A QUASIAROMATIC RING WITH AN H-BOND

(Presented by Academician A. N. Terenin on 18 VIII 1964)

In works (^{1}, ^{2}) it was shown that in systems with π-electrons the formation of an H-bond can lead to the appearance of a quasiaromatic (coplanar, six-membered) ring owing to the generalization (“delocalization”) of its six electrons: four π-electrons of the C=C and C=O bonds, as well as two p-electrons of the oxygen atom of the O–H group.

The energy of formation of the quasiaromatic ring (b), in comparison with the ring without conjugation (a), will differ by the amount $E_\pi = E_b - E_a$, characterizing the stabilization energy of system (b), arising as a result of electron generalization in the system

chemical scheme: transition from structure (a) to structure (b) with E_π

On the basis of i.r. spectral data, in (^{2}) it was found that $E_a \approx 1.38$ kcal, and $E_b = 16.35$ kcal (for the enol isomer of dibenzoylmethane).

Consequently, the total stabilization energy of the ring with an H-bond (b) of the enol form of dibenzoylmethane is approximately equal to 16 kcal.

In the present work we report the results of determining the heats of combustion of the enol form of dibenzoylmethane (I) and its ethyl ether (II)

chemical structures of compounds (I) and (II)

Having data on the heats of combustion of these compounds, one can, by means of the corresponding calculation, estimate the stabilization energy of the quasiaromatic ring with an H-bond (the calculation is given below).

Dibenzoylmethane was obtained by condensation of the ethyl ester of benzoic acid and acetophenone under the action of sodium ethylate according to Claisen (^{3}). The substance was purified through the copper salt and distilled in vacuum. The fraction with boiling point 215–217°/18 mm was recrystallized from methanol and dried in vacuum (sample I). A small portion of the substance obtained was burned, and the remainder was again distilled in vacuum and then burned (sample II). The melting point of sample II was 77-78°. Literature data ( ): m.p. 77-78°.

Ethyl ester of the enolic form of dibenzoylmethane (ω-(α-ethoxybenzyl)-acetophenone) was obtained by the action of an alcoholic solution of caustic potash on benzylacetophenone dibromide ( ). The substance was purified by repeated distillation in vacuum. A fraction with b.p. 218–220° (18 mm) was collected, and part of the substance was burned (sample I). The greater part of the substance from this fraction was again distilled in vacuum (sample II). M.p. of sample II 77–78°. Literature data ( ): m.p. 77.5–78°.

On combustion of samples I and II, both in the case of dibenzoylmethane (I) and in the case of the ethyl ester of its enolic form (II), concordant results were obtained, which is relative evidence of the purity of the substances studied.

The calorimetric apparatus and the measurement procedure used ( ) make it possible, when pure substances are available, to determine their heats of combustion with an accuracy of 0.02%. The heat equivalent of the calorimetric system was determined by combustion of standard benzoic acid. The heat of combustion of one gram of it under standard conditions was taken as 6318.1 cal (weight in vacuo, 1 cal 4.1840 J). The temperature of the calorimeter was measured with a platinum resistance thermometer.

The amount of substance burned was determined in the calorimetric experiments from the amount of CO_2 found in the combustion products by the method proposed in ( ). The ratio of the found amount of CO_2 ($CO_{2\,\mathrm{found}}$) to the amount of CO_2 calculated ($CO_{2\,\mathrm{calc}}$) from the weighed sample of substance taken for combustion can to a certain extent serve as a criterion of the purity of the substance and the completeness of the combustion reaction. Table 1 gives the experimental results for the determination of the heats of combustion of substances (I) and (II). In Table 1 the following notation is adopted: q_{Fe} –the amount of heat

Table 1

No. of experiments	Sample	Sample weight (weight in vacuo)	$CO_{2\,\mathrm{found}}/CO_{2\,\mathrm{calc}}$	Temperature rise in experiment, ΔR (in Ohms)	q_{Fe}	$q_{\mathrm{HNO_3}}$	$-\Delta U_B^{25}$, cal/g
1	I	0.37800	1.0009	0.19640	8.60	1.49	7880.2
2	I	0.52297	1.0003	0.27114	8.46	3.00	7877.8
3	II	0.54765	1.0004	0.28382	8.89	2.02	7876.0
4	II	0.49899	1.0000	0.25867	8.30	2.10	7880.4
5	II	0.46301	1.0006	0.24021	8.66	2.52	7878.7

No. of experiments	Sample	Sample weight (weight in vacuo)	$CO_{2\,found}/CO_{2\,calc}$	Temperature rise in experiment, ΔR (in Ohms)	q_{Fe}	q_{HNO_3}	$-\Delta U_B^{25}$, cal/g
6	II	0.51187	1.0001	0.26548	8.98	2.52	7881.5
Average			1.0004± 0.083				7879.1+ 1.6
1	I	0.43165	0.9987	0.23598	7.96	2.34	8320.0
2	I	0.45850	0.9987	0.25069	8.30	2.40	8321.3
3	II	0.43255	0.9987	0.23639	8.75	2.22	8315.5
4	II	0.41083	0.9999	0.22494	7.89	2.04	8321.8
5	II	0.40958	0.9993	0.22425	9.84	2.10	8322.1
6	II	0.40619	0.9993	0.22229	8.16	1.99	8322.8
7	II	0.40219	0.9992	0.22017	8.32	2.27	8324.2
8	II	0.37461	1.0004	0.20519	8.43	1.54	8319.0
Average			0.9993± 0.035				8320.8+ 1.2

* $-\Delta U_B^{25} = 1766.93$ kcal/mol; $-\Delta U_R^{25} = 1765.71$ kcal/mol; $-\Delta H_{\text{comb}}^{25} = 1766.9 \pm 0.4$ kcal/mol.

** $-\Delta U_B^{25} = 2099.47$ kcal/mol; $-\Delta U_R^{25} = 2098.11$ kcal/mol; $-\Delta H_{\text{comb}}^{25} = 2099.9 \pm 0.4$ kcal/mol.

···calories released upon combustion of the iron wire used to ignite the substance. The heat of combustion of 1 g of it was taken to be 1793 cal. q_{HNO_3} is the amount of heat released in the formation of nitric acid in the bomb from $H_2O(l)$, $O_2(g)$, $N_2(g)$. The heat of formation of an aqueous solution of HNO_3 was taken to be 13.81 kcal/mole. $\Delta U_{\mathrm{B}}^{25}$ is the isothermal heat of combustion, i.e., the change in internal energy upon combustion of one gram or one mole of substance under the conditions corresponding to the process taking place in the bomb. $\Delta U_{\mathrm{R}}^{25}$ is the change in internal energy upon combustion of a mole of substance at initial and final pressures equal to 1 atm. The quantity $\Delta U_{\mathrm{R}}^{25}$ was calculated from the experimentally obtained value $\Delta U_{\mathrm{B}}^{25}$ by introducing the Washburn correction. $\Delta H_{\text{comb}}^{25}$ is the change in enthalpy upon combustion of a mole of substance at a temperature of 25° and a pressure of 1 atm.

The error of the results is given as twice the standard error of the mean result ($2S$). $S = \sqrt{\Sigma\Delta^2/n(n-1)}$, where Δ is the deviation of the result of each experiment from the mean value, and n is the number of experiments.

Substance (II) can be obtained from substance (I) by carrying out the following processes: a) rupture of the "hydrogen bond" in the quasiaromatic ring; b) replacement of the H atom in the hydroxyl group of compound (I) by the C_2H_5

group.

Then $\Delta H_1 + \Delta H_a + \Delta H_b = \Delta H_2$, where ΔH_1 and ΔH_2 are the heats of combustion of substances (I) and (II), respectively; ΔH_a is the enthalpy of formation of the quasiaromatic ring with an H bond; ΔH_b is the enthalpy change associated with replacement of the hydrogen atom by a C_2H_5 group.

The quantities ΔH_1 and ΔH_2 are known; the quantity ΔH_b can be estimated from the increments of the corresponding bonds in heats of combustion, which are given in the work of Lovering and Laidler [10]:

$$-\Delta H_a = \Delta H_1 + \Delta H_b - \Delta H_2 = -1766.9 - 323.7 + 2099.9 = 9.3 \text{ kcal.} \qquad (1)$$

If one takes into account that the thermochemical value of the stabilization energy of the ring ΔH_a differs from the spectroscopic value by the stabilization energy of the conjugated system

$$> \mathrm{C} = \mathrm{C} - \mathrm{C} = \mathrm{O},$$

approximately equal to 5-6 kcal, then we can state a good agreement between the experimental results obtained by the two methods.

Analysis of the data on the keto-enol equilibrium of acetylacetone also leads to a value for the stabilization energy of the quasiaromatic ring with an H bond approximately equal to 9 kcal [11].

Thus, the thermochemical value obtained for the stabilization energy of the quasiaromatic ring with an H bond, approximately equal to 9 kcal, is in agreement with other data.

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Note: Figure translations are in progress. See original paper for figures.

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