ion and 8-hydroxyquinoline. Further measurements of this kind on other metallo-organic compounds should permit a generalization concerning the state of the soluble material.

The Solubility of Magnesium Oxinate

Since the concentration of magnesium oxinate in the *p*H 10 buffer is so low (Fig. 3), it is necessary to measure the absorption in the region of 250 mμ in order to estimate the solubility. It was found that Beer's law was obeyed up to 9 mg. of 8-hydroxyquinoline per liter of buffer at 250 *m*. As is evident from Fig. 3, at 250 mμ a correction is necessary when using Beer's law on the metallo-organic solution. This factor was estimated to be 3, and the resulting solubility was calculated to be 1×10^{-5} mole of magnesium oxinate per liter of buffer. This value is in fair agreement with the value 1.9×10^{-6} found by Stone and Furman[10] using the polarographic method, and probably has an undeterminable error due to the estimated factor.

Summary

The effect of *p*H on the ultraviolet absorption of aqueous and alcoholic solutions of 8-hydroxyquinoline has been investigated. The acid ionization constant has been determined by solubility and spectroscopic methods and found to be 4.2×10^{-11}. The nature of the soluble magnesium oxinate has been investigated through the ultraviolet absorption and the solubility has been measured in ammonia buffers of *p*H 10.

(10) K. G. Stone and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 596 (1944).

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[CONTRIBUTION NO. 1098 FROM GATES AND CRELLIN LABORATORIES OF CHEMISTRY AND KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Heats of Combustion of Cyclopentane, Cyclohexane, Cycloheptane and Cyclooctane

BY RALPH SPITZER[1] AND HUGH M. HUFFMAN[2]

Introduction

Information about the structure and energy of cyclic hydrocarbons is of considerable interest in connection with the problem of restricted rotation about the carbon–carbon single bond. According to the classic strain theory, both cyclopentane in the planar configuration and cyclohexane in either the chair or the boat form should be essentially strain-free because the bond angles are almost or exactly tetrahedral.

With the discovery of a force hindering rotation about carbon–carbon single bonds in open chain paraffins[3] it gradually became apparent[4] that the same force should operate in cycloparaffins with the result that either cyclopentane or cyclohexane should be destabilized depending on whether the restricting force is repulsive or attractive. In fact, one of the most useful theoretical results of this research is to help make the decision in favor of repulsion.

At the time this work was undertaken (1939–1940) there were no reliable heats of combustion on cycloparaffins and it was impossible to interpret the accurate work of Kistiakowsky and coworkers[4] on heats of hydrogenation of cycloölefins. Recently, however, making use of the unpublished results of this work and other data, Pitzer[5] has correlated the energy data on cyclic hydrocarbons on the basis of the concept of a non-planar cyclopentane molecule, first suggested by Aston,[6] *et al.*

Experimental

The Calorimeter.—The method and calorimetric system, which is of the non-adiabatic type, have been previously described.[7] The essential differences in the present technique were that a Parr double valve bomb was used, instead of the single valve bomb, to minimize gas leakage and the amount of reaction was determined both from the mass of the sample and, in some experiments, from measurement of carbon dioxide evolved in the combustion.

The mass of the sample was determined as the difference of two masses, the initial mass of filled ampoule plus platinum crucible and the final mass of glass residue plus platinum crucible. In the earlier experiments (with cyclopentane) it was observed that the final mass depended on the treatment of the glass residue. The mass determined after heating the crucible and contents on a hot plate was greater by as much as 0.4 mg. than found after igniting. This may have been due to some of the sample or products of combustion having been occluded in the glass residue. Because of the uncertainty in regard to the mass of the sample the results of the combustions of cyclopentane and cyclohexane based on the mass determination were given no weight in arriving at the final value, which is based solely on the carbon dioxide determination.

In later experiments on cycloheptane and cyclooctane, in which we used a 20- or 30-g. crucible in place of the 3-g. crucible used earlier, the weighings were quite reproducible and so analyses were run only occasionally.

The combustible impurities in the oxygen were removed by slow passage through a furnace containing vanadium pentoxide catalyst at 400° and then through Ascarite and Dehydrite absorbers to remove water and carbon dioxide.

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(3) Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

(4) Conn, Kistiakowsky and Smith, THIS JOURNAL, **61**, 1868 (1939). This possibility was first suggested to them by Schomaker.

(5) Pitzer, *Science*, **101**, 672 (1945).

(6) Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941).

(7) Huffman and Ellis, *ibid.*, **51**, 41 (1935).

TABLE I

EXPERIMENTAL DATA AT 25°

Subst.	No. of runs	No. dir. weighings	No. of analyses	Av. $-\Delta U_B/m$ from direct weighing	Av. $-\Delta U_B/m$ from analyses	Final average $-\Delta U_B/m$
C_5H_{10}	6	6	6	11,193.9 ± 2.8[a]	11,197.9 ± 3.3	11,197.9 ± 3.3
C_6H_{12}	6	4	6	11,107.2 ± 4.0[a]	11,110.0 ± 1.4	11,110.0 ± 1.4
C_7H_{14}	10	9	2			11,175.8 ± 2.3
C_8H_{16}	5	5	1			11,196.0 ± 2.1

[a] Not included in final average. See text for explanation. Uncertainties given are mean deviations.

TABLE II

SUMMARY OF DERIVED DATA AT 25°[a]

Subst.	Mol. wt.	Density	$-\Delta U_B$, kcal./mole	$-\Delta U_R$, kcal./mole	$-\Delta H_R$, kcal./mole	$-\Delta H_f^0$, kcal./mole	$\frac{d\Delta U_R}{dt}$[b], cal./mole/deg.
C_5H_{10}	70.130	0.7460	785.31 ± 0.30	785.14 ± 0.30	786.62 ± 0.30	25.23 ± 0.42	56
C_6H_{12}	84.156	.7781	934.97 ± .24	934.76 ± .24	936.53 ± .24	37.68 ± .42	67
C_7H_{14}	98.182	.8100	1097.26 ± .40	1097.02 ± .40	1099.09 ± .40	37.73 ± .56	78
C_8H_{16}	112.208	.8304	1256.28 ± .38	1255.99 ± .38	1258.35 ± .38	40.60 ± .60	89

[a] Errors are "uncertainty interval." [b] Temperature coefficient obtained from approximate heat capacity data and may be applied only over a range of 5 to 10°.

After the combustion, the contents of the bomb were discharged at about 200 cc. per minute through an absorption train consisting of a drying tube followed by three similar Turner absorbers each containing Ascarite, Dehydrite and phosphorus pentoxide. The third absorber was used as a tare and the second absorber which served as a guard gained weight only rarely. The bomb was flushed three times with pure oxygen.

Occasional tests were made for completeness of combustion by connecting to the absorbing train an apparatus similar to that described by Cook[8] for the colorimetric determination of carbon monoxide by hemoglobin. In only one run was any carbon monoxide found, and in that experiment evidences of spattering were obvious. In check experiments 0.2 cc. of carbon monoxide was easily detected.

The precision of the analytical method is shown by analyses made during calibration with benzoic acid. In 13 runs the ratio of carbon dioxide found to carbon dioxide calculated from the mass of benzoic acid was 0.99997 with a mean deviation of ±0.00008 and an extreme deviation of −0.00022.

Materials.—Professor G. B. Kistiakowsky of Harvard was kind enough to supply us with pure samples which were prepared from the end-products of his hydrogenation experiments by careful fractionation and were then sealed in bulbs under vacuum. Cyclohexane (b), which was originally prepared by the Shell Development Co., was supplied to us by Professor G. S. Parks of Stanford University. The physical constants of the samples, as determined by Kistiakowsky [except cyclohexane (b)] were, respectively, for cyclopentane, cyclohexane, cyclohexane (b), cycloheptane, and cycloöctane: melting points—not given, 6.42, 6.35, −12.2 and 14.5; $n^{20}D$ 1.4060, 1.4260, not given, 1.4446, and 1.4587.

Calibration, Units, etc.—The energy equivalent of the calorimeter was determined frequently by burning Bureau of Standards benzoic acid, samples 39e and 39f[9] having for its isothermal heat of combustion per gram under standard conditions at 25° the value of $-\Delta U_B/m = 26{,}428$ N. B. S. international joules. Under the conditions of our experiments (volume of bomb 358 cc., 0.1 g. water, oxygen pressure of 30 atm. and weight of benzoic acid about 1.023 g.) $-\Delta U_B/m$ is 26,425 international joules. Results are expressed in defined conventional calories (one defined cal. = 4.1833 int. joules).

We have taken the values of the heats of formation of liquid water and gaseous carbon dioxide at 25° to be 68,317 and 94,052 cal. per mole, respectively. Correction was made for nitric acid formed in the combustion using 14,340 cal. per mole for its heat of formation at constant volume from water, oxygen and nitrogen. Our titrations with brom cresol green as indicator were not influenced by dissolved carbon dioxide. All weights have been reduced to vacuum standard.

Presentation of the Data

Table I is a summary of the results. As mentioned above, the direct weighing values were not used in making the final averages for cyclopentane and cyclohexane. The uncertainties given in Table I are mean deviations.

In Table II are given the calculated quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$ and $-\Delta H_f^0$. These quantities all refer to one mole at 25°. $-\Delta U_B$ is the actual heat evolved, corrected to 25°, $-\Delta U_R$ is the heat evolved when the reaction occurs with all reactants and products in their standard states, $-\Delta H_R$ is the change in heat content at one atmosphere assuming the perfect gas laws to hold for oxygen and carbon and $-\Delta H_f^0$ is the standard heat of formation from the elements at one atmosphere. The uncertainties given in Table II correspond to the "uncertainty interval" of Rossini[10] and include an estimate of the uncertainty in the value of the heat of combustion of benzoic acid (0.01%) and in the heats of formation of H_2O and CO_2 (0.015 and 0.011%).

Table III presents the heats of combustion per mole and per CH_2 group of the cycloparaffins in the gaseous state.

Discussion

Table III shows that cyclohexane is roughly one kcal. per mole of CH_2 more stable than any of the other cycloparaffins. This result can be shown to be in semi-quantitative accord with the proposal that a potential similar to that restricting rotation in ethane acts in cycloparaffins. It is

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(8) Cook, *Ind. Eng. Chem., Anal. Ed.*, **12**, 661 (1940).

(9) Jessup, *J. Res. Natl. Bur. Standards*, **29**, 247 (1942).

(10) Rossini, *J. Wash. Acad. Sci.*, **29**, 440 (1939).

TABLE III

HEATS OF COMBUSTION OF CYCLOPARAFFINS IN THE GASEOUS STATE AT 25° IN KILOCALORIES PER MOLE

Substance	$-\Delta H_R$ (liq.)	$\Delta H_{vap.}$	$-\Delta H_R$ (gas)	$-\Delta H_R/n$ (gas)[b]
C_5H_{10}	786.6	7.0	793.6	158.7
C_6H_{12}	936.5	8.0	944.5	157.4
C_7H_{14}	1099.1	8.9[a]	1108.0	158.3
C_8H_{16}	1258.4	10.4[a]	1268.8	158.6

[a] Estimated by Trouton's rule. [b] n = number of CH_2 groups per molecule.

immediately obvious that the restricting force is repulsion between hydrogen atoms, otherwise, cyclopentane with hydrogen atoms on adjacent carbon atoms as close as possible would be the most stable cycloparaffin.

In order to calculate the expected difference in energy between the cycloparaffins we assume, as was first suggested by Schomaker and later in more detail by Pitzer[5] that cyclohexane, in the chair form, is the most stable cycloparaffin because the adjacent CH_2 groups are rotated by 60° with respect to each other. This configuration is the most stable in ethane and other straight chain hydrocarbons and it is reasonable to expect it to be the most stable in cycloparaffins.

Other cycloparaffins will be less stable than cyclohexane for one or both of two reasons: the C-C-C angles will not be exactly tetrahedral, leading to angular strain, or the angle of rotation of the CH_2 groups about the C-C bond will not be exactly 60°, leading to torsional strain.

Pitzer[5] calculated the equilibrium configuration of cyclopentane by moving one or two atoms out of the plane of the ring and computing the angular and torsional strains. Using for the torsional potential energy

$$V = \frac{V_0}{2}(1 + \cos 3\gamma) \text{ kcal. per mole}; \quad V_0 = 2.8 \qquad (1)$$

where γ is the torsional angle and using 6×10^{-12} ergs per radian^2 for A, the potential constant for deformation of the C-C-C angle, α, (Potential energy = $^1/_2\ A\ \alpha^2$), he obtained an equilibrium position which had energy 9.2 kcal. higher than cyclohexane. If we use the more accurate value of 10×10^{-12} for the angle potential constant, this value is raised to 10.7 kcal. compared with the experimental value of 6.5. A similar calculation for cyclooöctane leads to a destabilization of about 13.9 kcal. instead of 9.6 as observed. Inspection of Pitzer's table in reference 5 shows that (particularly if the C-C-C angle potential constant is raised) his calculated strain energies are always higher than those observed. This suggests either that V_0 in equation (1) should be lowered to about 1.9 for cycloparaffins or that the actual shape of the function should be changed.

Using another term in the Fourier expansion of V improves the agreement between experiment and theory.

$$V = \frac{V_0}{2}\left(3/4 + \cos 3\gamma + \frac{\cos 6\gamma}{4}\right); \quad V_0 = 2.8 \qquad (2)$$

The potential function leads to 8.2 and 9.6 kcal. destabilization for cyclopentane and cyclooöctane, respectively. A similar calculation cannot be made for cycloheptane because of its lack of symmetry but inspection of atomic models shows no great qualitative difference.

The only models of cyclooöctane which were investigated had either tetrahedral bond angles and vertical planes of symmetry, or deformed bond angles and a four-fold axis in addition to the planes of symmetry. The model with deformed angles had its minimum energy at an angle very close to tetrahedral and the minimum energy was practically identical with that calculated for the less symmetrical models. It is probable, therefore, that the neglect of models with even less symmetry does not lead to serious error in the calculated energy.

It should be emphasized that while these simple calculations do not prove the validity of the potential function (2) they do indicate strongly that the potential function (1) is not adequate for cycloparaffins.

Comparison with Other Work.—Moore, *et al.*,[11] obtained 934.96 kcal. per mole (corrected for change in heat of combustion of benzoic acid) for $-\Delta U_R$ of cyclohexane, in agreement with our result within experimental error. The Bureau of standards[12] obtained 786.54 and 936.88 for $-\Delta H_R$ of cyclopentane and cyclohexane, also well within our combined experimental errors. The agreement among three different laboratories within the small experimental error claimed by all is most gratifying.

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Summary

1. The heats of combustion and formation at 25° of cyclopentane, cyclohexane, cycloheptane and cyclooöctane are presented.

2. The heats of combustion are interpreted on the assumption that cyclohexane in the chair form has no strain energy while the other cycloparaffins are strained either by having their C-C-C angles different from tetrahedral or by not having adjacent CH_2 groups rotated 60° with respect to each other.

3. It is shown that the function $V = V_0 - (1 + \cos 3\gamma)/2$ with $V_0 = 2.8$ kcal. as the potential restricting internal rotation will not explain the experimental results.

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(11) Moore, Renquist and Parks, THIS JOURNAL, **62**, 505 (1940).

(12) Johnson, Prosen and Rossini, *Bur. Standards J. Res.*, **36**, 463 (1946).