M. P. KOZINA, M. Yu. LUKINA, N. D. ZUBAREVA, I. L. SAFONOVA,

S. M. SKURATOV, and Academician B. A. KAZANSKII

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Abstract

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M. P. KOZINA, M. Yu. LUKINA, N. D. ZUBAREVA, I. L. SAFONOVA, S. M. SKURATOV, and Academician B. A. KAZANSKII

HEATS OF COMBUSTION OF CERTAIN PHENYLCYCLOPROPANES

It is known that, in some chemical and physical properties, hydrocarbons of the cyclopropane series differ sharply from other cycloparaffins and resemble olefins. Like a double bond, a three-membered ring situated adjacent to an unsaturated grouping gives systems resembling conjugated ones ([1]).

It has proved impossible to explain the anomalous properties of cyclopropane from the standpoint of classical ideas about its structure; therefore its structure has repeatedly been discussed and up to the present remains a subject of debate. Consequently, the accumulation of experimental facts capable of confirming one or another point of view concerning the structure of cyclopropane is an important and interesting task. Much has already been done in this direction. Thus, confirmation of the most fundamental hypothesis, according to which the hybridization of the carbon atoms in cyclopropane is close to trigonal ([2–4]), is provided by work on calculating the force constant of C–H bonds ([5]), on measuring the H—C—H angle in cyclopropane ([6]), on studying the Raman spectra of conjugated hydrocarbons of this series ([7]), their reactivity ([8–11]), and others. In this connection, the study of the heats of combustion of cyclopropane hydrocarbons may be of considerable interest, especially since very little has so far been done in this direction ([12,13]).

In the present work we report the results of determining the heats of combustion of phenylcyclopropane, 1,1-diphenylcyclopropane, and two stereoisomeric 1,2-diphenylcyclopropanes. The synthesis of the hydrocarbons, their Raman spectra, and the study of their reactivity in the catalytic hydrogenation reaction were published earlier ([7–10]). These studies showed that in phenylcyclopropane and in the 1,2-diphenylcyclopropanes there is conjugation between the three-membered ring and the phenyl rings, whereas in 1,1-diphenylcyclopropane it is practically absent. The reasons for this phenomenon are discussed in those works.

It is known that the conjugation effect is also reflected in the heats of combustion of substances. Thus, for measured dienes having different arrangements of the double bonds, the lowest heats of combustion are observed for conjugated systems. It should be borne in mind that the magnitudes of the heats of combustion cannot by themselves give an unambiguous indication that precisely a

conjugation effect is present in the corresponding compounds, since other structural features—for example, steric interactions—may also change the magnitude of the heat of combustion. However, taken together with other facts (Raman spectra of light, behavior of substances in chemical reactions), the heats of combustion can be used to evaluate the conjugation effect in the substances under investigation.

The substances were burned in a calorimetric bomb, into which they were placed in sealed thin-walled glass ampoules. The method for measuring heats of combustion has been described previously ([14]). Table 1 gives the physico-chemical

chemical constants of all the above substances, the enthalpy changes (ΔH_c^{25}) in their combustion reactions, and the enthalpies of formation (ΔH_f^{25}), in kilocalories per mole (1 cal = 4.1840 absolute joules). The data refer to the liquid state of the substances (for cis-1,2-diphenylcyclopropane, to the supercooled state). The magnitudes of the errors are given as twice the standard deviation from the mean result.

The enthalpies of formation of these compounds from the elements at 25° were calculated on the basis of the experimental data obtained for their enthalpies of combustion and the known enthalpies of formation of (ΔH_f^{25})CO_2 (g) and H_2O (l), which were taken to be, respectively, 94.052 and 68.317 kcal/mole ([12]).

Table 1

Compound	B.p., °C	n_D^{20}	d_4^{20}	$-\Delta H_c^{25}$, kcal/mole	ΔH_f^{25}, kcal/mole	$\frac{CO_2 \text{ found}}{CO_2 \text{ calc.}}$
Phenylcyclopropane		1.5337	0.9415	1212.0 ± 0.2	19.0±0.2	0.9997
Trans-1,2-diphenylcyclopropane	15.3	1.5997	1.0346	1928.7 ± 0.6	39.7±0.6	1.0000 ± 0.0001
Cis-1,2-diphenylcyclopropane	36.7	1.5887	1.0290	1951.7 ± 0.2	42.7±0.2	1.0002 ± 0.0001
1,1-Diphenylcyclopropane		1.5878	1.0330	1933.3 ± 0.8	44.3±0.8	1.0004 ± 0.0001

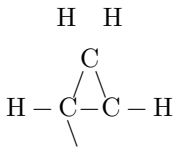
As is evident from Table 1, the ratio of the amount of carbon dioxide found analytically (absorption of CO_2 by Ascarite) in the combustion products to the amount of CO_2 calculated from the weighed sample of substance taken for combustion is close to unity, which is a criterion of the completeness of combustion and of the purity of the preparations used.

The results obtained make it possible to draw certain conclusions concerning the magnitude of the conjugation effect in these substances.

Estimation of the magnitude of conjugation in phenylcyclopropane. The magnitude of conjugation was obtained as the difference between the experimentally found heat of combustion of phenylcyclopropane and that calculated on the assumption that conjugation is absent. The calculation was carried out by summing the increments (contributions) of the phenyl and cyclopropyl radicals. The increment of the phenyl radical can easily be found from the values of the heats of combustion of various monoalkylbenzenes ([12]) and proves to be 749.7 ± 0.1 kcal/mole. The increment of the cyclopropyl radical can be found from the reliably established, recently determined heats of combustion of 1,1-dimethyl-2-alkylcyclopropanes ([13]), by subtracting from the experimental values of the heats of combustion the increments attributable: (a) to the alkyl radical and (b) to the two methyl groups attached to one carbon atom (the latter value proves to be very close whether it is estimated from 1,1-dimethylcycloalkanes or from 2,2- or 3,3-dimethylalkanes) ([12]). The heat-of-combustion increment of the cyclopropyl radical in this calculation proves to be 464.1 ± 0.5 kcal/mole. Thus, the value of the heat of combustion of phenylcyclopropane calculated from increments is 1213.8 ± 0.6 kcal/mole. The difference between the calculated heat of combustion (1213.8 kcal/mole) and the experimentally found value (1212.0 ± 0.2 kcal/mole) is 1.8 ± 0.8 kcal/mole and may be interpreted as a quantity characterizing conjugation in phenylcyclopropane. The result obtained shows that conjugation in this case is weaker than in conjugated dienes (about 6 kcal/mole).

Estimation of the relative conjugation effect in diphenylcyclopropanes. A calculation analogous to that indicated above cannot be carried out for disubstituted phenylcyclopropanes, since ···

there are no experimental data that make it possible to determine the increment of the heat of combustion of the radical



(C_3H_4)

Therefore, for the diphenylcyclopropanes it was necessary to confine ourselves only to a comparative estimate of the conjugation effect, i.e., to a comparison of their heats of combustion and heats of formation. The lowest heat of combustion is possessed by trans-1,2-diphenylcyclopropane, and the highest by 1,1-diphenylcyclopropane. The difference in the heats of formation between them is 4.6 kcal/mole; the difference in the heats of combustion between the cis- and trans-1,2-diphenylcyclopropanes is 3.0 kcal/mole. Consequently, the greatest conjugation is observed in trans-1,2-diphenylcyclopropane. This is in complete agreement with the conclusions regarding the degree of conjugation in these compounds drawn on the basis of conformational analysis of them and of their light-scattering combination spectra (7).

Moscow State University
named after M. V. Lomonosov

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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