PHYSICAL CHEMISTRY

S. M. SKURATOV, A. A. STREPICHEEV, S. M. SHTEHER, and A. V. VOLOKHINA

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

S. M. SKURATOV, A. A. STREPICHEEV, S. M. SHTEHER, and A. V. VOLOKHINA

ON THE ENTHALPY OF POLYMERIZATION OF CYCLIC FORMALS

(Presented by Academician A. A. Balandin, 25 V 1957)

The polymerization reaction of heterocyclic compounds is of undoubted interest from both the theoretical and the practical points of view. Many examples are known of sharp differences in reactivity in general and, in particular, in the ability to polymerize, among heterocyclic compounds of one and the same homologous series, depending on the number of members in the ring. Usually the 5- and 6-membered rings of each series prove to be considerably less reactive than the 7- and 8-membered rings of the same series under the same reaction conditions (rings with a larger number of members have scarcely been investigated).

Since both the attacking agent and the hetero bond being attacked remain formally the same in analogous reactions for all heterocycles of a given series, the causes of the sharp difference in the reactivity of individual representatives of the series should be sought in thermodynamics.

An attempt made by one of us (^1) at a general consideration of the polymerization reactions of heterocyclic compounds from the standpoint of thermodynamics could not go beyond establishing several general propositions; their development requires a large amount of experimental material, which is still lacking.

Recently the question of the change in isobaric potential in the polymerization reactions of cyclic compounds was examined in detail by Dainton and coauthors (^2). Using reliable experimental data and supplementing missing quantities by extrapolation with the aid of semiempirical equations, these authors calculated the values of ΔH, ΔS, and ΔZ for cycloalkanes (up to cyclooctane inclusive) and for polymethylene. Comparing the quantities obtained in these calculations, they could easily calculate the change in these functions for the hypothetical reaction of polymerization of cyclane (l) —polymethylene (l) at standard temperature.

However, the values of the standard entropy of cycloheptane and cyclooctane obtained by extrapolation in work (^2) differ substantially (by up to 9 kcal/mole· degree) from those determined experimentally by Finke and coauthors (^3).

Attempts to extend the conclusions obtained for cyclanes even to the simplest series of heterocyclic compounds (^4) lead to still less reliable results. In this field experimental material is almost entirely lacking, and its accumulation is highly necessary.

In a series of our works we set ourselves the task of obtaining experimental material on the enthalpy change in the process of polymerization of various series of heterocyclic compounds, mainly with a number of ring members from 5 to 8. The complete absence of data on the entropy of these compounds and, correspondingly,

···of the corresponding linear polymers makes it impossible to calculate the values of ΔZ for the polymerization reactions. However, we believe that data on enthalpy changes in these processes will undoubtedly also prove useful for explaining the differences in reactivity of heterocyclic compounds of this series.

In one of our papers (^{5}) we showed that, for a series of lactones (with the number of ring members from 5 to 8), the enthalpy of cyclization, i.e., the enthalpy change in the polymerization reaction, can qualitatively explain the difference in their ability to undergo this reaction.

After the equilibrium in the polymerization reactions of cyclic formals (with the number of ring members from 5 to 8) (^{6}) had been studied in detail, it was of undoubted interest to investigate the heats of combustion of these compounds and, by comparing the experimentally found heat of combustion with that calculated for the given compound from the increments of the atomic groups entering into it, to calculate the magnitude of the enthalpy of cyclization (as was done in (^{5}) for lactones). The method of carrying out such a calculation and its validity were discussed in (^{5}).

In addition, it was of interest to compare the magnitudes of the enthalpy of cyclization in the series of formals with the corresponding values for cycloalkanes, for which reliable data on heats of combustion, referred to the gaseous state, are available in the literature (^{7},^{8}) (in the case of lactones (^{5}) such a comparison could not be made because of the absence of reliable data on their heats of fusion or sublimation).

The procedure used for determining the heat of combustion, described by us earlier (^{9}), makes it possible to obtain results with an accuracy of 0.02–0.03%. All the objects investigated in the present work are liquids at room temperature; they were burned in a calorimetric bomb in sealed thin-walled glass ampoules. The physical constants of the substances studied and the experimental data obtained by us are given in Table 1.

Table 1

Compound	Formula	B.p., °C	n_D^{20}	d_4^{20}	$-\Delta H_c^{20}$, kcal/mole (liq.)	Heat of vaporization, kcal/mole	ΔH_c^{20}, kcal/mole (gas)
Ethylene formal	$\begin{array}{l} CH_2-O \\ \vert \\ CH_2-O \quad CH_2 \end{array}$	76.0	1.4002	1.0595	407.6	8.3	415.9
Trimethylene formal	$\begin{array}{l} CH_2-O \\ CH_2 \quad CH_2 \\ CH_2-O \end{array}$	103.5–104	1.4183	1.0319	557.4	9.4	566.8
Tetramethylene formal	$\begin{array}{l} CH_2-CH_2-O \\ \vert \\ CH_2-CH_2-O \quad CH_2 \end{array}$	117–117.5	1.4307	1.0023	719.4	9.8	729.2
Pentamethylene formal	$\begin{array}{l} CH_2-CH_2-O \\ CH_2 \quad CH_2 \\ CH_2-CH_2-O \end{array}$	134	1.4383	0.9886	884.0	10.7	894.7
Dibutyl formal	$C_4H_9-O-CH_2-O-C_4H_9$	180	1.4060	0.8340	1398.7	13.7	1412.4

The values of ΔH_c^{20} are the enthalpy changes, expressed in $kcal_{15^\circ}$, for isothermal (at 20°) combustion of the substances studied in the liquid state at a pressure of 1 atm and with the formation, as reaction products, of gaseous CO_2 and liquid H_2O.

The heats of vaporization of the substances studied at 20°, given in Table 1, were calculated by us with an accuracy of up to 1–2% from semiempirical relations ([10]).

The last column gives the heats of combustion at 20° referred to the gaseous state of the substances.

From the data obtained, the enthalpies of cyclization were calculated as the differences between the heats of combustion of the corresponding compounds in the gaseous state and the heats of combustion calculated for them additively from the increments of the corresponding groups. As the increment of the heat of combustion for the $-CH_2-$group, the value known from the literature for alkanes, 157.4 kcal, was adopted ([11]). The increment of the heat of combustion for the $-O-CH_2-O-$group was determined by comparing the heat of combustion of dibutyl formal found by us with the heat of combustion of normal octane ([11]): it proved to be equal to 94.9 kcal.

Table 2

Enthalpy of cyclization for hydrocarbons and formals (kcal/mole)

Number of ring members	Hydrocarbon	Formal
5	6.6	6.2
6	0.1	0.0
7	6.2	4.7
8	9.6	12.8

Table 2 gives the enthalpies of cyclization of cyclic hydrocarbons (7,8) and formals.

As is seen from Table 2, for both series of compounds the minimum enthalpy of cyclization is found for the 6-membered rings, and the maximum for the 8-membered rings.

The values of the enthalpy of cyclization for equal-membered alkanes and formals (except for the 8-membered ones) are close. It should be noted that the excess enthalpy of cyclic formals, just as of alkanes, decreases in the series 8 > 5 > 7 > 6. Quantitative studies of the polymer monomer equilibrium for cyclic formals (6) showed that their tendency toward polymerization depends on the number of members in the ring and decreases in the series 8 > 7 > 5 > 6, while 5- and 7-membered rings differ little in their ability to polymerize.

Comparing these data with the values of the enthalpy of cyclization obtained in the present work, it may be concluded that this quantity makes it possible to estimate the relative ability toward polymerization for compounds of the given series.

Moscow State University
named after M. V. Lomonosov

Received
16 V 1957

CITED LITERATURE

[1] A. A. Strepikheev, Dissertation, VNIIV, 1950.
[2] F. S. Dainton, T. R. E. Delvin, P. A. Small, Trans. Farad. Soc., **51**, 1710 (1955).
[3] H. L. Finke, D. W. Scott et al. J. Am. Chem. Soc. **78**, 5469 (1956).
[4] P. A. Small, Trans. Farad. Soc., **51**, 717 (1955).
[5] A. A. Strepikheev, S. M. Skuratov et al., DAN **102**, No. 1, 105 (1955).
[6] A. A. Strepikheev, A. V. Volokhina, DAN **99**, No. 3, 407 (1954).
[7] R. Spitzer, H. Huffman, J. Am. Chem. Soc., **69**, 211 (1947).
[8] Sj. Kaarsemaker, J. Coops, Rec. Trav. Chim., **71**, No. 2, 261 (1952).

[9] S. M. Skuratov, A. A. Strepikheev et al., Scientific Notes of Moscow State University, **164**, 73 (1953).
[10] W. Heukelom, Rec. Trav. Chim., **68**, 661 (1949).
[11] E. I. Prosen, F. D. Rossini, J. Res. Nat. Bur. Stand., **34**, 263 (1945).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.