I. B. RABINOVICH, V. I. TELNOI, L. M. TERMAN, A. S. KIRILLOVA

and Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV

1962

SovietRxiv

Abstract

Full Text

I. B. RABINOVICH, V. I. TELNOI, L. M. TERMAN, A. S. KIRILLOVA and Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV

HEATS OF DECOMPOSITION AND FORMATION OF DICYCLOHEXYL AND DIMETHYL PEROXYDICARBONATE

The thermal effects of the decomposition of organic peroxides are of independent interest, and can also be used as a criterion for judging the overall equations of these processes from the heats of formation of the reactants, or for calculating the thermochemical characteristics of the latter when the equations are known. Nevertheless, there are no experimental data in the literature on the heats of decomposition of the indicated substances. There are only a few values ([1]) for the hydroperoxides of ethyl and propyl, calculated thermochemically; moreover, the value obtained for the first of these compounds is unreliable, since in its calculation the heat of combustion of a product containing only 90% peroxide was used.

In the present work, the heats of decomposition of dicyclohexyl peroxydicarbonate in benzene, dibutyl phthalate, and isopropyl alcohol, and of dimethyl peroxydicarbonate in dibutyl phthalate, have been determined experimentally. The results are compared with data from thermochemical calculations carried out on the basis of the decomposition equations proposed in ([2]). In connection with these calculations we measured the heats of combustion, sublimation, and solution of dicyclohexyl peroxydicarbonate, the heats of combustion and solution of cyclohexanone and cyclohexanol, and from the data obtained calculated the heats of formation of these substances. In addition, from the heat of formation of dicyclohexyl peroxydicarbonate and the mean bond energies C—C and C—H, the heat of formation of dimethyl peroxydicarbonate was calculated. All thermochemical quantities below are expressed in calories; 1 cal = 4.1840 absolute joules.

The preparation of the peroxides has been described in ([3]). Dimethyl peroxydicarbonate was synthesized in the solvents in which the decomposition was studied. The substances and solutions used were thoroughly purified. The calorimeter proper for determining the heats of reactions was a Dewar vessel of 200 cm^3 capacity. It had an isothermal jacket, which was an automated liquid thermostat of 24 liters volume. Toluene or nitrobenzene served as the calorimetric liquid, their heat capacities being known ([4]). The heat equivalent of the calorimeter with the reaction test tube was determined from the heats of solution of potassium chloride and sodium carbonate, for which accurate data are available (⁵). The heat capacity of dilute solutions was taken as equal to the heat capacity of the corresponding solvent; the heat capacity of concentrated solutions was measured at 25°, i.e., under conditions in which decomposition of the peroxides studied is not observed during the measurement. (The volume of the peroxide solution in the reaction vessel was usually about 5% of the volume of the calorimetric liquid.)

The temperature was measured with graduated Beckmann thermometers, and its change during the experiment was determined graphically by the usual calorimetric method. In order to reduce to a minimum the correction for the change in the temperature of the calorimeter due to insertion of the reaction vessel, the experiments were carried out as follows. Two identical test tubes with exactly the same amount of the given peroxide, or of a specified solution of it, were placed for 15 min in an auxiliary thermostat, where the temperature was 0.2–0.3° higher than in the calorimeter. The test tubes were then removed simultaneously from the thermostat, and one of them was quickly placed in the calorimeter and the other in liquid nitrogen. After completion of the observations of the decomposition, the other test tube was also transferred to nitrogen. Then iodometrically

the peroxide content in both test tubes was determined, and the difference between the values obtained indicated the amount of peroxide decomposed in the calorimeter. Temperature corrections were checked by control experiments with solvent without peroxide. The temperature change due to the reaction was usually $\sim 2^\circ$. Each experiment was repeated 5–10 times. Table 1 gives the arithmetic mean results and the maximum scatter of the data.

Table 1

Thermal effects of peroxide decomposition according to calorimetric data

Substance	Solvent	Conc., mole %	Temp., °C	$-\Delta H$, kcal/mole
Dicyclohexyl peroxydicarbonate	–	99.5 (melt)	50	61 ± 4
Same	Dibutyl phthalate	10	50	54 ± 4
» »	Benzene	5	50	54 ± 4
» »	Isopropyl alcohol	1.3	50	64 ± 4
Dimethyl peroxydicarbonate	Dibutyl phthalate	40	50	59 ± 2
Same	»	55	40	59 ± 4

Heats of combustion were determined in a bomb calorimeter. The apparatus had a number of special devices for reducing heat exchange with the surroundings. The heat equivalent of the calorimeter was determined with standard benzoic acid obtained from VNIIM ($-\Delta H^{\mathrm{comb}} = 6323.8 \pm 5$ cal/g), with an accuracy of 0.06%. The corrections customary in measurements of heats of combustion were introduced.

The peroxide was burned in a mixture with benzoic acid in the form of tablets in a thin cellophane wrapper. The latter was used so that, during briquetting, the ratio of the components in the mixture would not change because of adhesion of grains to the press die. Preliminary experiments showed that for complete combustion of the peroxide its weight fraction in the mixture should be no more than 1/4. The heat of combustion of the cellophane used was accurately determined. In control experiments, tablets of pure benzoic acid in a cellophane wrapper were burned.

The heat of sublimation of dicyclohexyl peroxydicarbonate was calculated by means of a plot $\lg p = f(T)$, where T is the temperature and p is the vapor pressure, which was studied by the Knudsen effusion method in the range $20 \div 40^{\circ}$.* The heats of solution were determined in a calorimeter similar to the instrument used for measuring heats of reaction.**

In the calculations, values of the standard heats of formation of CO_2 and H_2O, respectively 94.05 and 68.32 kcal/mole [6], were used. The results are given in Table 2.

According to the data of G. A. Razuvaev and L. M. Terman [2], during the thermal decomposition of organic percarbonates in an inert solvent, carbon dioxide is evolved and radicals of the type RO· are formed, which disproportionate. On this basis, the decomposition of dicyclohexyl peroxydicarbonate in the pure state and in dibutyl phthalate or benzene solution can be expressed by the overall equation:

$$C_6H_{11}OC(O)OOC(O)OC_6H_{11} \rightarrow 2CO_2 + C_6H_{11}OH + C_6H_{11}O. \qquad (1)$$

From calculation using the heats of formation of the reagents, and using the data of Table 2, for the thermal effect of reaction (1) in benzene solution one obtains $-\Delta H = 74 \pm 5$ kcal/mole.

Upon decomposition of dicyclohexyl peroxydicarbonate in isopropyl alcohol, according to data [2], carbon dioxide is evolved and radicals RO· are formed, as in an inert solvent. However, in alcohol these radicals— do not disproportionate, but dehydrate the solvent. The overall equation will be:

---

* These measurements were carried out in our laboratory by N. A. Kozlov.

** The heats of solution were determined by E. G. Kalashnikova.

$$C_6H_{11}OC(O)OOC(O)OC_6H_{11} + CH_3CHOHCH_3 \rightarrow 2CO_2 + 2C_6H_{11}OH + CH_3COCH_3. \quad (2)$$

In this case, from a calculation based on heats of formation using the corresponding data of Table 2 and the values of the heats of formation of carbon dioxide and isopropyl alcohol ($-\Delta H^{\mathrm{f}}_{\ell} = 76.2$ kcal/mol (^{7})), for the heat effect of reaction (2) one obtains $-\Delta H = 82 \pm 5$ kcal/mol.

Table 2

Heats of combustion ($-\Delta H^{\mathrm{c}}$), vaporization ($-\Delta H^{\mathrm{vap}}$), solution ($-\Delta H^{\mathrm{soln}}$), and formation ($-\Delta H^{\mathrm{f}}$) of dicyclohexyl peroxydicarbonate and the products of its decomposition, in kcal/mol. Indices: k —standard condensed phase, g —gas phase, soln. —solution; $t = 25°$, $p = 1$ atm.

Substance	$-\Delta H^{\mathrm{c}}$	ΔH^{vap}	ΔH^{soln}*	$-\Delta H^{\mathrm{f}}_{\mathrm{k}}$	$-\Delta H^{\mathrm{f}}_{\mathrm{g}}$	$-\Delta H^{\mathrm{f}}_{\mathrm{soln}}$*
Dicyclohexyl peroxydicarbonate	1805 ± 5	24 ± 0.5	In benzene 6.0 ± 0.1 In isopropyl alcohol 8.7 ± 0.1	263 ± 5	239 ± 5	In benzene 257 ± 5 In isopropyl alcohol 254 ± 5
Cyclohexanone	845.2 ± 0.5		In benzene -0.25 ± 0.01	60.7 ± 0.5		In benzene 60.9 ± 0.5
Cyclohexanol	890.6 ± 0.5**		In benzene 1.12 ± 0.02 In isopropyl alcohol 0.18 ± 0.02	83.6 ± 0.5		In benzene 82.5 ± 0.5 In isopropyl alcohol 83.4 ± 0.5
Acetone			In isopropyl alcohol 1.35 ± 0.02	59.3***		In isopropyl alcohol 57.9

---

* The concentration of the solutions in benzene is 5 mole %, in isopropyl alcohol

1 mole %, which corresponds to the conditions of the calorimetric measurements of the heats of decomposition (Table 1).
** For ΔH^{c} of cyclohexanol, the value −890.8 kcal/mol had previously (7) been obtained, which agrees well with our value.
*** According to data (8).

The calculated values of the heats of decomposition refer to 25°, whereas the experimental values (Table 1) refer to 50°. However, since the heat effect of a chemical reaction depends comparatively weakly on temperature, in the present case the temperature correction is probably within the error limits of both the calculation and the experiment. Thus, the results of the calculations of the heat effects of reactions (1) and (2) are approximately 20 kcal/mol greater than the corresponding values of the heats of decomposition of the peroxide measured directly, and this difference is twice as large as the sum of the errors of calculation and experiment. Hence, apparently, it follows that, in addition to processes (1) and (2), which in (2) were established by chemical analysis of the decomposition products, other reactions involving the peroxide also proceed in the solutions studied. This conclusion agrees with the data of the authors (2), who found in the decomposition products of dicyclohexyl peroxydicarbonate in benzene and isopropyl alcohol substances that are secondary with respect to reactions (1) and (2), respectively.

For the decomposition of dimethyl peroxydicarbonate in an indifferent solvent, by analogy with (1), we have:

$$CH_3OC(O)OOC(O)OCH_3 \rightarrow 2CO_2 + CH_3OH + HCHO. \tag{3}$$

In order to calculate the heat effect of reaction (3), we calculated in the following way the heat of formation of dimethyl peroxydicarbonate (M), proceeding from the experimental value (Table 2) of the corresponding quantity for dicyclohexyl peroxydicarbonate (C) and some other thermochemical data.

1) $\sum \Delta H^{\text{form}}_{\text{at,C}} - \Delta H^{\text{form}}_{\text{g,C}} = \Delta H^{\text{atom}}_{\text{C}} = 3896 + 239 = 4135$ kcal/mole, where ΔH^{atom} denotes the enthalpy of atomization of the given compound in the gaseous state, equal to the sum of the average energies (E) of all its atomic bonds, and the subscript g indicates reference to the gas phase. For the enthalpies of formation of the atoms ($\Delta H^{\text{form}}_{\text{at}}$) C, H, and O, the values 170.9; 52.09; and 59.54 kcal/g-atom, respectively, were taken, as given in (9), from which the data of (10) differ only slightly.

2) $\Delta H^{\text{atom}}_{\text{C}} - 12E(\text{C—C})_{\text{cyclohex}} - 16E(\text{C}_{\text{aliph}}\text{—H}) = \Delta H^{\text{atom}}_{\text{M}} = 4135 - 991 - 1579 = 1565$ kcal/mole, where the subscript cyclohex denotes cyclohexane. The value $E(\text{C}_{\text{aliph}}\text{—H})$, 98.70 kcal, was taken from (9). The value $E(\text{C—C})_{\text{cyclohex}}$ was calculated:

$$\sum \Delta H^{\text{form}}_{\text{at,cyclohex}} - \Delta H^{\text{form}}_{\text{g,cyclohex}} = \Delta H^{\text{atom}}_{\text{cyclohex}} = 1650.5 + 29.4 = 1679.9 \text{ kcal/mole;}$$

$$E(\text{C—C})_{\text{cyclohex}} = \frac{1}{6}\left[\Delta H^{\text{atom}}_{\text{cyclohex}} - 12E(\text{C}_{\text{aliph}}\text{—H})\right] = 82.6 \text{ kcal.}$$

The value $\Delta H^{\text{form}}_{\text{g,cyclohex}}$ was taken from ([11]).

3) $\sum \Delta H^{\text{form}}_{\text{at,M}} - \Delta H^{\text{atom}}_{\text{M}} = \Delta H^{\text{form}}_{\text{g,M}} = 1353 - 1565 = -212$ kcal/mole. The accuracy of this value is about ±5 kcal/mole.

Next we estimated the heat of the gas → solution process (solvent–dibutyl phthalate, benzene) for dimethyl peroxydicarbonate as $-\Delta H^{\text{soln}} = 10$ kcal/mole, with the error of this value probably no greater than 2 kcal/mole.* Then the heat of formation referred to solution for this peroxide is

$$-\Delta H^{\text{form}}_{\text{soln,M}} = 222 \text{ kcal/mole}$$

with an assumed maximum error of 7 kcal/mole.

For liquid methyl alcohol, $-\Delta H^{\text{form}}_{\ell} = 57.02$ kcal/mole ([6]). We took its heat of dissolution in dibutyl phthalate (benzene), with an assumed accuracy of 0.5 kcal/mole, to be equal to the corresponding heat of dissolution of ethyl alcohol: $\Delta H^{\text{soln}} \cong 2$ kcal/mole ([6]). Hence, for methyl alcohol,

$$-\Delta H^{\text{form}}_{\text{soln}} = 55 \text{ kcal/mole.}$$

For the heat of formation of formaldehyde referred to solution in water, ([6]) gives the value $-\Delta H^{\text{form}}_{\text{soln}} = 42.5$, and for solution in methyl alcohol: $-\Delta H^{\text{form}}_{\text{soln}} = 42.7$ kcal/mole. On this basis we assumed that, with an error not exceeding 2 kcal/mole, for formaldehyde in dibutyl phthalate solution we have

$$-\Delta H^{\text{form}}_{\text{soln}} = 42 \text{ kcal/mole.}$$

Using the indicated values of the heats of formation of the reactants, calculation of the thermal effect of reaction (3) gives the result

$$-\Delta H = 63 \text{ kcal/mole,}$$

with the error probably not exceeding 10 kcal/mole.

Thus, the results of the calorimetric determination of the heat of decomposition (59 kcal/mole, Table 1) and of its calculation from the heats of formation, according to equation (3), agree within the limits of the corresponding errors.

Scientific Research Institute of Chemistry
at N. I. Lobachevsky Gorky State University

Received
21 X 1961

REFERENCES

1. E. J. Harries, Proc. Roy. Soc., A173, 126 (1939).

2. G. A. Razuvaev, L. M. Terman, ZhOKh, 30, 2387 (1960); G. A. Razuvaev, L. M. Terman, G. G. Petukhov, DAN, 136, 628, 1349 (1961).

3. F. Strain, W. E. Bissinger et al., J. Am. Chem. Soc., 72, 1254 (1950).

4. I. Timmermans, Physico-Chemical Constants of Pure Organic Compounds, N. Y., 1950.

5. E. V. Britske, A. F. Kapustinskii et al., *Thermal Constants of Inorganic Substances*, Publishing House of the Academy of Sciences of the USSR, 1949.

6. D. D. Wagman, W. H. Evans et al., Select. Val. Chem. Thermodyn. Prop., Natl. Bur. Stand., Circ. 500, 1952.

7. S. Parks, J. R. Mosley, P. V. Peterson, J. Chem. Phys., 18, 152 (1950).

8. R. E. Pennington, K. A. Kobe, J. Am. Chem. Soc., 79, 300 (1957).

9. T. L. Cottrel, *The Strengths of Chemical Bonds*, 2nd Ed., Butterworths Sci. Publ., 1958; J. H. S. Green, Quart. Rev., 15, 125 (1961).

10. G. I. Levi, A. A. Balandin, Izv. AN SSSR, OKhN, 1960, No. 2, 157.

11. J. E. Kilpatrick, H. G. Werner et al., J. Res. Nat. Bur. Stand., 39, 523 (1947).

* The estimate was made on the basis of the heats of vaporization and dissolution of certain substances comparatively close to the given peroxide in molecular composition and structure.

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

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