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Abstract

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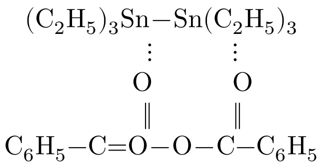
Thermochemistry of the Interaction of Hexaethyldistannane with Benzoyl Peroxide

Recently G. A. Razuvaev, N. S. Vyazankin, and O. A. Shchetkova (^{1}) established that hexaethyldistannane in benzene solution at room temperature reacts with benzoyl peroxide, forming triethyltin benzoate. The reaction is expressed by the equation

$$(C_2H_5)_6Sn_2 + (C_6H_5COO)_2 \rightarrow 2(C_2H_5)_3SnOCOC_6H_5. \qquad (1)$$

Since neither benzoyl peroxide nor hexaethyldistannane decomposes by itself at room temperature, their facile interaction is explained by the formation of an intermediate complex or other complexes with four- or eight-membered rings. Hexaethyldiplumbane reacts analogously with benzoyl peroxide.



$$\begin{array}{c} (C_2H_5)_3Sn-Sn(C_2H_5)_3 \\ \vdots \qquad \vdots \\ O \qquad O \\ \| \qquad \| \\ C_6H_5-C=O-O-C-C_6H_5 \end{array}$$

In the present work the thermochemistry of the reaction between hexaethyldistannane and benzoyl peroxide was studied; for methodological reasons dibutyl phthalate was used as the solvent. The main aim was to determine the thermal effect by two routes: directly, i.e., from the heat evolved in the reaction, and from the heats of combustion of the reactants, according to equation (1). It was borne in mind that agreement of the corresponding results would be convincing evidence for the absence of side processes. In addition, it was of interest to compare the strength of the atomic bonds broken and formed in the reaction, and also to compare the bond energies Sn—Sn and Sn—C.

The direct determination of the thermal effect of the reaction was carried out with a precision adiabatic calorimeter described by S. M. Skuratov (^{2}). The apparatus was improved by introducing three additional jackets, which made it easier to attain adiabaticity of the thermal regime.

A solution of benzoyl peroxide was placed directly in the calorimetric vessel, while the hexaethyldistannane, before mixing, was in an evacuated ampoule lowered into the same vessel. The heat associated with mixing the distannane with the peroxide solution and with breaking the ampoule was determined and taken into account.

The heat capacity of the calorimetric system, including the peroxide solution and the ampoule with distannane, was determined before each experiment. For this purpose the method of heating by an electric current was used, and the apparatus customary in calorimetry was employed.**

The initial concentration of the reactants was of the order of 0.1 mol/l. The experiments were carried out at 40°, since at lower temperatures the reaction proceeds very slowly. The duration of an experiment was about 10 h. During this time the concentration of the starting substances decreased by approximately 20%, the temperature increase in the calorimeter was about 2°, and the amount of heat evolved was 35–40 cal.; the accuracy of determination of this quantity was about 1%. Control experiments showed that the heat evolved when only a solution of hexaethyldistannane or only a solution of benzoyl peroxide was kept in the calorimeter for 10 h at 40° amounted to less than 0.5% of the thermal effect of the reaction between these substances.

The 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 from standard benzoic acid ($\Delta H^r = 6323.8 \pm 5$ cal/g), with an accuracy of 0.1%. Corrections customary in measuring heats of combustion were introduced. The accuracy of the apparatus and procedure was checked by determining the heats of combustion of chemically pure benzene and glycerol. Our values for these substances agreed with the corresponding literature data (^{3}) to within 0.1%. Since A. A. Balandin et al. (^{4}), by X-ray structural analysis of the combustion products of tetraethyltin, showed that combustion in the calorimetric bomb proceeds to the formation of tin dioxide without admixture of its oxide or metallic tin, we assumed that the combustion process of hexaethyldistannane proceeds in the same way.

Analysis of mixtures of hexaethyldistannane and benzoyl peroxide was carried out iodometrically. First, the distannane was titrated with iodine solution (the reaction proceeds with formation of triethyltin iodide). Then, to determine the peroxide, an excess of potassium iodide was added, the solution was acidified, and the liberated iodine was titrated with hyposulfite. The accuracy of this analytical method is 2–3%.

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* A. S. Kirillova took part in the synthesis of hexaethyldistannane and in the analysis of the reaction mixtures.

** In the calculations it was assumed that 1 cal = 4.1840 J.

The synthesis of hexaethyldistannane is described in (5), and that of triethyltin benzoate in (1). All substances used were thoroughly purified. In fractional distillation of the distannane, a fraction boiling between 161 and 162° at 23 mm Hg was collected; n_D^{20} 1.5377. The benzoate had m.p. 78–79°. Tetraethyltin boiled at 177.8° (760 mm) and had n_D^{20} 1.4716. Corresponding literature data: 175–178.5° and 1.4717–1.4722 (4).

The results of the calorimetric measurements are given in Table 1. From these data it follows that the average value of the thermal effect of the reaction in solution is

Table 1

Data of direct measurements of the thermal effect

Experiment No.	Peroxide reacted, mmol	Stannane reacted, mmol	$-\Delta H$ measured, cal	$-\Delta H$ of reaction, kcal/mol, from peroxide	$-\Delta H$ of reaction, kcal/mol, from stannane	$-\Delta H$ of reaction, kcal/mol, mean
1	0.375	0.395	40.6	108	103	105 ± 3
2	0.355	0.385	41.3	117	107	112 ± 5
3	0.310	0.335	35.1	113	104	108 ± 4

$$-\Delta H^{\text{soln.}}_{\text{react.}} = 108 \pm 5 \text{ kcal}$$

per 1 mole of hexaethyldistannane or benzoyl peroxide. This value pertains to the experimental temperature 40°. However, calculation showed that the correction for reducing ΔH to 25° lies within the experimental error of the thermal-effect value.

Data on the heats of combustion are given in Table 2. In addition to the reagents (1), tetraethyltin was studied. Its heat of combustion was needed for calculating the Sn—C bond energy, since the literature data (4,6) for this quantity differ considerably.

Table 2

Heats of combustion

Substance	$-\Delta H$, kcal/mol, by authors	$-\Delta H$, kcal/mol, literature data	Substance	$-\Delta H$, kcal/mol, by authors	$-\Delta H$, kcal/mol, literature data
$(C_2H_5)_4Sn$	1551 ± 3	1546 (4)	$(C_6H_5COO)_2$		

Substance	$-\Delta H$, kcal/mol, by authors	$-\Delta H$, kcal/mol, literature data	Substance	$-\Delta H$, kcal/mol, by authors	$-\Delta H$, kcal/mol, literature data
$(C_2H_5)_6Sn_2$	2379 ± 3	1523 (6)	$(C_2H_5)_3SnOOCC_6H_5$	1007 ± 1	1552 (3)

Calculation of the thermal effect of reaction (1) from the authors' data on the heats of combustion of hexaethyldistannane and triethyltin benzoate, and from the value adopted in the literature (3) for the heat of combustion of benzoyl peroxide,* gives the result: $-\Delta H^{\text{st. s}}_{\text{react}} = 117 \pm 5$ kcal per 1 mole of any of the starting substances at 25°. This value refers to the reaction between liquid hexaethyldistannane and solid benzoyl peroxide with formation of solid triethyltin benzoate, i.e., to the reagents in their standard states (st. s.). The thermal effect of the reaction in solution can be calculated from equation (2), if the heats of solution of the reagents ($\Delta H_{\text{p-p}}$) in dibutyl phthalate are known:

$$\Delta H^{\text{p-p}}_{\text{react}} = \Delta H^{\text{st. s}}_{\text{react}} - \Delta H^{\text{pb}}_{\text{p-p}} - \Delta H^{\text{heds}}_{\text{p-p}} + 2\Delta H^{\text{btet}}_{\text{p-p}} \tag{2}$$

(where the subscripts denote: p-p—solution, st. s—standard state, pb—benzoyl peroxide, heds—hexaethyldistannane, btet—triethyltin benzoate).

Special experiments to determine these heats,** carried out in the adiabatic calorimeter described above at 25°, gave the following results:

Benzoyl peroxide	$\Delta H^{\text{pb}}_{\text{p-p}} = 6.9$ kcal/mole
Hexaethyldistannane	$\Delta H^{\text{heds}}_{\text{p-p}} = 0.9$ kcal/mole
Triethyltin benzoate	$\Delta H^{\text{btet}}_{\text{p-p}} = 7.1$ kcal/mole

Taking these data into account, from (2) it follows that the thermal effect of process (1) in solution is $-\Delta H^{\text{p-p}}_{\text{react}} = 111 \pm 5$ kcal per 1 mole of peroxide or distannane (25°). Consequently, calculation of the thermal effect of the process of interaction of hexaethyldistannane with benzoyl peroxide from the heats of combustion of the reactants according to equation (1) gave a result in good agreement with the value of the same thermal effect obtained by directly carrying out the reaction in the calorimeter. Hence it is clear that the reaction studied proceeds in an indifferent solvent only according to equation (1).

From the heats of combustion and vaporization of the liquids studied, and from literature data on the heats of formation of the combustion products (9) and individual atoms, the heats of formation were calculated for the condensed ($\Delta H^{\text{form}}_{\text{k}}$) and gaseous ($\Delta H^{\text{form}}_{\text{g}}$) phases, as well as the heats of atomization of tetraethyltin and hexaethyldistannane, and also the heats of formation of solid benzoyl peroxide and triethyltin benzoate (Table 3). For the heat of atomization of carbon, the value 171.3 kcal/g-atom, now considered reliable, was taken (10, 4). The heats of atomization of hydrogen (52.1 kcal/g-atom) and tin (70 kcal/g-atom) were taken from ([11]).

The heat of vaporization of tetraethyltin was calculated by the empirical Klyages formula ([12]). The heat of vaporization of hexaethyldistannane was calculated by the Clausius-Clapeyron equation, proceeding from the fact that at 23 mm Hg this substance boils at about 161.5°, and at 17 mm—about 154°. The accuracy of the data in Table 3 is several kilocalories per mole.

From the heats of atomization of tetraethyltin and the average values of the bond energies C—H (98.75 kcal) and C—C (82.87 kcal) ([13]), the energy of the Sn—C bond was calculated. In a similar way the energy of the Sn—Sn bond in hexaethyldistannane was calculated, with the assumption that, to an accuracy of 1 kcal, the Sn—C bond in this compound has the same energy as in tetraethyltin. The following results were obtained: for the Sn—C bond in $(C_2H_5)_4Sn$, 46.9 ± 1 kcal (literature data 48.4([4]) and 53.9 ([6])***); for Sn—Sn in $(C_2H_5)_2Sn_2$, 50 ± 10 kcal; for Sn—O in $(C_2H_5)_3SnOCOC_6H_5$, 95 ± 10 kcal.

* Breitengbach and Derkosch ([7]) give, for ΔH^c of benzoyl peroxide, the value 1560, and in ([8]) 1564 kcal/mole. However, from ([7]) it follows that these values cannot be considered reliable.

** The integral heats of solution of 0.1 mole of substance in 1 kg of solvent were determined.

*** These values were calculated by us from the corresponding data of works ([4], [6]), proceeding from the currently accepted heat of atomization of carbon, 171.3 kcal/g-atom.

The value of the Sn—C bond energy in tetraethyltin obtained by the authors, and the corresponding value cited by A. A. Balandin and co-workers (4), differ by 1.5 kcal. Therefore the average value of 47.6 ± 0.8 kcal, used by us in the subsequent calculations, may be considered correct, while the value following from the data of Long and Norrish (6) is apparently too high by 6 kcal.

For the Sn—Sn bond energy in hexaethyldistannane, the value 50 ± 10 kcal was obtained by the route indicated above. Previously this quantity had not been determined. Pedley, Skinner, and Chernik (14) calculated the heat of formation of $(CH_3)_6Sn_2$ from data on the heats of bromination of this compound and of $(CH_3)_4Sn$, and from the heats of formation of Br_2, CH_3Br, and $(CH_3)_4Sn$. By further calculation from average bond energies, they found that the Sn—Sn energy in $(CH_3)_6Sn_2$ is probably ∼ 40 kcal. In doing so it was assumed that the Sn—C energy in $(CH_3)_6Sn_2$ and $(CH_3)_4Sn$ is the same. In addition, other errors in the calculation amount to about 5 kcal, so that the total possible error is apparently 10 kcal. Since the error in our calculation of the Sn—Sn energy in $(C_2H_5)_6Sn_2$ is also probably 10 kcal, we do not exclude the possibility of the lower limit of this energy, i.e., 40 kcal.

Table 3

Heats of formation and atomization. 25°
(in kcal/mole)

Substance	$-\Delta H_f^{obr}$	ΔH_{par}	$-\Delta H_f^{obr}$	ΔH of atomization
$(C_2H_5)_4Sn$	24	12	12	2494
$(C_2H_5)_6Sn_2$	52	15	37	3396
$(C_6H_5COO)_2$	106			
$(C_2H_5)_3SnOCOC_6H_5$	137			

The Sn—O bond energy in triethyltin benzoate can be calculated approximately from the O—O (13) and Sn—Sn bond energies and the thermal effect of reaction (1), if the latter is referred to the reagents in the gas phase; for this it is necessary to know their heats of sublimation. Judging from the corresponding heats of solution, there are grounds to assume that twice the heat of sublimation of triethyltin benzoate exceeds the sum of the heat of sublimation of benzoyl peroxide and the heat of vaporization of hexaethyldistannane by 5 ± 5 kcal. In this case it follows that the Sn—O energy is 95 ± 10 kcal.

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1. G. A. Razuvaev, N. S. Vyazankin, O. A. Shchepetkova, ZhOKh, **30**, 2498 (1960).
2. S. M. Skuratov, Koll. zhurn., **9**, 133 (1947).
3. M. S. Kharasch, *J. Res. Nat. Bur. Stand.*, **2**, 359 (1929).
4. A. A. Balandin, E. I. Klabunovskii et al., Izv. AN SSSR, OKhN, 1958, No. 1.
5. A. N. Nesmeyanov, K. A. Kocheshkov, V. P. Puzyrev, ZhOKh, **7**, 118 (1937).
6. L. H. Long, R. G. W. Norrish, *Proc. Roy. Soc.*, A **187**, 337 (1946).

7. J. W. Breitenbach, J. Derkosch, *Monatsh. Chem.*, **81**, 689 (1950).
8. J. W. Breitenbach, J. Derkosch, *Monatsh. Chem.*, **82**, 177 (1951).
9. F. Rossini et al., *Select. Val. Chem. Thermodyn. Prop.*, Nat. Bur. Stand., Circ. 500, 1952.
10. V. N. Kondrat' ev, *Usp. khim.*, **26**, 861 (1957); J. D. Morrison, H. E. Stanton, *J. Chem. Phys.*, **28**, 9 (1958).
11. T. Kottrell, *Strength of Chemical Bonds*, IL, 1956; L. Brewer, R. F. Potter, *J. Chem. Phys.*, **21**, 2012 (1953).
12. F. Klages, *Ber.*, **82**, 358 (1949).
13. G. I. Levi, A. A. Balandin, Izv. AN SSSR, OKhN, 1960, No. 2, 157.
14. J. B. Pedley, H. A. Skinner, C. L. Chernik, *Trans. Farad. Soc.*, **53**, 1612 (1957).

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