

for  $C_7H_{11}OClSi$ : C 46.5; H 9.5; Si 15.5;  $MR_D$  50.5; equiv.wt. 181.)

*N-Phenylurethan.* 2.3 g (0.019 mole) of phenyl isocyanate and 2.6 g (0.015 mole) of (A) were warmed for 5 minutes on a boiling water bath. The mixture was allowed to stand at room temperature until crystallization occurred. The crystal cake was boiled with 10 ml of petroleum ether (b.p. 100–110°) and the insoluble diphenylurea removed by filtration. The filtrate was cooled in ice and the obtained crystals were collected on a filter and recrystallized from petroleum ether. The yield of crystals melting at 77.5–78° was 3.2 g (0.011 mole). (Found: C 56.3; H 7.4; Si 9.3; equiv.wt. 298 \*. Calc. for  $C_{14}H_{22}O_2ClNSi$ : C 56.1; H 7.4; Si 9.3; equiv.wt. 300.)

4-Trimethylsilylbutylene-1,2 oxide (B) from (A). 100 g (0.55 mole) of (A) were dissolved in 200 ml of ether and refluxed for 3 h with 80 g (2.0 moles) of finely powdered sodium hydroxide. The mixture was filtered and the precipitate washed several times with ether. The ether was removed by distillation and the residue was fractionated at 20 mm Hg. 56 g (0.39 mole) of 4-trimethylsilylbutylene-1,2-oxide were collected at 58–59°.  $n_D^{20} = 1.4276$ ,  $d_4^{20} = 0.8452$ . (Found: C 58.2; H 11.3; Si 19.0;  $MR_D$  43.9. Calc. for  $C_7H_{16}OSi$ : C 58.2; H 11.2; Si 19.5;  $MR_D$  43.9.)

*Addition product with aniline.* 2.0 g of (B) dissolved in 30 ml of ethanol were dropped into a stirred solution of 14.0 g of freshly distilled aniline in 50 ml of ethanol and 15 ml of water. The mixture was allowed to stand for 3 days. The ethyl alcohol was distilled off until two layers were formed. After cooling to room temperature the organic layer was separated and the water layer extracted with ether. The ether and the remaining ethanol were removed from the combined ether layers by distillation at ordinary pressure and the excess of aniline at 2 mm Hg. The residue solidified on cooling and was crystallized four times from petroleum ether (b. p. 30–50°). 2.0 g (60 %) of crystals melting at 52.5–53° were obtained. (Found: C 64.8; H 9.7; Si 11.8. Calc. for  $C_{13}H_{23}NOSi$ : C 65.8; H 9.8; Si 11.8.)

4-Trimethylsilylbutylene-1,2-oxide from 4-trimethylsilylbutene-1. (III). 16.2 g (0.091 mole) of N-bromosuccinimide and 11.6 g (0.091 mole) of 4-trimethylsilylbutene-1 were shaken with

100 ml of water until all the N-bromosuccinimide had dissolved. The solution was extracted with ether and the combined ether portions were treated with alkali according to the method above. 4.2 g (0.030 mole) of (III) were obtained.

The addition product with aniline was prepared in the same way as above for the oxide (B). M. p. 53–53.5°.

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## Corrected Heats of Combustion of Organic Iodine Compounds

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In his dissertation<sup>1</sup> Karlsson\* has shown convincingly that combustion in a calorimetric bomb of iodine containing compounds forms only elemental iodine besides carbon dioxide and water\*\*. He further estimated that the heats of sublimation and solution of the iodine under his experimental conditions (liquid phase in the bomb 20 ml water) were very small (0.05 and 0.1 cal, respectively) and considered them negligible. For the heats of solution of the carbon dioxide appropriate corrections, however, were not applied, since the method of calculation of these was worked out and described after the publication of Karlssons dissertation (Smith *et al.*<sup>3</sup>).

Owing to the experimental conditions used by Karlsson, and the iodine compounds chosen by him, the last mentioned corrections are mostly very small as will be shown below. Thus his values of combustion are more accurate than should be expected from the considerable quantity of water present in the bomb during the

\* The equivalent weights were determined by hydrolysis with ethanolic sodium hydroxide and titration of the formed chloride ions with silver nitrate solution.

\* Now Karrman.

\*\* Concerning other investigations of this problem, see Ref.<sup>2</sup>.

combustion. It may be mentioned here that his values are not published elsewhere than in his dissertation.

For the recalculation of his data I have applied eqn 2 in Ref.<sup>3</sup>. This equation, the result of experiments with chlorine compounds, in which a HCl-containing bomb solution is formed, was nevertheless used even here, as considered exact enough for the very small corrections occurring in this case.

In Karlssons *calibration* experiments also the above mentioned quantity of water was present in the bomb. The standard being benzoic acid and almost all the compounds burnt aromatic, the errors in the heat equivalent and in the heats of combustion of the compounds tend to cancel. Among the aromatic compounds the iodotoluenes have the maximum-correction (0.4 cal/g). For the only non-aromatic compound, iodocyclohexane, the correction has been calculated to 0.7 cal/g.

In Table 1 developed heat is considered *positive*, as done in the dissertation. Notations in the table: In the first column "No." refers to the table numbers in Ref.<sup>1</sup>; in the second the names of the compounds

are given, "l" = liquid, "s" = solid, and in the third the heats of combustion (cal/g; const. volume) determined by Karlsson. In the fourth column "Corr.CO<sub>2</sub>" denotes the calculated correction (cal/g) for the heat of solution of carbon dioxide; the fifth contains the correction to weight in vacuum ("Corr. vac.") and the sixth ("Heats of comb, corr.") the final corrected heats. Temperature 20°. — For computing the heats of combustion in the gaseous state of the compounds, the heats of vaporization and sublimation in Ref.<sup>1</sup>, Tables 89 and 90, can be used.

Compounds, which are liquid at 20°, were burnt with cellophane cover. This method gives too low results (see Ref.<sup>3</sup>, p. 79). The resulting errors will of course diminish with rising boiling points of the compounds (see also Ref.<sup>4</sup>, p. 196).

The table shows that the corrections caused by the heat of solution of carbon dioxide, especially for the solid compounds, are very small and negligible, this, as already mentioned, depending on the fact that the errors in the determination of the heat equivalent and the heat of combustion of the compounds mostly almost cancel.

Table 1. Heats of combustion of iodine compounds.

No.	Compound	Heat of comb. uncorr. cal/g <sup>a</sup>	Corr. CO <sub>2</sub> cal/g	Corr. <sup>b</sup> vac. cal/g	Heat of comb. corr. cal/g
41	Iodobenzene (l)	3 738.9 ± 0.6	0.2	—1.9	3 737.2 ± 0.6
42	<i>o</i> -Iodotoluene (l)	4 199.9 ± 0.6	0.4	—2.4	4 197.9 ± 0.6
43	<i>m</i> - " (l)	4 200.8 ± 0.4	0.4	—2.4	4 198.8 ± 0.4
44	<i>p</i> - " (l)	4 188.1 ± 1.2	0.3	—2.3	4 186.0 ± 1.2
45	<i>o</i> -Iodobenzoic acid (s)	3 052.8 ± 0.4	—0.05	—1.2	3 051.5 ± 0.4
46	<i>m</i> - " (s)	3 039.0 ± 0.6	—0.1	—1.2	3 037.7 ± 0.6
47	<i>p</i> - " (s)	3 039.5 ± 0.8	—0.1	—1.2	3 038.2 ± 0.8
48	<i>o</i> -Iodomethylbenzoate (l)	3 562.2 ± 1.5	0.1	—1.8	3 560.5 ± 1.5
49	<i>m</i> - " (s)	3 530.6 ± 0.6	0.1	—1.8	3 528.9 ± 0.6
50	<i>p</i> - " (s)	3 523.0 ± 0.9	0.0	—1.8	3 521.2 ± 0.9
51	<i>o</i> -Diiodobenzene (l)	2 259.1 ± 0.4	0.1	—0.8	2 258.4 ± 0.4
52	<i>o</i> - " (s)	2 248.8 ± 1.2	0.1	—0.8	2 248.1 ± 1.2
53	<i>m</i> - " (s)	2 259.3 ± 1.7	0.1	—0.8	2 258.6 ± 1.7
54	<i>p</i> - " (s)	2 240.2 ± 1.0	0.1	—0.8	2 239.5 ± 1.0
55	<i>o</i> -Iodophenol (s)	3 237.0 ± 1.4	0.1	—1.5	3 235.6 ± 1.4
56	<i>m</i> - " (s)	3 238.2 ± 1.2	0.1	—1.5	3 236.8 ± 1.2
57	<i>p</i> - " (s)	3 237.6 ± 1.0	0.1	—1.5	3 236.2 ± 1.0
58	$\alpha$ -Iodonaphthalene (l)	4 793.5 ± 1.5	0.2	—2.7	4 791.0 ± 1.5
59	$\beta$ - " (s)	4 777.8 ± 1.8	0.2	—2.7	4 775.3 ± 1.8
60	Iodocyclohexane (l)	4 360.1 ± 0.9	0.7	—2.6	4 358.2 ± 0.9

<sup>a</sup> Not corrected to weight in vacuum.

<sup>b</sup> These corrections are given by Karlsson only for the heat of combustion per mole.

Compounds with an appreciable carbon dioxide correction are in the liquid state and Karlssons values (see above) of the heats of combustion are certainly somewhat too low (perhaps except for  $\alpha$ -iodonaphthalene with a very high boiling point). The plus-correction in the heats for the liquid compounds thus will diminish the error in question.

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