THERMOCHEMICAL INVESTIGATIONS ON METHYL-SUBSTITUTED BENZOIC ACIDS: I. TOLUIC ACIDS

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The thermochemical study of the methyl-substituted benzoic acids has been undertaken as a contribution to the basic thermodynamic information on pure organic compounds. This paper contains the thermochemical data of the three first members of this series: the toluic acids. The unit of energy upon which values reported in this paper are based is the absolute joule. The relation 1 cal = 4·1840 J is used. The molecular weight of carbon dioxide is taken as 44·011.

METHOD AND APPARATUS

The heats of combustion of the compounds were determined by burning the solid acids in the form of pellets in oxygen in a bomb, at constant volume. The procedure is similar to that described by Prosen[1]. The samples were weighed and placed in a platinum crucible in the bomb, 1 ml of water was added to the bomb, and the bomb was flushed and filled with purified oxygen to 30 atm pressure at 25°C. The sample was ignited by means of an iron wire fuse, 0·012 cm in diameter and 6 cm long, coiled above the sample. The amount of reaction was determined from the mass of carbon dioxide formed in the combustion. The heat of reaction was referred to the final calorimetric temperature of 28°C. Experiments with standard benzoic acid were carried out to determine the energy equivalent of the calorimetric system. A series of calorimetric combustion experiments was made with each of the three toluic acids. The same calorimetric system, platinum resistance thermometer and Mueller bridge were used for all the experiments.

A check on the completeness of reaction was afforded by the ratio, r, of carbon dioxide produced in the combustion to the stoichiometric amount of carbon dioxide calculated from the mass of toluic acid, corrected to vacuum, and its density. The density used for the three toluic acids was 1·30 g/cm³. The average values of r were always very close to 1·0000.

Materials

The *ortho-*, *meta-* and *para-*toluic acids from British Drug Houses, Ltd (England) were purified first by vacuum sublimation and then by zone-melting, with a simple and efficient device developed in this laboratory. The qualitative control of purity of the three toluic acids, by heating curves, according to the method of Skau[2], showed that those compounds were of a high degree of purity.

EXPERIMENTAL RESULTS

The results of a series of calibration experiments using N.B.S. standard benzoic acid are given in *Table 1*, which shows the experiment number, the mass of benzoic acid burned (corrected to vacuum), the deviation, Δe_1, of the energy equivalent from that of the standard calorimeter system, the corrected temperature rise ΔR_c, the ignition energy correction q_i, the nitric acid correction q_n, the energy equivalent E_s, and the deviation from the mean.

The values of q_n were computed from the amount of nitric acid formed using the value 57·8 kJ/mole for the standard heat of formation of nitric acid from nitrogen, oxygen, and liquid water. The values of q_i were obtained from separate ignition experiments in which a standard mass of 5·60 mg of iron was burned (standard $q_i = 41·1$ J) but are corrected to the actual mass of iron burned in each experiment using 7·5 J/mg for the heat of combustion of iron. (On the experiments Nos. 1 and 2 another iron wire was used with a standard mass of 8·30 mg of iron.) The value of Δe_1 for each experiment was computed from the heat capacity of benzoic acid taken as 1·21 J g^{-1} °C^{-1} at 26·5°C converted to J/Ω on the resistance thermometer used.

From the data in *Table 1*, the energy equivalent of the standard calorimeter system E_s is computed as follows:

$$E_s = [(-\Delta E_{B,\,28°C}\ m_s + q_i + q_n)/\Delta R_c] - \Delta e_1 \text{ J}/\Omega$$

where $-\Delta E_{B,\,28°C} = 26431·8$ J/g is the heat of combustion of standard benzoic acid under the actual bomb conditions.

Table 1. Calibration experiments with benzoic acid

Expt No.	Mass of benzoic acid (g)	Δe_1 (J/Ω)	ΔR_c (Ω)	q_i (J)	q_n (J)	E_s (J/Ω)	Deviation from mean (J/Ω)
1	1·60272	19·2	0·300232	62·4	2·3	141296·4	− 8·9
2	1·60327	19·2	0·300306	61·5	2·6	141308·0	+ 2·7
3	1·60290	19·2	0·300089	43·2	1·7	141313·6	+ 8·3
4	1·60248	19·2	0·300042	42·0	3·0	141299·1	− 6·2
5	1·60238	19·2	0·300006	42·2	1·9	141304·3	− 1·0
6	1·60240	19·2	0·299975	42·0	1·9	141320·0	+ 14·7
7	1·60136	19·2	0·299800	41·8	2·7	141312·8	+ 7·5
8	1·60209	19·2	0·299947	42·0	2·7	141308·5	+ 3·2
9	1·60167	19·2	0·299890	42·1	2·6	141298·4	− 6·9
10	1·60260	19·2	0·300077	42·1	2·6	141292·2	− 13·1

Mean, 141305·3
S.D. of mean, ± 5·6

Table 2 lists the data for the calorimetric combustion experiments of the three toluic acids. Δe_2 is the deviation from the standard calorimetric system; $Q_{28°C} = (E_s + \Delta e_2)\Delta R_c$ is the isothermal heat liberated by the process which took place in the bomb; and $-\Delta E_{B,28°C} = Q_{,28°C} - q_i - q_n$ is the heat of combustion in the bomb process.

Table 2.   Combustion experiments with toluic acids

Expt. No.	Mass of carbon dioxide (g)	Δe_2 (J/Ω)	ΔR_c (Ω)	$Q_{28°C}$ (J)	q_i (J)	q_n (J)	$-\Delta E_B$, 28°C (J/g of CO₂)	Mean value $-\Delta E_B$ (J/g of CO₂)
				o-Toluic acid				
1	3·80624	18·8	0·296702	41931·1	41·7	6·1	11003·9	
2	3·96951	19·6	0·309387	43724·1	40·0	6·1	11003·4	
3	3·86876	26·0	0·301652	42632·9	42·1	7·6	11006·9	11005·0
4	3·86323	26·0	0·301172	42565·0	42·8	6·5	11005·2	± 0·6
5	3·86426	26·0	0·301263	42577·9	41·9	7·3	11005·7	
				m-Toluic acid				
1	3·86434	25·3	0·300494	42469·0	42·4	6·5	10977·3	10978·1
2	3·85449	25·2	0·299777	42367·6	43·0	6·8	10978·8	±0·8
3	3·89990	−17·3	0·303236	42843·6	41·8	3·4	10974·2	10975·2
4	3·86532	−17·4	0·300616	42473·4	41·8	3·7	10976·6	±0·7
5	3·88144	−17·4	0·301815	42642·8	40·3	4·3	10974·8	
				p-Toluic acid				
1	3·87614	18·3	0·301220	42569·5	41·7	6·5	10970·0	
2	3·87233	18·3	0·300978	42535·3	42·1	8·8	10971·3	
3	3·87169	18·2	0·300810	42511·5	43·0	8·0	10966·9	10968·7
4	3·86532	18·2	0·300372	42449·6	42·7	8·7	10968·9	± 0·9
5	3·87671	18·3	0·301176	42563·3	42·0	8·4	10966·2	

The values of Δe_2 were computed from the heat capacities: 12·8, 12·1 and 12·0 J g^{-1} Ω^{-1} for *o*-, *m*- and *p*-toluic acid, respectively[3], and the heat capacity of any parts of the calorimeter which were changed during the course of this investigation.   Thus, in combustion experiments 3, 4 and 5 of the *o*-toluic acid and 1 and 2 of the *m*-toluic acid a transitory modification of the bomb was introduced, which is reflected in the related Δe_2 values.

As complete combustion of the *m*-toluic acid was very difficult at the standard pressure of 30 atm, the *m*-toluic acid combustion experiments 3, 4 and 5 were performed with the bomb filled with purified oxygen to 20 atm pressure* at 25°C.   This explains the difference in the Δe_2 values and the two mean values of $-\Delta E_{B, 28°C}$ for the *m*-toluic acid.

In *Table 3* the following quantities are given for each of the compounds: the mean value of $-\Delta E_{B, 28°C}$, from *Table 2*, expressed in kilojoules per mole of acid; $-\Delta E_{28°C}^\circ$, the decrement in internal energy in the ideal bomb process; $-\Delta H_{c, 28°C}^\circ$, the heat of combustion at constant pressure at 28°C; $-\Delta H_{c, 25°C}^\circ$, the heat of combustion at constant pressure at 25°C; and ΔH_f°, the heat of formation at constant pressure at 25°C.

* The deviation from the standard calorimeter system due to the difference between 30 and 20 atm pressure of oxygen ($\Delta e = 35·83$ J/Ω) was computed from the volume of the bomb (0·387 l.) and the heat capacity of oxygen at constant volume taken as 20·96 J mole^{-1} °C^{-1} converted to J/Ω on the resistance thermometer used.

*Table 3.* Heats of combustion and formation of the toluic acids

Compound (cryst.)	$-\Delta E_B^\circ$, 28°C (kJ/mole)	$-\Delta E^\circ$, 28°C (kJ/mole)	$-\Delta H_C^\circ$, 28°C (kJ/mole)	$-\Delta H_C^\circ$, 25°C		ΔH_f°, 25°C (kcal/mole)
				(kJ/mole)	(kcal/mole)	
o-Toluic acid	3874·73 ± 0·77	3872·02 ± 0·77	3874·53 ± 0·77	3875·00 ± 0·77	926·14 ± 0·18	− 99·55 ± 0·22
m-Toluic acid	3865·26 ± 0·81 3864·24 ± 0·81	3862·33 ± 0·81	3864·84 ± 0·81	3865·34 ± 0·81	923·84 ± 0·19	− 101·84 ± 0·23
p-Toluic acid	3861·95 ± 0·93	3859·24 ± 0·93	3861·75 ± 0·93	3862·26 ± 0·93	923·10 ± 0·22	− 102·58 ± 0·26

The uncertainties in the heats of combustion assigned to the values in *Table 3* were calculated from the relation:
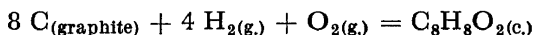
$$\text{uncertainty} = [(0{\cdot}01)^2 + (2\sigma E_S)^2 + (2\sigma\Delta E_B)^2 + (0{\cdot}01)^2]^{\frac{1}{2}}$$

where σ represents the standard deviation of the mean for the specified measurement, and all deviations are expressed as percentages of the measured quantity. The first term, 0·01 per cent, is the assigned uncertainty in the certified value of the heat of combustion of the standard benzoic acid. The second term, 0·01 per cent, is arbitrarily assigned to allow for systematic error in the measurements.

The heats of combustion refer to the reaction:

$$C_8H_8O_{2(c.)} + 9\ O_{2(g.)} = 8\ CO_{2(g.)} + 4\ H_2O_{(l.)}$$
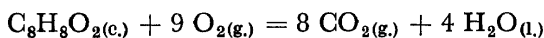
The heats of formation refer to the reaction:

$$8\ C_{(graphite)} + 4\ H_{2(g.)} + O_{2(g.)} = C_8H_8O_{2(c.)}$$

The heats of formation were calculated from the heats of combustion using the values −68·317 ± 0·010 kcal/mole for the heat of formation of liquid water and −94·052 ± 0·011 kcal/mole for the heat of formation of carbon dioxide.

References

[1] E. J. Prosen. Chap. 6 in *Experimental Thermochemistry*, Ed. F. D. Rossini, Interscience, New York (1956)

[2] E. L. Skau. *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1932)

[3] D. H. Andrews, G. Lynn and J. Johnston. *J. Am. Chem. Soc.*, **48**, 1274 (1926)