HEATS OF COMBUSTION OF FIVE ALKYL PHENYL KETONES

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As a contribution to the determination of fundamental thermodynamic properties of pure organic compounds a group of alkyl phenyl ketones has been selected for study.

METHOD AND APPARATUS

The heats of combustion of the compounds were determined by burning the liquid alkyl phenyl ketones in oxygen in a bomb, at constant volume. The procedure is similar to that described by Prosen[1], followed by us in other studies[2].

Materials

The methyl, ethyl and propyl phenyl ketones were commercial products. The iso- or *tert*-butyl phenyl ketones were synthesized in this laboratory. The five ketones were purified first by vacuum distillation, in a column of fifty theoretical plates, and then by fractional melting, with an apparatus developed in this laboratory from a simpler device described by Nicholson[3]. The qualitative control of purity by heating curves, following the method of Skau, showed that these compounds were very pure.

EXPERIMENTAL RESULTS

The results of a series of calibration experiments using N.B.S. standard benzoic acid are given in *Table 1*. The tabulated data were obtained as in the following paper[2]. The values of q_i were obtained from separate ignition experiments in which a standard mass of 8·30 mg of iron was burned (standard $q_i = 62$ J).

Table 1. Data from calibrating 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	1·59823	19·2	0·299388	61·7	1·7	141294	− 25
2	1·59794	19·2	0·299233	62·0	1·9	141343	+ 25
3	1·59979	19·2	0·299624	61·8	2·0	141322	+ 3
4	1·60135	19·2	0·299945	63·8	1·9	141313	− 6
5	1·59822	19·2	0·299342	62·4	2·7	141320	+ 1
						Mean, 141319	
						S.D. of mean, ± 8	

In *Table 2* the results of five series of combustion experiments with the alkyl phenyl ketones are given. These data were obtained as in the following paper[2].

In *Table 3* the heats of combustion and formation of the five alkyl phenyl ketones are given. These data and their uncertainties were computed as in the following paper[2].

CONCLUSIONS

On comparing the heats of combustion of the alkyl phenyl ketones with the corresponding values for the liquid alkylbenzenes, reported by Prosen, Johnson and Rossini[4], the following conclusions can be drawn.

Table 2. Data from combustion experiments with alkyl phenyl ketones

Expt. No.	*Mass of carbon dioxide* (g)	Δe_3 (J/Ω)	ΔR_c (Ω)	$Q_{28°C}$ (J)	q_i (J)	q_n (J)	$-\Delta E_B$ (28°C) (J/g of CO_2)	*Mean value* $-\Delta E_B$ (J/g of CO_2)
				Methyl phenyl ketone				
1	3·62191	24·4	0·302301	42728·2	63·4	2·5	11779·0	
2	3·62318	24·4	0·302359	42736·6	61·5	2·1	11777·7	11779·4
3	3·63150	24·4	0·303132	42845·8	64·2	2·4	11780·0	± 0·7
4	3·62991	24·4	0·303011	42828·6	62·4	2·4	11781·0	
				Ethyl phenyl ketone				
1	3·51073	23·4	0·301502	42615·1	62·3	2·5	12120·1	
2	3·51625	23·4	0·301935	42676·3	61·4	2·3	12118·7	12120·5
3	3·51463	23·4	0·301895	42670·6	61·9	2·9	12122·4	± 0·8
4	3·51244	23·4	0·301670	42638·8	64·0	2·1	12120·6	
				Propyl phenyl ketone				
1	3·41445	22·6	0·299881	42386·8	47·0	2·1	12399·6	
2	3·41632	22·7	0·300023	42406·9	50·3	2·1	12397·7	12400·0
3	3·41379	22·6	0·299922	42392·6	50·4	2·0	12402·7	± 1·5
				Isobutyl phenyl ketone				
1	3·33339	22·0	0·297763	42086·1	60·9	2·3	12606·7	
2	3·34221	22·0	0·298664	42213·6	61·9	2·5	12611·2	
3	3·34344	22·1	0·298686	42216·3	61·1	2·5	12607·7	12608·8
4	3·33878	22·0	0·298275	42158·5	61·2	2·4	12607·9	± 0·9
5	3·33968	22·0	0·298421	42180·5	61·5	2·3	12610·6	
				tert-Butyl phenyl ketone				
1	3·42902	22·6	0·306826	43367·2	61·7	4·2	12627·9	
2	3·42394	22·6	0·306458	43315·3	61·1	3·0	12632·0	12632·3
3	3·37080	22·2	0·301694	42641·8	61·4	3·1	12631·2	± 2·1
4	3·36889	22·2	0·301686	42640·7	62·6	2·3	12637·9	

Table 3. Heats of combustion and formation of alkyl phenyl ketones

Compound (*liq.*)	$-\Delta E_B$ 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 (kJ/mole)	$-\Delta H_c^\circ$ 25°C (kcal/mole)	ΔH_f° 25°C (kcal/mole)
Methyl phenyl ketone	4147·39 ± 0·89	4144·95 ± 0·89	4148·71 ± 0·89	4148·95 ± 0·89	991·62 ± 0·21	− 34·06 ± 0·25
Ethyl phenyl ketone	4800·90 ± 1·05	4798·28 ± 1·05	4803·29 ± 1·05	4803·66 ± 1·05	1148·10 ± 0·25	− 39·95 ± 0·30
Propyl phenyl ketone	5457·36 ± 1·69	5454·66 ± 1·69	5460·83 ± 1·69	5461·32 ± 1·69	1305·29 ± 0·40	− 45·13 ± 0·45
Isobutyl phenyl ketone	6104·19 ± 1·39	6101·23 ± 1·39	6108·74 ± 1·39	6109·36 ± 1·39	1460·17 ± 0·33	− 52·62 ± 0·39
tert-Butyl phenyl ketone	6115·54 ± 2·26	6112·57 ± 2·26	6120·09 ± 2·26	6120·70 ± 2·26	1462·88 ± 0·54	− 49·91 ± 0·60

(a) The increments in the heats of combustion per CH_2 group added to the chain in the liquids methyl phenyl ketone and methylbenzene have the same value of 156·5 kcal/mole. This identity of increments in the heats of combustion per CH_2 group added to the chain is again reproduced in the liquids propyl phenyl ketone and propylbenzene with the same value of 154·9 kcal/mole.

(b) The increments in the heats of combustion per CH_2 group added to the chain in the liquids ethyl phenyl ketone and ethylbenzene have an unexpected difference of 1 kcal/mole: 157·2 kcal/mole and 156·2 kcal/mole, respectively.

(c) There is an important difference between the heats of isomerization for the liquid state at 25°C of the following reactions:

Isobutyl phenyl ketone ⟶ *tert*-Butyl phenyl ketone −2·7 kcal/mole

Isobutylbenzene ⟶ *tert*-Butyl benzene +0·2 kcal/mole

Finally, from the heat of combustion of benzyl methyl ketone, measured by Springall and Nicholson[5, 3], and our experimental results, the heat of isomerization of the following reaction for the liquid state at 25°C has been computed:

Ethyl phenyl ketone ⟶ Benzyl methyl ketone −3·6 kcal/mole

References

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

[2] M. Colomina, R. Pérez-Ossorio and M. L. Boned. " Thermochemical investigations on methyl-substituted benzoic acids: I. Toluic acids ". This Symposium, *Pure and Appl. Chem.*, **2**, No. 1–2, 137 (1961)

[3] G. R. Nicholson, M. Szwarc and J. W. Taylor. *J. Chem. Soc.*, **1954**, 2767

[4] E. J. Prosen, W. H. Johnson and F. D. Rossini. *J. Research Nat Bur. Standards*, **36**, 455 (1946)

[5] H. D. Springall and R. T. White. *J. Chem. Soc.*, **1954**, 2764