

*Heats of Combustion and Molecular Structure. Part II.\* The Mean Bond Energy Term for the Carbonyl System in Certain Ketones.*

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The heats of combustion ( $-\Delta H_c^\circ$ ) of diacetyl, benzil, benzyl methyl ketone, and dibenzyl ketone, together with the corresponding latent heats of evaporation (or sublimation),  $L_g^\circ$ , have been determined, and used to derive the mean bond energy terms for the carbonyl system,  $\bar{E}(\text{C}=\text{O})$ , in these compounds. The significance of these results is briefly considered.

DURING a thermochemical investigation in 1950, of C-O and C=O compounds, we were requested by Dr. Szwarc to include diacetyl and benzyl methyl ketone. The heats of combustion of these compounds, needed in his kinetic investigations, were accordingly measured and reported to Dr. Szwarc in May 1950. They are now recorded with those for the related substances, benzil and dibenzyl ketone.

#### EXPERIMENTAL

*Materials.*—Diacetyl, supplied by Light and Co. Ltd., was dried (CaO) and fractionated to give a product, b. p. 88.5—89.0°/750 mm. This product was again fractionated from anhydrous calcium oxide and a fraction of b. p. 88.0—88.2°/758 mm. was collected. Henderson, and Heilbron (*Ber.*, 1914, 47, 887) give b. p. 87—88°/760 mm.

Benzil, supplied by Towers and Co. Ltd., was recrystallised four times from 90% ethanol. Fine yellow prisms were obtained, m. p. 94.5—94.9° (corr.). Limpricht and Schwanert (*Annalen*, 1868, 145, 338) give m. p. 95°.

\* Part I, *Trans. Faraday Soc.*, in the press.

Benzyl methyl ketone (reagent quality), supplied by British Drug Houses Ltd., was fractionated from pure dry calcium oxide under reduced pressure, the first fraction being rejected. A fraction of b. p. 96.0—96.2°/9 mm. was collected. Rupe, Metzger, and Volger (*Helv. Chim. Acta*, 1925, 8, 851) give b. p. 98—100°/10 mm.

*Dibenzyl ketone.* The crude yellow acidic material supplied by Light and Co. Ltd. was dissolved in ether, extracted several times with dilute aqueous sodium carbonate, and washed free from alkali. The ether solution was dried (MgSO<sub>4</sub>), passed through alumina to remove the yellow colour, and concentrated under reduced pressure, whereafter the dibenzyl ketone crystallised, which recrystallised three times from light petroleum [b. p. 40—60°; previously dried

TABLE 1.†

$m_{(vac.)}$ (g.)	$\Delta$	$\theta_m$	Corr. (fuse) (cal.)	Corr. (HNO <sub>3</sub> ) (cal.)	Corr. (carbon) (cal.)	$E'$ (cal./deg.)	$C$ (cal./deg.)	$-\Delta U_b$ (kcal./mole)
<i>Diacetyl. M, 86.09.</i>								
1.2491	2.274°	4.25°	71.8	3.2	2.4	3188	0.9	494.7
1.2664	2.303	4.45	71.8	3.4	1.6	3193	0.9	495.0
1.3060	2.373	4.47	71.8	3.5	1.6	3193	0.9	494.7
<i>Benzil. M, 210.22.</i>								
0.9801	2.384	4.32	71.8	2.1	0.8	3190	0.5	1615.2
0.9268	2.259	4.25	71.8	2.1	0.8	3188	0.5	1617.3
0.9818	2.383	4.49	71.8	2.4	0.8	3194	0.5	1614.2
0.9843	2.392	4.57	71.8	2.2	—	3195.5	0.5	1616.8
<i>Benzyl methyl ketone. M, 134.17.</i>								
0.8611	2.338	4.53	71.8	1.5	—	3195	0.6	1152.4
0.9116	2.470	4.49	71.8	1.8	1.6	3194	0.7	1150.7
0.9529	2.584	4.42	71.8	4.2	1.5	3192	0.7	1150.8
0.8776	2.377	4.59	71.8	2.8	0.8	3196	0.6	1150.5
<i>Dibenzyl ketone. M, 210.26.</i>								
0.8396	2.336	4.43	—	2.2	—	3192.5	0.8	1867.3
0.7643 *	2.404	4.65	808.3	11.5	0.8	3198	0.8	1868.2
0.8415	2.342	4.40	—	2.8	0.8	3192	0.8	1868.4

\* Combustion carried out with a gelatin capsule as a container.

† Symbols (see Springall, White, and Cass, *loc. cit.*):  $m_{(vac.)}$  is the mass (*in vacuo*) of the sample burnt in the run;  $\Delta\theta$  is the corrected temperature rise;  $\theta_m$  is the mean temperature (Beckmann thermometer); Corr. (fuse), Corr. (HNO<sub>3</sub>), and Corr. (carbon) are the corrections to be applied for (i) combustion of the larger fuses used for liquids, (ii) the formation of nitric acid, and (iii) the production of unburnt carbon;  $E'$  is the heat capacity of the calorimeter-bomb system (including the fuse correction for solids);  $C$  is the isothermal correction (Washburn, *J. Res. Nat. Bur. Stand.*, 1933, 10, 525), and  $-\Delta U_b$  is the decrease in intrinsic energy during the combustion reaction conducted at the actual calorimeter jacket temperature and at 30 atm. initial pressure and is given by:

$$-\Delta U_b = M/m[(E' + C)\Delta\theta - \text{corr. (fuse)} - \text{corr. (HNO}_3\text{)} + \text{corr. (carbon)}] \times 10^{-3} \text{ kcal./mole.}$$

TABLE 2.\*

Compound	$-\Delta U_b$ mean (kcal./mole)	Standard deviation ( $-\Delta U_b$ ) (%)	Overall uncertainty interval (%)	Washburn corr. $w$ (kcal./mole)	$\Delta nRT$ (kcal./mole)	$-\Delta H_c^\circ$ (kcal./mole)
Diacetyl .....	494.8	0.022	0.036	0.3	-0.3	494.8 ± 0.2
Benzil .....	1615.9	0.043	0.050	1.2	-0.9	1615.6 ± 0.8
Benzyl methyl ketone	1151.1	0.038	0.046	0.7	-1.2	1151.6 ± 0.6
Dibenzyl ketone .....	1868.0	0.019	0.032	1.1	-1.8	1868.7 ± 0.6

\* Symbols:  $w$  is the Washburn correction (Washburn, *loc. cit.*) to convert  $-\Delta U_b$  into the corresponding  $-\Delta U_{298}$  term (at 298° C and 1 atm. initial pressure);  $\Delta n$  is the increase in the number of moles of gas in the reaction;  $-\Delta H_c^\circ$  is the decrease in enthalpy in the combustion reaction at 298° C and 1 atm., the "heat of combustion," and is given by:

$$-\Delta H_c^\circ = -\Delta U_b - w - \Delta nRT \text{ (see Springall, White, and Cass, } loc. cit.).$$

(LiH<sub>2</sub>) as fine colourless needles, m. p. 33.0—33.5°. Stobbe, Russwurm, and Schulz (*Annalen*, 1899, 308, 175) give m. p. 34—35°. As dibenzyl ketone decomposes fairly rapidly, especially when exposed to light and air, the product was pelleted as soon as all the light petroleum had been removed *in vacuo*, over phosphoric oxide.

*Combustion Calorimetry.*—The substances were burnt under 30 atm. pressure of oxygen in the Mahler–Cook stainless steel bomb, the temperature changes being recorded by a Beckmann thermometer. The apparatus, experimental procedure, and the method of calculation are described elsewhere (Springall, White, and Cass, *Trans. Faraday Soc.*, in the press). The results are in Table 1.

*Estimations of Latent Heat (Standard State to Vapour),  $L_g^{st}$ .*—These were made from vapour pressure–temperature measurements in an apparatus developed from Balston's (*Trans. Faraday Soc.*, 1947, 43, 54). [We now use the apparatus described by Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 84.] The results obtained were: diacetyl, 8.6; benzil, 20.9; benzyl methyl ketone, 13.2; dibenzyl ketone, 21.3 kcal./mole.

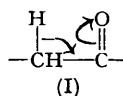
## DISCUSSION.

The values of  $-\Delta H_c^0$  found for diacetyl and for benzil are considerably lower than the values (503.3 and 1624.6 kcal./mole respectively) reported in Kharasch's compilation (*J. Res. Nat. Bur. Stand.*, 1929, 2, 359). Results for benzyl methyl ketone and for dibenzyl ketone have not been previously reported. Recent data are available for acetone (Miles and Hunt, *J. Phys. Chem.*, 1941, 45, 1346) and for ethyl methyl ketone and benzophenone (Parks, Mosley, and Peterson, *J. Chem. Phys.*, 1950, 18, 152). All these  $-\Delta H_c^0$  and the corresponding  $L_g^{st}$  terms are listed in Table 3 together with the corresponding mean C:O bond energy terms;  $\bar{E}(\text{C:O})$  was derived (see Springall, White, and Cass, *loc. cit.*) by using (a) the  $-\Delta H_f^0$  terms, carbon dioxide 94.05, and water 68.32 kcal./mole, (b) the heats of atomisation,  $\Delta H_a$ ,  $C_{\text{graphite}}$  171.7,  $\frac{1}{2}H_{2(g)}$  52.09,  $\frac{1}{2}O_{2(g)}$  59.16 kcal./g.-atom (these are the currently accepted "best" values, see, e.g., "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand. Circular 500, Washington, 1952), (c) the mean bond energy terms,  $\bar{E}$ , C–C 83.1, CH:CH (*cis*) 148.2, C–H 98.85 kcal./mole, and (d) the resonance energy,  $E_r$ , for the  $C_6H_5-C$  system 38.9 kcal./mole.

TABLE 3. *Energy term (in kcal./mole).*

Compound	$-\Delta H_c^0$	$-\Delta H_f^0$	$L_g^{st}$	$\bar{E}(\text{C:O})$	Compound	$-\Delta H_c^0$	$-\Delta H_f^0$	$L_g^{st}$	$\bar{E}(\text{C:O})$
Acetone .....	427.9	59.2	7.4	179.2	Dibenzyl ketone	1868.7	20.3	21.3	180.5
Ethyl methyl ketone .....	582.8	66.7	8.3	180.9	Benzophenone ...	1556.4	7.9	20.4	179.5
Benzyl methyl ketone .....	1151.6	36.45	13.2	178.1	Diacetyl .....	494.8	86.4	8.6	176.5
					Benzil .....	1615.6	42.7	20.9	180.8

The general agreement found among the  $\bar{E}(\text{C:O})$  terms for the monoketonic compounds is good. The mean value, 179.6 kcal./mole, is reasonably concordant with Pauling's value of 152 kcal./mole ("The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1940, p. 131) when account is taken of the different values used here for heats of atomisation and the other bond-energy terms.



With the diketones we feel that the low value of  $\bar{E}(\text{C:O})$  for diacetyl is significant and is probably due to the suppression of the enol-type hyperconjugation (I) by the mutual polarisation of the adjacent carbonyl groups. No detailed consideration can be given at this stage but the work is being continued.

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