The Heats of Formation of Diacetyl and of Benzyl Methyl Ketone in the Vapour Phase.

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The heats of combustion, vaporization, and formation of diacetyl and benzyl methyl ketone have been determined. Special apparatus for purification of the compounds by crystallization has been described and its performance demonstrated on benzene, diacetyl, and benzyl methyl ketone.

Heats of formation, $\Delta H_f(\mathrm{R})$, of free radicals R can be obtained from studies of bond dissociation energies, $D(\mathrm{R{-}R})$, since the heat of formation of a radical R may be obtained from equation (1) :

$$\Delta H_f(\mathrm{R}) = \tfrac{1}{2}[D(\mathrm{R{-}R}) + \Delta H_f(\mathrm{R_2})] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

or from equation (2)

$$\Delta H_f(\mathrm{R}) = D(\mathrm{R{-}R'}) + \Delta H\,(\mathrm{RR'}) - \Delta H\,(\mathrm{R'}) \quad . \; . \; . \; . \quad (2)$$

if $\Delta H_f(\mathrm{R'})$ has been determined independently.

Solution of these equations requires a knowledge of the heat of formation of the parent compound, *i.e.*, $\Delta H_f(\mathrm{R_2})$ or $\Delta H_f(\mathrm{RR'})$.

There have been some attempts to determine the dissociation energies $D(\mathrm{MeCO{\cdot}COMe})$ in diacetyl and $D(\mathrm{PhCH_2{\cdot}COMe})$ in benzyl methyl ketone in order to evaluate the heat of formation of the acetyl radical. The heats of combustion of diacetyl and of benzyl methyl ketone were kindly measured in 1950 by Springall and White, at our request. As the figures were much lower than we expected it was decided to repeat the determinations independently, with even more rigorous purification of the compounds and separate determinations of the heats of combustion and vaporization. It will be observed (see Springall and White, preceding paper) that almost identical heats of combustion were obtained.

Experimental

Purification of the Compounds.—(a) *Crystallization apparatus.* The apparatus (Fig. 1) is essentially a container *A* with a sintered-glass plate. An upward stream of dry nitrogen which was passed through the plate supported a liquid above it and ensured efficient mixing of the liquid whose temperature was measured within ±0·01° by a double-junction copper–constantan thermocouple immersed in it. A cooling-bath *B* enables the rate of cooling to be controlled. When the liquid cooled and had partly crystallized, suction was applied and the mother-liquor collected in the flask below. On rotation of the collecting " pig " through 180° the crystalline material was collected separately after warming. Alternatively the nitrogen stream could be started before the crystals melted and crystallization repeated several times, a small quantity of mother-liquor being removed each time until the material on the sintered plate was sufficiently pure.

The performance of the apparatus was checked by purifying " AnalaR " benzene. Fig. 2 shows the rising m. p. and increasing constancy of the melting temperature. The crystals from the fourth crystallization should be extremely pure, as judged by the almost horizontal direction of the fourth cooling curve, and lack of further increase of the m. p.

(b) *Purification of diacetyl.* Diacetyl was distilled through an 18" × 17 mm. column packed with 1/16" Dixon rings (metal gauze), as supplied by Griffin and Tatlock. The efficiency of the column was estimated at 33 theoretical plates with a carbon tetrachloride–benzene mixture. The fraction collected boiled within 1°. On crystallization as in (a), after the first crystallization of about 80 g. about 20 ml. of mother-liquor were sucked off. Three further crystallizations were made, about 10 ml. of mother-liquor being removed each time. The crystals were then melted and recrystallized without pre-saturation of the nitrogen stream * and hence without the possibility of reintroducing the impurities. The final crystallization took place within 0·05°. The mother-liquor and crystals from this fifth crystallization were sealed in ampoules.

(c) *Purification of benzyl methyl ketone.* The commercial product supplied by L. Light & Co., Ltd., was converted into its semicarbazone (m. p. 187°; recorded values range between 186° and 194°). The latter was crystallized from hot ethanol, about 50% of the semicarbazone dissolved being collected. The ketone was regenerated by refluxing of the semicarbazone with an excess of 12% sulphuric acid, followed by steam-distillation. The colourless oil obtained was dried, and then distilled in a vacuum through the column described above. The middle fraction (about 60% of charge) was redistilled in a high vacuum out of contact with grease, to remove any grease contamination, and crystallized as above.

The m. p. was −15°. The erroneous value (+27°) is reported in Heilbron's " Dictionary of Organic Compounds."

Heats of Combustion.—Heats of combustion were determined in an isothermal bomb calorimeter apparatus of Dickinson type (*Bull. Bur. Stand.*, 1915, **11**, 189), the calorimeter having previously been calibrated by combustion of benzoic acid (National Bureau of Standards sample No. 39g). The bomb had a capacity of 540 c.c., and the temperature of the calorimeter was measured by means of a platinum resistance thermometer in conjunction with a Smith's difference bridge. Soda-glass ampoules were completely filled with diacetyl or benzyl methyl ketone by means of a hypodermic syringe, and then sealed. Filled ampoules were pressure tested at 30 atmosphere (equal to the initial oxygen pressure in the bomb), and those surviving were used for combustion. The weight of liquid used, which depended on the size of the individual ampoule, was 1·4—1·7 g. for diacetyl and 1·5—1·8 g. for benzyl methyl ketone. To assist bursting, the ampoules were smeared locally with a small quantity (about 0·02 g.) of petroleum jelly which was ignited by means of a platinum wire and cotton-thread fuse. Corrections to the gross heat evolved were made for the heats of combustion of the cotton and petroleum jelly (previously determined), the joule heat in the platinum wire, and the heat produced in the formation of a small quantity of nitric acid in the bomb from residual nitrogen in the oxygen. Corrections were also made for very small quantities of residual carbon found fused into the remains of the ampoule in a number of combustion experiments. The weights of the samples for combustion were corrected for buoyancy by using measured densities at 20° of 0·973 g./c.c. (diacetyl) and 1·003 g./c.c. (benzyl methyl ketone). The weights were corrected in addition for the measured water content of the samples, *viz.*, 0·084% (diacetyl) and 0·21% (benzyl methyl ketone). Corrected sample weights were converted into moles by using molecular

FIG. 1.

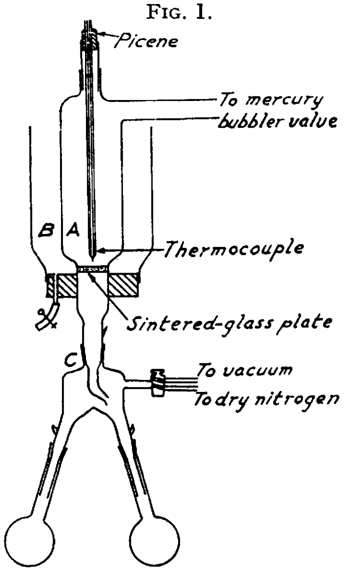
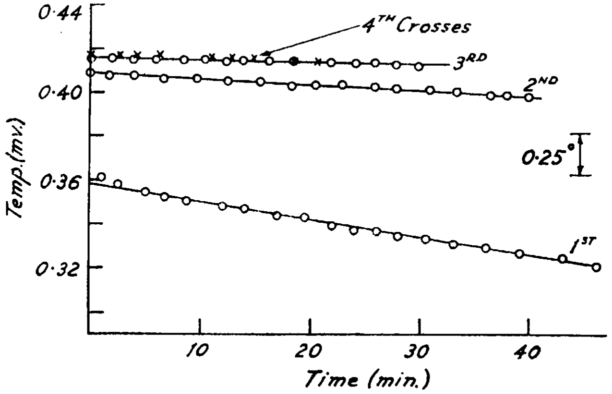


FIG. 2.



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* In the previous crystallizations the nitrogen stream was pre-saturated with diacetyl vapour to avoid local cooling of the liquid and consequent blocking of the plate.

weights of 86·088 (diacetyl) and 134·170 (benzyl methyl ketone). The molar energy change in the bomb process, U_B, was corrected to the standard heat of combustion at 25° and 1 atm., $\Delta H_c°$, by Washburn's method (*J. Res. Nat. Bur. Stand.*, 1933, **10**, 525). The estimated error in the mean value of $\Delta H_c°$ was calculated by combining the combustion error (twice the standard error of the mean $\Delta H_c°$), the benzoic acid calibration error, and the water content determination error of the sample.

Heats of Vaporization.—The latent heat of vaporization of diacetyl was determined by measurement of its vapour pressure in the range 0—20°, where it lay between about 12 and 39 mm. Pressures of this order could conveniently be measured directly on a mercury manometer. An equation of the form $\log_{10} p = A + B/T$ was fitted by least squares to the set of values obtained for vapour pressure (p mm.) against $1/T$ (°K), and the values of the constants were found to be $A = 8{\cdot}63772$ and $B = -2066{\cdot}09$. From the Clapeyron–Clausius equation the heat of vaporization was therefore $\Delta H_v = (2066{\cdot}09 \times 10^{-3}) \,.\, \boldsymbol{R} \,.\, \ln 10 =$ 9·45 kcal./mole at the mean temperature of the set of measurements, 9·96° C, with a standard error in the slope of the straight line of ±0·22 kcal./mole. In the absence of data on the specific heats of liquid and gaseous diacetyl this value of ΔH_v was corrected to the saturation condition at 25°, on the assumption that $\mathrm{d}(\Delta H_v)/\mathrm{d}T = -0{\cdot}0136$ kcal. deg.$^{-1}$ mole^{-1}, the mean value for a number of paraffin hydrocarbons of chain length similar to that of diacetyl ("Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., 1949). The additional correction from saturation pressure to 1 atmosphere at 25° is insignificant. The standard latent heat of vaporization at 25° and 1 atm. was thus calculated at be $\Delta H_v° = 9{\cdot}25 \pm 0{\cdot}22$ kcal./mole.

The latent heat of vaporization of benzyl methyl ketone was determined from the observed variation of vapour pressure with temperature in the range 0—55° approximately. A radioactive ionization gauge, of the type described by Downing and Mellen (*Rev. Sci. Instr.*, 1946, **17**, 218) but modified so that it could be heated above ambient temperature, was used. This apparatus gives an ionization current proportional to the vapour pressure of a given compound for pressures up to about 10 mm. Actual vapour pressure need not be known for the purpose of determining latent heats. Four separate sets of measurements were made and the heat of vaporization calculated by the Clapeyron–Clausius equation. Correction to 25° and 1 atm. was made as for diacetyl and the four values of $\Delta H_v°$ obtained gave as mean 12·78 ± 0·06 kcal./mole.

Heats of Formation.—Standard heats of formation (liquid), $\Delta H_f°$ (l), were calculated from the standard heats of combustion $\Delta H_c°$, with the values −94·052 and −68·317 kcal./mole (*op. cit.*) for the heats of formation respectively of carbon dioxide (g) and water (l). The results are as tabulated (1 calorie = 4·1840 absolute joules).

Compound	$-\Delta H_c°$ (kcal./mole)	$\Delta H_f°$ (l) (kcal./mole)
Diacetyl	493·81 = 0·19	−87·35
Benzyl methyl ketone	1151·65 = 0·40	−36·40

Combining these values for the heats of formation in the liquid state with the respective heats of vaporization gives the following standard heats of formation in the vapour phase, $\Delta H_f°$ (g) :

Compound	$\Delta H_f°$ (g) (kcal./mole)
Diacetyl	−78·10
Benzyl methyl ketone	−22·62

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