Enthalpies of Vaporization of some β-Diketones

By **Roger J. Irving** * and **Manuel A. V. Ribeiro da Silva**, Chemistry Department, University of Surrey, Guildford GU2 5XH

Molar enthalpies of vaporization of six β-diketones have been measured at 298·15 K by a direct calorimetric method; for 1,1,1,5,5,5-hexafluoropentane-2,4-dione, ΔH_v^0 = 7·31 ± 0·03 kcal mol^{-1}, 1,1,1-trifluoropentane-2,4-dione, 8·90 ± 0·4, 2,6-dimethylheptane-3,5-dione, 13·40 ± 0·04, 2,2-dimethylheptane-3,5-dione, 13·59 ± 0·03, 2,2,6-trimethylheptane-3,5-dione, 13·80 ± 0·05, and for 2,2,6,6-tetramethylheptane-3,5-dione, ΔH_v^0 = 14·23 ± 0·03 kcal mol^{-1}. The relationship between the enthalpy of vaporization and the normal boiling point is briefly discussed.

ACETYLACETONE and the β-diketones, in general, form co-ordination compounds with a wide range of metals. Many of these complexes are readily volatile and amenable to thermodynamic study in the vapour state. Thermodynamic data on the β-diketones themselves are scarce.

We now present information on the enthalpies of vaporization of six β-diketones, chosen because they exist predominantly in the enol form in the liquid state.

EXPERIMENTAL

Materials.—The compounds were prepared by methods described in the literature [1,2] and were purified by successive fractional distillations, under vacuum, through a Vigreux column, the midfraction from each one being used for a further fractionation, and then stored under nitrogen in the dark. Hexafluoroacetylacetone was dehydrated using the method of Belford *et al.*,[3] purified by successive fractional distillations and stored over phosphorus pentaoxide under nitrogen in the dark.

The purity of each compound was checked by g.l.c. using two different columns; no impurity could be detected.

Enthalpy measurements were carried out in the LKB Vaporization Calorimeter 8721-3 which was charged with *ca.* 0·2 g of compound. The experimental procedure is described in previous papers.[4,5]

Normally, sufficient sample was weighed into the calorimeter to permit three successive determinations. Unsatisfactory results were obtained if less than 0·05 g remained in the calorimeter, presumably because of poor thermal contact between calorimeter and sample. For both trifluoroacetylacetone and hexafluoroacetylacetone it proved essential to clean and refill the calorimeter for each determination as some decomposition took place after *ca.* 3 h.

The amount of heat (Q) supplied to the calorimeter through the heater resistance (R_h = 49·895) is given by the relation $Q = (R_h I_h^2 t)/4{\cdot}1840$ where the heating current (I_h) is evaluated by measuring the potential drop E (in volts) across a standard resistance R_s (9·998 Ω). Since $I_h = E/R_s$ and substituting R_h and R_s by their values, one obtains $Q = KE^2t$, where K is a constant for the particular calorimeter ($K = 0{\cdot}119297$); the molar enthalpy of vaporization is calculated from the relationship $\Delta H_v = Q/n$, where n is the amount of substance evaporated (in mol).

In a typical experiment with 1,1,1-trifluoropentane-2,4-dione $E = 0{\cdot}2010$ V, $n = 4{\cdot}874 \times 10^{-4}$ mol, $t = 900{\cdot}24$ s.

Much smaller quantities of the higher-boiling compounds were vaporized and the heating current was reduced: for a typical experiment with 2,2-dimethylheptane-3,5-dione, $E = 0{\cdot}1002$ V, $n = 7{\cdot}933 \times 10^{-5}$ mol, $t = 900{\cdot}04$ s.

Thermochemical functions are expressed in terms of the 'thermochemical calorie' (1 thermochemical calorie = 4·184 J exactly) and refer to the isothermal process at 298·15 K and the true mass. The uncertainty interval is twice the standard deviation of the mean (six determinations were made for each compound).

The calorimeter was tested by determining the enthalpy of vaporization of n-decane and n-undecane as described in a previous paper.[4]

The results are presented in the Table.

DISCUSSION

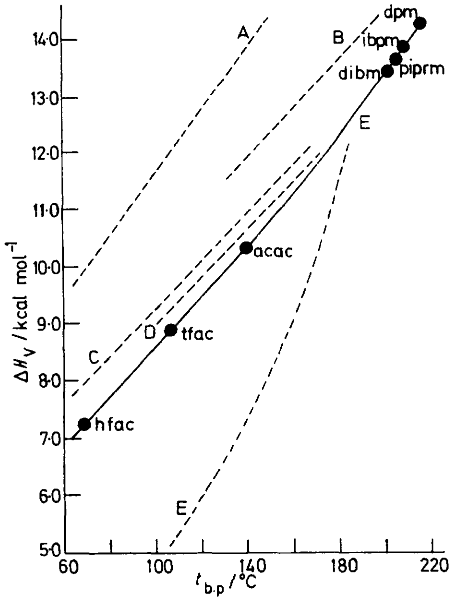
In recent years the application of n.m.r. techniques to the study of the keto–enol tautomeric equilibrium has provided values for the enol percentage of different β-diketones, in the pure liquid state, at different temperatures.[6] The 'best values' are reported in the Table.

Enthalpies of vaporization (298·15 K) of some β-diketones

β-Diketone *	Normal $t_{b.p.}$/°C	Enol %	ΔH_v^0 / kcal mol^{-1}
acac	140	81·4 [10]	+10·33 ± 0·05 [10]
hfac	70	100 [7]	+7·31 ± 0·03
tfac	107	97 [7]	+8·90 ± 0·04
dibm	199—201 [a]	95·8 [8]	+13·40 ± 0·04
piprm	203—204 [a]	93·4 [8]	+13·59 ± 0·03
ibpm	206—208 [a]	97 [9]	+13·80 ± 0·05
dpm	214—216 [a]	98·0 [8]	+14·23 ± 0·03

[a] Reduced to normal pressure using the Dreisback tables.[11]

* acac = pentane-2,4-dione; hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dione tfac = 1,1,1-trifluoropentane-2,4-dione; dibm = 2,6-dimethylheptane-3,5-dione; piprm = 2,2-dimethylheptane-3,5-dione; ibpm = 2,2,6-trimethylheptane-3,5-dione; dpm = 2,2,6,6-tetramethylheptane-3,5-dione



Relationship between boiling point and enthalpy of vaporization: A, alcohols (ROH); B, alkoxyacetates ($ROCH_2{\cdot}CH_2{\cdot}OAc$); C, *O*-esters ($RCO_2R'$); D, *S*-esters + ketones (RCOSR' + RCOR'), E; lower carboxylic acids (RCO_2H)

The values of the molar enthalpies of vaporization refer to the isothermal vaporization (298·15 K) of the pure liquid (keto–enol) to the real gas (keto–enol) formed under its saturated vapour pressure. Neither the keto–enol composition of the vapour nor the enthalpy of enolization of these compounds is known. For acetylacetone [10] the heat of enolization of the vapour is −2·4 kcal mol^{-1} and for the liquid it is −2·7 kcal mol^{-1}.

On this basis even assuming complete conversion to

---

[1] J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.

[2] K. R. Kopecky, D. C. Nonhebel, G. Morris, and G. S. Hammond, *J. Org. Chem.*, 1962, **27**, 1036.

[3] R. L. Bedford, A. E. Martell, and M. Calvin, *J. Inorg. Nuclear Chem.*, 1956, **2**, 11.

[4] R. J. Irving, *J. Chem. Thermodynamics*, 1972, **4**, 793.

[5] I. Wadsö, *Acta Chem. Scand.*, 1966, **20**, 536.

[6] L. W. Reeves, *Canad. J. Chem.*, 1957, **35**, 1351.

[7] J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, 1964, **86**, 2105.

[8] H. Koshimura, J. Saito, and T. Okubo, *Bull. Chem. Soc. Japan*, 1973, **46**, 632.

[9] G. K. Schweitzer and E. W. Benson, *J. Chem. and Eng. Data*, 1968, **13**, 452.

[10] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1970, **24**, 589.

[11] R. R. Dreisbach, 'Pressure–Volume–Temperature Relationships of Organic Compounds,' Handbook Publishers Inc., Ohio, 1952, 3rd edn.

the enol in the vapour state, it is calculated that the values for the vaporization of pure liquid to real gas for all compounds in the Table are the same as for liquid (100% enol) to gas (100% enol) within the experimental error quoted.

Correlation between ΔH_v^0 *and Normal Boiling Points*.—A plot of the β-diketones (see Figure) shows all seven falling on a smooth weakly convex curve of equation $\Delta H_v^0 = 4{\cdot}85 + 3{\cdot}15 \times 10^{-2}t_{\text{b.p.}} + 5{\cdot}65 \times 10^{-5}t_{\text{b.p.}}^2$.

Some of Wadsö's [12-16] results are plotted together with the results obtained in the present work showing that the β-diketone curve lies very close to the families of slightly associated compounds, suggesting that the β-diketones have a very low or even non-existent degree of association. This is to be expected, as the enolic hydrogen of the β-diketones forms an intramolecular hydrogen bond with the ketonic oxygen.

If Wadsö's relationship, $\Delta H_v = 5{\cdot}0 + 0{\cdot}041t_{\text{b.p.}}$, is used to calculate the heats of vaporization of the β-diketones, reasonable results are obtained, the maximum variations occurring at the two extremes, hfac being 0·6 kcal mol^{-1} more exothermic, and dpm 0·4 kcal mol^{-1} less exothermic than the experimentally determined values.

It is interesting to note that the increment of a methylene group on a secondary carbon increases the ΔH_v by +0·2 kcal mol^{-1} and the increment of a methylene group on a tertiary carbon increases the ΔH_v by 0·4 kcal mol^{-1}. These increments are remarkably close to those of the much more thoroughly studied aliphatic ketone series.

One of us (M. A. V. R. S.) expresses his gratitude to the Calouste Gulbenkian Foundation, Lisbon, for financial support and to the Chemistry Department of the Faculty of Sciences of Oporto University and to the ' Instituto de Alta Cultura,' Portugal, for leave of absence.

[4/1844 *Received*, *9th September*, 1974]

---

[12] I. Wadsö, *Acta Chem. Scand.*, 1966, **20**, 544.

[13] I. Wadsö, *Acta Chem. Scand.*, 1969, **23**, 2061.

[14] P. B. Howard and I. Wadsö, *Acta Chem. Scand.*, 1970, **24**, 145.

[15] J. Konicek and I. Wadsö, *Acta Chem. Scand.*, 1970, **24**, 2612.

[16] K. Kusano and I. Wadsö, *Acta Chem. Scand.*, 1971, **25**, 219.