Heats of Formation of Aliphatic Ketones: Structure Correlation Based on Environment Treatment

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Summary The difference between the heat of formation of an aliphatic ketone and that of the isotopological alkane is separated into a carbonyl group contribution and topological perturbations from its ordered environment.

Recently Sellers[1] analysed the heats of formation of α- and β-substituted aliphatic ketones and proposed a relationship based on an Allen type bond energy scheme[2] using parameters determined by Nelander and Sunner.[3] Skinner's [*S*] terms which correct for the destabilising effect of steric hindrance[4] were not included. In Sellers' view, then, the differences between experimental and calculated values are a measure of the steric effects upon the heats of formation. Thus, for 2,2,4,4-tetramethylpentan-3-one, the difference of 4·7 kcal/mol is attributed to the steric interaction between the two t-butyl groups.

We report now, in addition to new experimental data, an original method for the calculation of ΔH°_f for ketones, based on the graphs of the ketones and the isotopological saturated hydrocarbons, *i.e.* alkanes with the same graph as the ketones, where >CMe replaces >C=O.

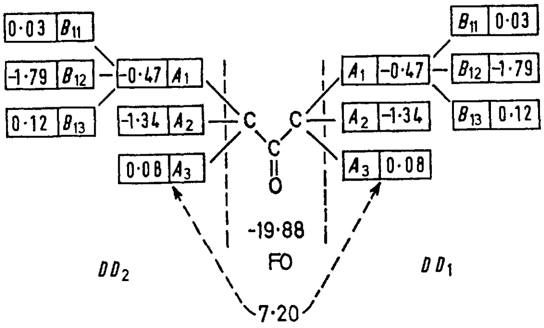

Figure. *Topological perturbations to the heat of formation. The total for a given ketone is the difference between its heat of formation and that of the alkane with the same graph. Thus for* 3,3-*dimethylpentan*-2-*one:* ΔH°_f (*ketone*) = *focus* + $A_1 + A_2 + A_3 + B_{11}$ + ΔH°_f (alkane) = − 19·88 − 0·47 − 1·34 + 0·08 + 0·03 − 51·42 = − 73·00 kcal/mol.

Table

Heats of formation of aliphatic ketones.[a] (*Mean deviation between experimental and calculated values,* 0·20 kcal/mol; *correlation coefficient,* 0·999)

Compound	DEL[b] DD_1	DEL[b] DD_2	ΔH°_f(gas) in kcal/mol for ketones: Expt.	ΔH°_f(gas) in kcal/mol for ketones: Calc.	ΔH°_f(gas) in kcal/mol for alkanes[c]
3-Methylpentan-2-one	(2100)	(0000)	−67·90 ± 0·32	−67·90	−46·24
4-Methylpentan-2-one	(1110)	(0000)	−69·60 ± 0·34	−69·05	−46·94
Heptan-4-one	(1100)	(1100)	−71·30 ± 0·31	−71·20	−50·44
3,3-Dimethylpentan-2-one	(3100)	(0000)	−72·60 ± 0·41	−73·00	−51·42
4,4-Dimethylpentan-2-one	(1111)	(0000)	−76·60 ± 0·45	−76·46	−54·47
3,3,4-Trimethylpentan-2-one	(3110)	(0000)	−78·50 ± 0·41	−78·18	−54·81
3,3,4,4-Tetramethylpentan-2-one ..	(3111)	(0000)	−83·10 ± 0·42	−82·95	−59·70

[a] Full experimental details will be published elsewhere. [b] DEL (ref. 5b) describes the state of occupancy of the different sites in the environment of the carbonyl group. [c] Since data were not available for all the isotopological alkanes their heats of formation were calculated from the existing data (19 alkanes[6]) by an interpolation method which has been previously described: J. E. Dubois and D. Laurent, *Compt. rend.*, 1967, **265C**, 780; 1968, **266C**, 608; 1969, **268A**, 405.

The difference between the heat of formation of a ketone and that of the isotopological alkane is not constant. Thus, for acetone and 2-methylpropane, the value is 19·88 kcal/mole whereas for 2,2,4,4-tetramethylpentan-3-one and the corresponding alkane the difference is only 16·14 kcal/mol. The perturbation due to the presence of the carbonyl group is, therefore, a function of its environment. This environment can be organised by application of the DARC system[5] into a series of concentric shells, the centre being identified as the 'focus' FO (see Figure). For ketones it is convenient to take the focus as ⋟C–CO–C⋞ and to consider that the difference in the heats of formation is made up of a contribution due to the focus together with increments associated with different topologically defined sites in the alkyl group environments DD_1 and DD_2† and interaction terms.

The results of applying this procedure are shown in the Table and in the Figure. The graph is based on the heats of formation for 21 ketones of which 14 were taken from the literature (1,6—8) and 7 were determined in this laboratory (see Table).

The greater part of the ΔH°_f difference (19·88 kcal/mol) is seen to be associated with the focus but topological contributions cause this difference to vary over nearly 11 kcal/mol. Of particular interest is the interaction term of 7·20 kcal/mol which is required when both A_3 positions are occupied, as in highly hindered ketones such as 2,2,4,4-tetramethylpentan-3-one. This puts a higher value on the importance of steric effects than does Sellers' calculation. Similar large interaction terms have been found in studies of the i.r.[9] and u.v.[10] spectra of this and related ketones.

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† Equivalent sites in DD_1 and DD_2 are assigned the same increment.

In the group additivity scheme[8] a group is defined as an atom and its ligands, but next-nearest neighbour or more remote effects are not considered except by the introduction of special corrections. In the topological treatment described here, all interactions are in principle calculable and the precision of the calculation depends only on the size of the available ketone and reference alkane populations. Extension of this work to more highly substituted ketones[11] is in progress.

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