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THERMOCHEMICAL DATA OF CARBONYL COMPOUNDS VIA THEIR BOND SEPARATION ENERGIES

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Two types of equivalents for the aldo and the keto groups have been developed, the Schleyer and the bond separation energy (*BSE*) equivalents. The equivalents were used to give the heats of formation and the *BSE* of unstrained models. These equivalents were then used in the calculations of the strain energies for aldehydes and ketones. The results obtained were compared with MM2 values. The equivalents were also used in calculations of the stabilization (destabilization) energies for conjugated carbonyl compounds. The results obtained correlate well with the available experimental data.

INTRODUCTION

Heats of formation, ΔH_f, of unstrained models are usually obtained by the summation of strain-free group equivalents. Franklin[1] and Benson *et al.*[2] separately developed group equivalents for most organic compounds and Schleyer *et al.*[3] developed a set of group equivalents for alkanes. The conventional strain energy, *SE*, is defined as the difference between the experimental ΔH_f and that of the unconstrained model.[4] In this work, the *SE*s are named according to the equivalents from which they were calculated. For example, the Schleyer *SE* means that it was calculated via the Schleyer equivalents. Allinger *et al.*[5] developed general and strain-free bond equivalents. For a given compound, the summation of the general equivalents reproduces the experimental heat of formation while that of the unstrained model is obtained by the summation of the strain-free equivalents. The *SE* is the difference between the two summations. The *SE*s calculated via the two types of Allinger bond equivalents are named MM2 *SE*s.

Another comparable method used for the calculation of the *SE*s is the bond separation energy (*BSE*) method.[6] In this method, the *SE* is calculated via the equation

$$SE = \sum_{i=1}^{k} N_i X_i - BSE_{\text{exptl}} \ (\text{kcal mol}^{-1}) \qquad (1)$$

where N_i is the number of groups of type i, X_i the equivalent for group i and K the number of different groups in the molecule. The summation term of equation (1), $\Sigma N_i X_i$, is the *BSE* for the unstrained model and BSE_{exptl} is the experimental *BSE* for the compound. The definition and the method of calculation of BSE_{exptl} are explained in detail elsewhere.[6,7] *BSE* equivalents have been developed for CH_3, CH_2, CH, C, $H_2C{=}$, HC= and C= groups.[6] This method has successfully reproduced the thermochemical data for alkanes and alkenes.[6] Therefore, there is real convenience in extending this method to other classes of organic compounds. The aim of this work was the development of *BSE* equivalents for the aldo and the keto groups. Consequently, the *SE*s of carbonyl compounds can be calculated via equation (1). The values obtained in this work are compared with MM2 *SE*s. The developed *BSE* equivalents are also used in the calculations of the stabilization (destabilization) energies for conjugated carbonyl compounds, the results being compared with the available experimental data.

Schleyer *et al.* used their equivalents for alkanes and the Benson equivalents for the alkenes to calculate the *SE*s for alkenes. This set of equivalents will be referred to as Schleyer equivalents. To include other classes of organic compounds in the Schleyer equivalents, equivalents for the aldo and the keto groups have been developed in this work. The results obtained via these equivalents are compared with those calculated via the *BSE* equivalents and with the available experimental data.

Both *BSE* equivalents and Schleyer equivalents for the aldo and the keto groups are derived to reproduce the *SE*s for propanal and butan-2-one. These com-

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pounds were chosen because the enthalpy differences between the conformers of each compound are known. This knowledge is necessary for the calculation of their *SE*s. Therefore, the calculations of *SE*s for propanal and butan-2-one will be discussed before the method of the derivation of the equivalents.

Calculation of SE of propanal

Microwave spectroscopy[8,9] revealed that the eclipsed conformer of propanal is more stable than the *gauche* conformer by 0·9 kcal mol^{-1}. The CCCO dihedral angle is 0·0° in the former and either 60° or 280° in the latter. Entropy favours the *gauche* conformer by $R \ln 2$. The free energy difference, ΔG, between the two conformers is 0·49 kcal mol^{-1} as calculated via equation (2) at 298 K. Applying equation (3) at 298 K indicates that the population of the gauche is 30%. This population yields an *SE* for propanal of 0·27 kcal mol^{-1}.

$$\Delta G = \Delta H - T\,\Delta S \qquad (2)$$

$$\Delta G = -RT \ln K_{eq} \qquad (3)$$

Calculation of SE of butan-2-one

IR spectroscopy, electron diffraction and microwave spectroscopy show that the *trans* conformer of butan-2-one is more stable than the *gauche* conformer by 0·7 kcal mol^{-1}.[9] The *trans* conformer is the one in which the two methyls are *trans* to each other whereas they are *gauche* to each other in the *gauche* conformer. Applying the same procedure described above gives an *SE* for butan-2-one of 0·27 kcal mol^{-1}.

Derivation of the group equivalents

The *BSE* equivalents are derived via equation (1). The *SE*s of propanal and butan-2-one are calculated above. The BSE_{exptl} are the experimental enthalpy changes for reactions (3) and (4).

$$CH_3CH_2CHO + 2CH_4 \rightarrow 2CH_3CH_3 + H_2CO \qquad (3)$$

$$CH_3CH_2COCH_3 + 3CH_4 \rightarrow 3CH_3CH_3 + H_2CO \qquad (4)$$

These enthalpy changes are 14·14 and 20·02 kcal mol^{-1}, respectively. The experimental heats of formation of reactants and products used are those reported by Cox and Pilcher,[10] except for propanal, where the value reported by Pedley and Rylance[11] is used in the calculations. This choice was built on the fact that the Pedley and Rylance value (−44·79 kcal mol^{-1}) is closer to the MM2 value (−44·39 kcal mol^{-1})[5] than the Cox and Pilder value (−45·45 kcal mol^{-1}).[10] Using *BSE* equivalents for CH_3 and CH_2 groups[6] gives aldo and keto *BSE* equivalents of 11·59 and 21·40 kcal mol^{-1}, respectively. These values are given in Table 1 together with the previously obtained *BSE* equivalents for alkanes and alkenes.

Table 1. Strain-free heats of formation (Schleyer) and the *BSE* equivalents

	Equivalent (kcal mol^{-1})	
Group	*BSE*	Schleyer
H_3C	0·07[a]	−10·05[b]
H_2C	2·75[a]	−5·13[b]
HC	7·42[a]	−2·16[b]
C	13·11[a]	−0·30[b]
$H_2C{=}$	0·0[a]	6·26[c]
$HC{=}$	5·36[a]	8·59[c]
$C{=}$	11·29[a]	10·34[c]
$HC{=}O$	11·59	−29·88
$C{=}O$	21·40	−32·06

[a] Ref. 6
[b] Ref. 3.
[c] Ref. 2.

Schleyer equivalents for the aldo and the keto groups were also developed to reproduce the *SE*s of propanal and butan-2-one. These equivalents are also listed in Table 1.

RESULTS AND DISCUSSION

Schleyer and *BSE* strain energies were calculated for a large number of aldehydes and ketones from their experimental heats of formation. The MM2 heats of formation of cyclobutanone, cyclopentane and cyclohexane carboxaldehydes were used because their experimental heats of formation are not available.

Schleyer and *BSE* *SE*s for aldehydes and acyclic ketones are given in Tables 2 and 3, respectively. The MM2 *SE*s, reported by Allinger *et al.*,[5] are also given for comparison. The r.m.s. deviations of the Schleyer and *BSE* *SE*s relative to MM2 values are 0·79 and 0·56 kcal mol^{-1} for aldehydes and acyclic ketones, respectively. Hence the Schleyer and *BSE* *SE*s correlate well with the corresponding MM2 strain energies for both aldehydes and acyclic ketones.

The *SE*s of cyclic ketones calculated via Schleyer and *BSE* equivalents are listed in Table 4. The results show that the MM2 *SE*s are much higher than the others. It seems that MM2 strain energies are overestimated for cyclic ketones. The MM2 *SE*s of *cis*- and *trans*-bicyclo[3.3.0]octanes are 13·56 and 19·98 kcal mol^{-1}, respectively.[13] The corresponding Schleyer *SE*s are 12·4 and 18·7 kcal mol^{-1} as calculated from the experimental heats of formation reported by Pedley *et al.*[14] It is known that the angle bending is unfavourable at the carbonyl in cyclopentanone, but the removal of the eclipsing interaction by replacing a CH_2 by a carbonyl

Table 2. Calculations of strain energies for aldehydes[a]

Molecular formula	Molecule	ΔH_f°(g)	Observed *BSE*	$\sum_{i=1}^{k} n_i x_i$	*SE* Schleyer[b]	*SE* *BSE*[b]	*SE* MM2[c]
C_2H_4O	Acetaldehyde	−39·73[d]	11·43	11·66	0·20	0·23	0·0
C_3H_6O	Propanal	−44·79[e]	14·14	14·41	0·27	0·27	0·27
C_4H_8O	Butanal	−49·59[e]	16·59	17·16	0·60	0·57	0·52
C_4H_8O	2-Methylpropanal	−51·53[e]	18·53	19·15	0·61	0·62	1·11
$C_5H_{10}O$	Pentanal	−54·45[f]	19·10	19·91	0·87	0·81	0·70
$C_6H_{10}O$	Cyclopentanecarboxaldehyde	−43·55[g]	21·39	30·01	9·01	8·62	8·83
$C_6H_{12}O$	Hexanal	−59·37[h]	21·67	22·66	1·08	0·99	0·88
$C_6H_{12}O$	3,3-Dimethylbutanal	−63·89[g]	26·19	27·66	1·57	1·47	1·00
$C_7H_{12}O$	Cyclohexanecarboxaldehyde	−55·32[g]	30·81	32·76	2·37	1·95	2·25
$C_7H_{14}O$	Heptanal	−63·1[d]	23·05	25·41	2·48	2·36	1·06
$C_8H_{16}O$	Octanal	−69·23[h]	26·83	28·16	1·48	1·33	1·24
$C_8H_{16}O$	2-Ethylhexanal	−71·6[e]	29·20	30·15	1·06	0·95	3·34
$C_9H_{18}O$	Nonanal	−74·16[h]	29·41	30·91	1·68	1·50	1·41
$C_{10}H_{20}O$	Decanal	−79·09[h]	31·99	33·66	1·88	1·67	1·58

[a] All energies in kcal mol^{-1}.
[b] This work.
[c] Ref. 5.
[d] Ref. 10.
[e] Ref. 11.
[f] Ref. 12.
[g] MM2 value reported in Ref. 5.
[h] Experimental value reported in Ref. 5.

carbon is more important and hence the ketone has a lower *SE* than the hydrocarbon.[5] The MM2 *SE*s of *cis*- and *trans*-bicyclo[3.3.0]octan-3-ones are 16·85 and 19·38 kcal mol^{-1}, respectively (Table 4). Both values are either higher than or very close to those of the corresponding hydrocarbons, although it is expected that they will be lower in comparison to that observed with cyclopentanone and cyclopentane. Similar arguments could be used for *cis*- and *trans*-hydrindan-2-ones and most of the other compounds listed in Table 4.

The stabilization (destabilization) energies of 28 conjugated carbonyl compounds were calculated (Table 5). MM2 stabilization energies are not included because there are no general and strain-free bond equivalents for alkenes. The equivalents were used to reproduce strain energies. However, if there is a resonance stabilization energy in a specific compound, the equivalents will give the algebraic sum of the resonance and strain energies. Therefore, the results in Table 5 represent the net balance between resonance stabilization and strain destabilization energies. For example, Herndon[19] concluded, from photoelectron spectra, that the resonance stabilization energy in cyclopropenone is 23·2 kcal mol^{-1}. Greenberg *et al.*[15] estimated that the strain energy of cyclopropenone is 67 kcal mol^{-1}. Hence cyclopropenone has a destabilization energy of about 44 kcal mol^{-1}. This value is in fair agreement with the destabilization energy obtained via Schleyer and *BSE* equivalents as shown in Table 5.

The equivalents give a stabilization energy for tropone of 9·0–9·5 kcal mol^{-1}. Correction for the *cis* configuration by 1 kcal mol^{-1} for each double bond gives a resonance stabilization energy in tropone of 12·0–12·5 kcal mol^{-1}. The corresponding value reported by Herndon[19] from photoelectron spectra is 10·8 kcal mol^{-1}.

Shiner *et al.*[17] reported that 2,4- and 2,5-cyclohexadien-1-ones, the keto tautomers of phenol, have resonance stabilization energies. Unfortunately, they did not report the values. The results in Table 5 show that the stabilization energy is 14·5 kcal mol^{-1} in the linearly conjugated dienone and 10·5 kcal mol^{-1} in the cross-conjugated dienone. The resonance stabilization in each is higher by 2 kcal mol^{-1} owing to the *cis* configuration at the two double bonds.

The results obtained (Table 5) are in good agreement with the experimental values resulting from hydrogenation experiments. These experiments show that the resonance stabilization energies in benzaldehyde and *p*-benzoquinone are 35 and 3 kcal mol^{-1}, respectively.[20] After the consideration of the *cis*-configuration corrections, the stabilization energies in benzaldehyde and *p*-benzoquinone will be 32 and 1 kcal mol^{-1}, respectively. The experimental stabilization energy of benzaldehyde is reproduced by Schleyer and *BSE* equivalents whereas that of the quinone is only reproduced by *BSE* equivalents, as shown in Table 5.

The results in Table 5 also show that the aliphatic

Table 3. Calculations of strain energies for acyclic ketones[a]

Molecular formula	Molecule	ΔH_f°(g)	Observed *BSE*	$\sum_{i=1}^{k} n_i x_i$	*SE* Schleyer[b]	*SE* *BSE*[b]	*SE* MM2[c]
C_3H_6O	Acetone	−51·90[d]	21·25	21·54	0·26	0·29	0·0
C_4H_8O	Butan-2-one	−57·02[e]	24·02	24·29	0·27	0·27	0·05
$C_5H_{10}O$	Pentan-2-one	−61·92[d]	26·57	27·04	0·50	0·47	0·28
$C_5H_{10}O$	Pentan-3-one	−61·76[f]	26·41	27·04	0·66	0·63	0·29
$C_5H_{10}O$	3-Methylbutan-2-one	−62·76[e]	27·41	29·03	1·61	1·62	1·36
$C_6H_{12}O$	Hexan-2-one	−66.87[d]	29·17	29·79	0·68	0·62	0·46
$C_6H_{12}O$	Hexan-3-one	−66.51[d]	28·81	29·79	1·04	0·98	0·51
$C_6H_{12}O$	2-Methylpentan-3-one	−68·38[d]	30·68	31·78	1·12	1·10	1·70
$C_6H_{12}O$	3,3-Dimethylbutan-2-one	−69·28[d]	31·58	34·79	3·28	3·21	2·57
$C_7H_{14}O$	2,2-Dimethylpentan-3-one	−74·99[d]	34·94	37·54	2·70	2·60	2·76
$C_7H_{14}O$	2,4-Dimethylpentan-3-one	−74·40[d]	34·35	36·52	2·18	2·17	2·74
$C_8H_{16}O$	2,2,4-trimethylpentan-3-one	−80·84[d]	38·44	42·28	3·93	3·84	5·31
$C_9H_{18}O$	Nonan-5-one	−82·44[d]	37·69	38·04	0·50	0·35	0·74
$C_9H_{18}O$	2,6-Dimethylheptan-4-one	−85·47[f]	40·72	42·02	1·37	1·30	1·91
$C_9H_{18}O$	2,2,4,4-Tetramethylpentan-3-one	−82·65[f]	37·90	48·04	10·31	10·14	9·61
$C_{10}H_{20}O$	2,2,5,5-Tetramethylhexan-3-one	−94·15[d]	47·05	50·79	3·94	3·74	3·56
$C_{11}H_{22}O$	2,2,6,6-Tetramethylheptan-4-one	−100·67[f]	51·22	53·54	2·55	2·32	[g]

[a] All energies in kcal mol^{-1}.
[b] This work.
[c] Ref. 5.
[d] Refs 10 and 11.
[e] Ref. 10.
[f] Ref. 11.
[g] Not reported.

Table 4. Calculations of strain energies for cyclic ketones[a]

Molecular formula	Molecule	ΔH_f°(g)	Observed *BSE*	$\sum_{i=1}^{k} n_i x_i$	*SE* Schleyer[b]	*SE* *BSE*[b]	*SE* MM2[c]
C_4H_6O	Cyclobutanone	−18·80[d]	1·34	29·65	28·65	28·31	29·03
C_5H_8O	Cyclopentanone	−46·03[e]	26·22	32·40	6·55	6·18	6·40
$C_6H_{10}O$	Cyclohexanone	−54·04[e]	31·88	35·15	3·67	3·27	2·79
$C_7H_{12}O$	Cycloheptanone	−59·1[f]	34·59	37·90	3·74	3·31	6·51
$C_8H_{12}O$	*cis*-Bicyclo[3.3.0]octan-3-one	−55·0[f]	43·68	49·99	7·03	6·31	16·85
$C_8H_{12}O$	*trans*-Bicyclo[3.3.0]octan-3-one	−49·4[f]	30·08	49·99	12·63	11·91	19·38
$C_8H_{12}O$	Bicyclo[2.2.2]octan-2-one	−53·1[f]	41·78	49·99	8·93	8·21	11·42
$C_8H_{14}O$	Cycloctanone	−64·9[f]	38·04	40·65	3·07	2·61	8·97
$C_9H_{14}O$	*cis*-Hydrindan-2-one	−59·66[g]	45·99	52·74	7·50	6·75	9·25
$C_9H_{14}O$	*trans*-Hydrindan-2-one	−59·56[g]	45·89	52·74	7·60	6·85	8·58
$C_{10}H_{16}O$	*cis*-8-Methylhydrindan-2-one	−68·59[g]	52·57	58·50	6·76	5·93	9·46
$C_{10}H_{16}O$	*trans*-8-Methylhydrindan-2-one	−65·77[g]	49·75	58·50	9·58	8·75	11·56
$C_{15}H_{28}O$	Cyclopentadecanone	−99·1[f]	55·79	59·90	4·78	4·11	[h]
$C_{17}H_{32}O$	Cyclopentadecanone	−110·0[f]	62·0	65·40	4·14	3·40	[h]

[a] All energies in kcal mol^{-1}.
[b] This work.
[c] Ref. 5.
[d] MM2 value reported in Ref. 5.
[e] Ref. 10.
[f] Refs 10 and 11.
[g] Ref. 11.
[h] Not reported.

Table 5. Calculations of stabilization (destabilization) energies of conjugated carbonyl compounds[a]

Molecular formula	Molecule	ΔH_f°(g)	Observed *BSE*	$\sum_{i=1}^{k} n_i x_i$	*SE*	
					Schleyer[b]	*BSE*[b]
$C_2H_2O_2$	Ethanedial	−50·66[b]	14·3	23·2	9·1	8·9
C_3H_2O	Cyclopropenone	+33[c]	−15·4	32·1	47·9	47·5
C_3H_4O	Propenal	−18·0[d]	20·0	16·95	−2·9	−3·0
$C_3H_4O_2$	Propane-1,2-dione	−64·8[b]	26·1	33·1	7·2	7·0
C_4H_6O	But-2-enal	−24·76[e]	24·4	22·4	−2·0	−2·0
$C_4H_6O_2$	Butane-2,3-dione	−78·20[f]	37·1	42·9	6·0	5·8
$C_5H_8O_2$	Pentane-2,4-dione	−90·47[f]	47·1	45·7	−1·1	−1·4
C_6H_6O	Cyclohexa-2,4-dien-1-one	−17 ± 3[g]	60·2	45·6	−14·2	−14·6
C_6H_6O	Cyclohexa-2,5-dien-1-one	−13 ± 3[g]	56·2	45·6	−10·2	−10·6
$C_6H_4O_2$	*p*-Benzoquinone	−29·4[e]	64·6	64·2	0·4	−0·4
C_7H_6O	Benzaldehyde	−8·8[b]	82·4	49·7	−32·2	−32·7
C_7H_6O	Tropone	+10·5[e]	63·1	53·6	−9·0	−9·5
C_8H_8O	Acetophenone	−20·71[b]	91·9	59·6	−31·9	−32·3
$C_9H_{10}O$	1-Phenylpropan-1-one	−25·98[b]	94·8	62·3	−32·0	−32·5
$C_9H_{10}O$	1-Phenylpropan-2-one	−23·52[b]	92·4	62·3	−29·6	−30·1
$C_{10}H_{12}O$	1-Phenylbutan-1-one	−30·63[b]	97·1	65·1	−31·6	−32·0
$C_{10}H_6O_2$	1,4-Naphthoquinone	−26·5[b]	133·2	97·5	−34·6	−35·7
$C_{11}H_{14}O$	3-Methyl-1-phenylbutan-1-one	−38·41[b]	102·6	69·8	−32·5	−32·8
$C_{13}H_{10}O$	Benzophenone	+14·1[e]	159·0	97·6	−60·4	−61·4
$C_{14}H_{12}O$	1,2-Diphenylethanone	+5.3[e]	165·4	100·3	−64·1	−65·1
$C_{14}H_8O_2$	9,10-Anthraquinone	−22·8[b]	201·0	130·8	−68·8	−70·2
$C_{14}H_8O_2$	9,10-Phenanthraquinone	−33·3[b]	211·5	130·8	−79·3	−80·7
$C_{14}H_{10}O_2$	Diphenylethanedione (benzil)	−13·26[b]	175·9	119·0	−55·7	−56·9
$C_{15}H_{10}O$	Diphenylcyclopropenone	86 ± 4[h]	130·6	120·2	−9·2	−10·4
$C_{15}H_{14}O$	1,3-Diphenylpropan-2-one	+1·2[f]	167·2	103·1	−63·1	−64·1

[a] All energies in kcal mol^{-1}.
[b] Refs 10 and 11.
[c] *Ab initio* value reported in Ref. 15.
[d] Ref. 16.
[e] Ref. 11.
[f] Ref. 10.
[g] Ref. 17.
[h] Ref. 18.

1,2-diones have destabilization energies. For example, the destabilization energies for ethanedial, propane-1,2-dione and butane-2,3-dione are 8·9, 7·0 and 5·8 kcal mol^{-1}, respectively, as calculated from the *BSE* equivalents. This can be attributed to the electrostatic repulsion between the adjacent carbonyl carbons. The decrease in the destabilization energies in the diones is due to the inductive effect of the methyl group.

CONCLUSION

Schleyer and *BSE* equivalents for the aldo and the keto groups have been derived only from thermochemical data of propanal and butan-2-one. In spite of this, the *SE*s calculated via these equivalents for aldehydes and acyclic ketones correlate well with the MM2 *SE*s. Schleyer and *BSE* equivalents give lower *SE*s than the MM2 values for cyclic ketones. However, it is believed that the MM2 *SE*s are overestimated. The present calculations also show that Schleyer and *BSE* equivalents successfully reproduce the available experimental data for conjugated carbonyl compounds.

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