

DISSOCIATION ENERGIES OF METAL-CARBON BONDS AND THE EXCITATION ENERGIES OF METAL ATOMS IN COMBINATION

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Volatile methyl compounds are formed by the majority of elements standing up to six places before a rare gas, so that as a class they represent all groups and periods of the Periodic System with the exception of Group I. Accordingly, the volatile methyls provide a particularly suitable class of compounds for a comparative study of the covalent bonds which the metals and non-metals concerned form with carbon; and this study in turn throws light on the magnitudes of the internal excitation energies possessed by these elements when engaged in covalent bonding. Former approaches to this problem have been almost entirely theoretical.

For convenience, the term "metal-carbon bond" will be used throughout this paper to denote all bonds of the type stated, whether the element linked to carbon is a metal or not.

MEAN DISSOCIATION ENERGIES

The heats of formation of the methyl compounds are required for calculating the mean metal-carbon dissociation energies, and, in the case of the highly reactive, spontaneously inflammable liquids or gases under discussion, their determination has provided unusual experimental difficulties. Two distinct lines of approach to this problem have proved successful. One, originally due to Skinner and his co-workers, has made use of bromination or iodination in non-aqueous media in specially designed apparatus. The other, employed by several investigators (including the present author), relies on a special technique for opening thin-walled glass ampoules in oxygen under pressure in a bomb calorimeter. Waddington and his collaborators have improved on this by introducing a rotating bomb, and this has been applied to the cases of the methyls of lead and sulphur. With all methods, considerable difficulty has been encountered in obtaining pure or even complete reactions, and a careful analysis of the products is in general necessary to obtain reliable heats of reaction. In some reactions a small element of uncertainty is introduced through the possibility of solid products being produced in an energy-rich form or doubtful crystalline state.

Notwithstanding these difficulties, it has usually proved possible by these methods to obtain heats of formation of the methyl compounds with an accuracy that corresponds to limits of error of ± 1 kcal or less in the mean dissociation energies of the metal-carbon bonds. However, in a number of cases uncertainties in auxiliary thermochemical data, especially heats of atomization, introduce larger possible errors.

To reduce the latter as far as possible, published values for the heats of formation have been recalculated, where appropriate, with the help of the most up-to-date thermochemical data, and a weighted mean selected in cases where there have been more than one determination. The values so obtained have been adjusted for the respective heats of vaporization of the liquid compounds at 25°C and listed for the gaseous species in *Table 1*. In the case of aluminium trimethyl, which is mainly dimeric in the vapour phase, adjustment has also been made for the heat of dimerization.

Table 1. Heats of formation of the volatile methyls and total energies of removal of methyl radicals

Methyl M (CH ₃) _n	— $\Delta H_{f298.15}^{\circ}$ for gas (kcal/mole)	Ref.	Heat of atomization (25°C) of element M (kcal/g-atom)	Total energy of removal of all Me radicals (kcal/mole)
ZnMe ₂	— 13.26	1, 2	31.18	82.9
CdMe ₂	— 26.4	1, 3	26.97	65.6
HgMe ₂	— 20.78	4, 5	14.71	58.9
BMe ₃	+ 29.8	1, 6	135.2	262.5
AlMe ₃	+ 13.9*	1	77.4	188.8
GaMe ₃	+ 9.1	7, 8	65.8	172.4
CMe ₄	+ 39.67	9	171.4	341.1
SiMe ₄	+ 49.5	10	105	284.5
SnMe ₄	+ 11.2	10-12	71.9	213.1
PbMe ₄	— 32.6	13	46.34	143.7
NMe ₃	+ 4.1	14	112.95	214.5
PMe ₃	+ 23.2	14	75.18	195.9
AsMe ₃	— 3.7	15	60.64	154.4
SbMe ₃	— 9.2	16	60.8	149.1
BiMe ₃	— 45.8	17	49.5	101.2
OMe ₂	+ 44.3	18	59.56	168.9
SMe ₂	+ 8.88	19	66.75	140.6
ClMe	+ 20.634	20	28.942	82.1
BrMe	+ 9.563	21	26.85	68.9
IMe	— 3.6	5	25.48	54.4

* Monomeric species.

To calculate the mean dissociation energies, the heats of atomization of the respective elements are required, and the values used are likewise listed in *Table 1*. Also required is the heat of formation of the free methyl radical. This is best calculated from the bromination work²² of Kistiakowsky and Van Artsdalen, which, when combined with the most recent thermochemical data, gives 101.6 kcal/mole at 0°K for *D*(CH₃—H), corresponding to 102.5 at 25°C and —32.5 for the heat of formation of CH₃. From the latter value and the quantities listed in columns 2 and 4 of *Table 1*, the energy required to strip all the methyl radicals from each molecule, that is, to dissociate all the metal carbon bonds and leave the metal atom in its ground state, has been calculated (column 5). Experimental values are lacking for the methyls of indium, thallium, germanium, selenium, tellurium and fluorine.

DISSOCIATION ENERGIES OF METAL-CARBON BONDS

The variation in the dissociation energies is more readily grasped by reference to *Table 2*, where the mean values per bond are arranged by groups and periods, according to the number of places the metal atom stands in front of a rare gas. An estimated value for $D(\text{F}-\text{CH}_3)$, based on the heats of formation of other organic fluorine compounds, has been added. This variation in the mean dissociation energy $D_m(\text{M}-\text{C})$ must be ascribed principally to the change in the contribution made by the atom M.

Table 2. Mean M—C dissociation energies for the volatile methyls (in kcal)

	BMe ₃ 87.5	CMe ₄ 85.3	NMe ₃ 71.5	OMe ₂ 84.4	FMe (~ 120)
	AlMe ₃ 62.9	SiMe ₄ 71.1	PMe ₃ 65.3	SMe ₂ 70.3	ClMe 82.1
ZnMe ₂ 41.5	GaMe ₃ 57.5	GeMe ₄ —	AsMe ₃ 51.5	SeMe ₂ —	BrMe 68.9
CdMe ₂ 32.8	InMe ₃ —	SnMe ₄ 53.3	SbMe ₃ 49.7	TeMe ₂ —	I Me 54.4
HgMe ₂ 29.5	TlMe ₃ —	PbMe ₄ 35.9	BiMe ₃ 33.7		

Table 3. Valence-state energies for the free atoms (in eV)

	B 5.52	C 8.26	N 1.19	O 0.50	F 0.02
	Al 4.65	Si 6.22	P 0.70	S 0.30	Cl 0.04
Zn 4.49	Ga 5.75	Ge 6.8	As 0.67	Se 0.38	Br 0.15
Cd 4.26	In (5.5)	Sn —	Sb 0.57	Te 0.52	I 0.31
Hg 5.56	Tl 7.31	Pb —	Bi 0.86		

On viewing the dissociation energies from the point of view of the Periodic System as a whole, it is seen that, whereas there is a basic underlying regularity, in that, generally speaking, the dissociation energies decrease as the number of the period increases, being greatest in the upper right-hand corner and least in the lower left-hand, there are nevertheless marked irregularities. For example, relative to the contributions of its vertical neighbours, that of cadmium is low. Likewise the contribution of aluminium appears to be even more decidedly low. On the other hand the contributions of antimony and tin appear on a like basis to be higher than their position in the Periodic System would warrant. These irregularities are in general far too large to be ascribed to experimental error, but nowhere are they sufficiently great to change the vertical order in the magnitude of the dissociation energies.

Viewed horizontally, the contributions from silicon and gallium are seen to be distinctly high within their respective periods. However, the Group V elements probably all make weaker contributions than their Group IV neighbours, which is contrary to the general trend. Indeed, the deficiency is exceptionally large in the case of nitrogen, which makes by far the poorest contribution of all the first-row elements here considered. Quantitatively, the mean dissociation energy in NMe_3 is about 16 per cent lower than in CMe_4 , instead of being a few per cent higher.

EXCITATION ENERGIES OF COMBINATION

The most reasonable explanation is that the forementioned irregularities, which appear to be superimposed on an underlying regularity, are due to the varying internal excitation energy as one passes from one atom to the next. This intra-atomic energy has frequently been referred to as the "valence-state energy", but this expression will not be used here in the foregoing sense, since it has also been employed for the energy levels of hypothetical states of free (uncombined) atoms, and it is necessary to make a distinction between the two uses. Accordingly, the term "excitation energy of combination" or "chemical excitation energy" is more appropriate where combined atoms are under discussion.

Logically, the mean dissociation energies derived thermochemically cannot be identified with the true or intrinsic bond energies of the respective bonds, because on the detachment of all the methyl groups the methyl radicals reorganize and the central atom falls back to the ground state with the release of the previously mentioned excitation energy. Hence the mean dissociation energy is a net quantity, and for the compound $\text{M}(\text{CH}_3)_n$ is less than the intrinsic bond energy E_1 by an amount equal to the sum of R , the reorganization energy of the methyl radical, plus the n th part of V , the excitation energy of combination of the central atom M , that is,

$$E_1(\text{M}-\text{C}) = D_m(\text{M}-\text{C}) + R_{\text{CH}_3} + V_{\text{M}}/n$$

Whereas R may be nearly constant, or at least would not be expected to vary unsystematically, V unquestionably varies considerably with the number and nature of the electronic orbitals available on passing from one atom to its neighbour. Consequently, an anomalously low value of D_m will indicate that V for the central atom is higher than for its neighbours, and *vice versa*. This last statement is only valid if it can be assumed that the intrinsic bond energies (E_1 values) vary systematically with the position of the central atom M in the Periodic System; but that they do so to an exceptionally good approximation is strongly implied by the orderly variation in other bond properties for the volatile methyl compounds. This conclusion is reached whether one turns to bond lengths or stretching force constants (only in the case of HgMe_2 is the metal-carbon force constant seriously anomalous).

In general, therefore, anomalously low D_m values correspond to higher V values; and that we are not dealing with valence-state energies of uncombined atoms is again emphasized by comparison of *Table 2* with *Table 3*, in which calculated²³⁻²⁵ atomic valence-state energies are listed.

DISSOCIATION ENERGIES OF METAL-CARBON BONDS

The two are seen to bear surprisingly little relation. For example, the D_m values in *Table 2* reveal that the excitation energy of the combined atom is much greater for nitrogen than for carbon, whereas for the free atom in the calculated valence state, the reverse is true.

INDIVIDUAL DISSOCIATION ENERGIES

For polyvalent atoms, further light may be shed on the excitation energy of combination by comparing the mean dissociation energies with individual dissociation energies. For certain of the methyls, it has proved possible to obtain individual dissociation energies from the measured activation energies in pyrolytic and other kinetic studies at elevated temperatures. Inherent in the method is an uncertainty of order $\pm RT$ and there may be larger errors, but that the method is capable of giving reliable values is seen in the case of methyl bromide, where the activation energy²⁶ of 67.0 ± 2 kcal agrees to within experimental error with the thermochemical dissociation energy of 68.9 kcal.

Experimental values of activation energies so far available are listed in *Table 4*. In general, where the compound decomposes by a first-order mechanism liberating methyl radicals, the activation energy can be identified with the energy absorbed in the process



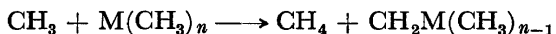
Table 4. Dissociation energies of the first metal-carbon bonds of the methyls

<i>Methyl</i>	D_m (kcal)	D_1 (kcal) <i>estimated from kinetic data</i>				
ZnMe ₂	41.5	47.2 ⁽²⁷⁾				
CdMe ₂	32.8	43.5 ⁽²⁸⁾	45.8 ⁽²⁹⁾			
HgMe ₂	29.5	51.3 ⁽³⁰⁾	51.5 ⁽³¹⁾	>42 ⁽³³⁾	50.1 ⁽²⁹⁾	57.9 ⁽³⁴⁾
BMe ₃	87.5	—				
AlMe ₃	62.9	~ 78* ⁽³⁵⁾				
GaMe ₃	57.5	—				
CMe ₄	85.3	98.8* ⁽²⁶⁾	100* ⁽³⁷⁾	83.0* ⁽³⁸⁾		
SiMe ₄	71.1	78.8 ⁽³⁹⁾				
SnMe ₄	53.3	82.4 ⁽⁴⁰⁾				
PbMe ₄	35.9	(>36.9 ⁽⁴¹⁾)	23.5 ⁽⁴²⁾	28.2 ⁽⁴³⁾		
NMe ₃	71.5	100.4* ⁽⁴⁴⁾	50.8 ⁽⁴⁵⁾			
PMe ₃	65.3	—				
AsMe ₃	51.5	54.6 ⁽⁴⁶⁾				
SbMe ₃	49.7	57.0 ⁽⁴⁷⁾				
BiMe ₃	33.7	44.03 ⁽⁴⁷⁾				
OMe ₂	84.4	98.0* ⁽⁴⁸⁾	81.1 ⁽⁴⁵⁾			
SMe ₂	70.3	—				

* Value estimated on the basis of a chain mechanism of order 3/2.

that is to say, may be equated with D_1 , the dissociation energy of the first metal-carbon bond. But this is apparently not the case with the first-row elements, where the methyl compounds decompose to give products containing double bonds. Thus neopentane gives mainly methane plus

isobutylene^{36, 49}, while NMe_3 and OMe_2 likewise give $\text{CH}_2=\text{NCH}_3$ ⁴⁴ and $\text{CH}_2=\text{O}$ ⁴⁸ among other products. Accordingly, the values for the first-row elements are not to be directly equated with dissociation energies, but in the higher periods the identification is reasonable, and here it is seen that the D_1 values are almost universally higher than the mean dissociation energies (the low values for PbMe_4 ^{42, 43} are associated with unreasonable pre-exponential factors and are probably erroneous, the true value almost certainly exceeding that for PbEt_4 ⁴¹). AlMe_3 is a special case, in that its thermal decomposition is by a chain mechanism³⁵ of order 3/2. In such cases the apparent energy of activation E_a (45 kcal for AlMe_3) is equal to $\frac{1}{2}D_1 + E_2$, where E_2 is the activation energy of the step



CMe_4 ($E_a = 59.4$ ³⁶, 60 ³⁷, 51.5 kcal³⁸) and NMe_3 ($E_a = 59$ kcal⁴⁴) both decompose by a precisely analogous mechanism of order 3/2, while OMe_2 ($E_a = 58.5$ kcal⁴⁸) apparently also has a three-halves order⁵⁰. Since the amount of methane formed during photolysis of AlMe_3 at 29° and 120°C ³⁵ suggests that E_2 here is ~ 6 kcal, whereas for CMe_4 , NMe_3 and OMe_2 E_2 is known to be respectively 10.0 ⁵¹, 8.8 ⁵² and 9.5 kcal⁵², the D_1 values for these four compounds are readily calculated and have been included in *Table 4*. The values derived for NMe_3 and OMe_2 by a mirror technique⁴⁵ would seem to be erroneous.

DISCUSSION

Although individual dissociation energies are lacking for a number of methyl compounds, while for others they are in some doubt, the most striking factor about the values listed in *Table 4*, taken as a whole, is that they differ markedly from the mean dissociation energies derived previously. In general they are larger, and this is precisely the state of affairs to be expected if the various polyvalent elements in Groups II to VI inclusive possess internal excitation energies in combination, since these elements would not return to the ground state on the rupture of a single bond, the state relative to which the mean dissociation energies are measured. The quantitative data discussed here therefore provide very strong evidence indeed for the reality of excitation energies of combined atoms, and this is perhaps the most important qualitative conclusion to be drawn from this study. The suggestion of the existence of such excitation energies is of course not new, but never before has it been verified for such a large number of elements.

It is, however, far more difficult to make any kind of quantitative pronouncement concerning this excitation energy. Quantitatively, the individual dissociation energies (D_1 values) will exceed the mean dissociation energies (D_m values) by an amount equal to the n th part of V , the excitation energy, less R' , the energy of reorganization of the molecular fragment MR_{n-1} liberated on its formation from the molecule MR_n , that is

$$D_1 - D_m = V_M/n - R'$$

Merely to multiply $D_1 - D_m$ by n will give a fair estimate of the excitation energy V of element M only if R' is small.

DISSOCIATION ENERGIES OF METAL-CARBON BONDS

This last condition is only likely to be realized with the elements in Group II. In this group, as in Groups III and IV, the excitation energy incorporates the energy of promotion of an *s* electron, as well as hybridization effects (which do not involve further electronic promotion). When only one of the bonds in, say, zinc dimethyl is ruptured, the zinc atom is not able to change its promoted state and recouple its electrons as an *s*² pair, neither will it change its valency angle. Accordingly *R'* may well be small with the methyl compounds of zinc, cadmium and mercury, in which case approximate values may be derived for *V* (Table 5) by ignoring *R'* and equating *V* to 2(*D*₁ - *D*_m). (Where alternative *D*₁ values are available, those derived from experiments with the unadulterated compound at higher pressures and lower temperatures have been selected as preferable.) The method has already been used by Pauling⁵³ in calculating the internal excitation energy of divalent oxygen.

Table 5. Approximate internal excitation energies of covalently bound zinc, cadmium and mercury

<i>Element</i>	<i>Compound</i>	<i>D</i> ₁ (kcal)	<i>D</i> _m (kcal)	<i>V</i> ≈ 2(<i>D</i> ₁ - <i>D</i> _m) (eV)
Zn	ZnMe ₂	47.2	41.5	~ 0.5
Cd	CdMe ₂	43.5	32.8	~ 0.9
Hg	HgMe ₂	51.3	29.5	~ 1.9

It is emphasized that these values for the excitation energies are tentative only. Nevertheless, they differ so widely from the values listed in Table 3, that it is again abundantly clear that we are not here dealing with the valence-state energies of uncombined atoms. Without making the most extravagant assumptions, no kind of agreement can be obtained, and, with the values listed in Table 3, the ZnMe, CdMe and HgMe radicals would be thermochemically unstable. Indeed, a fundamental reason can be suggested to explain why the two energies cannot be equated, namely that the method of calculating the valence-state energies of free atoms does not, indeed cannot, allow for the contribution to the internal excitation energy of the changed interaction terms (involving bonding and non-bonding electrons) caused by the additional electrons in the valence shell of the combined atom. Thus, for example, the energy of promotion of an *s* electron in molecular surroundings will not be the same as for a free atom.

In Groups III and IV, the reorganization energy *R'* may be appreciable, because, with the rupture of one bond, the bond angles and, conceivably, even the symmetry of the molecular fragment MR_{*n*-1} may change. It is difficult even to predict the sign of *R'*, so that no reliable estimates of excitation energies are provided by the data for these groups. *R'* may be markedly negative in the case of SnMe₄, for example, as otherwise the intrinsic bond energy would be abnormally high compared with other bond properties.

In groups higher than IV, excitation energies of combination are not connected with the energies required to uncouple and promote individual *s* electrons, but with hybridization effects which involve a change in the

orbital of the s^2 pair equivalent to a partial promotion. The amount of this promotion can vary on the rupture of a bond, and this will affect R' . Accordingly, even with the divalent element oxygen, the position is far less favourable for numerical treatment than with zinc, and the excitation energy which can be derived from the data for OMe_2 by the foregoing method (~ 1.2 eV) will at best be semi-quantitative. The difference between this and Pauling's value⁴⁹ (0.78 eV) derived from old energy data for the H_2O molecule must—in so far as it is not due to sheer experimental error—be ascribed to the difference in reorganization energies of the OMe and OH radicals. If these are positive, as seems more likely in Groups V and VI where a partial demotion of the lone pairs of electrons is probably involved on the rupture of the first bond, then it may be better to regard both estimates as lower limits. Likewise the value that can be derived from NMe_3 for nitrogen (~ 3.8 eV) is probably best regarded as a lower limit. It is to be noted that the valence-state energy of the free nitrogen atom is very much smaller, though it must be emphasized that the latter is calculated for a non-hybridized state, whereas if hybridization were also taken into account for the free atom, the discrepancy would probably not be so large.

To conclude, a study of the known dissociation energies for the methyl compounds reveals that the internal excitation energy to be associated with an atom in a valence state is not the same for the combined as for the free atom. Until a theoretical method of reliably computing reorganization energies is available, inferences regarding the excitation energies of combined atoms remain qualitative, or, at best, semi-quantitative.

Note added in proof

For OMe_2 , a recent further investigation⁵⁴ of the pyrolysis has provided experimental confirmation that the decomposition mechanism is of order $3/2$, as considered likely in the foregoing (cf. *Table 4* and text). The observed activation energy, E_a , is 55.6 kcal, which, with $E_2 = 9.5$ kcal, furnishes the improved value, $D_1 = 92.2$ kcal.

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DISSOCIATION ENERGIES OF METAL-CARBON BONDS

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