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THE STRENGTHS OF CERTAIN COVALENT METAL BONDS

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A method has been evolved for measuring the heats of combustion of spontaneously inflammable substances in the bomb calorimeter and applied to the following compounds: zinc dimethyl, zinc diethyl, zinc di-*n*-propyl, zinc di-*n*-butyl, cadmium dimethyl, boron trimethyl and aluminium trimethyl. The samples used were subjected to very thorough purification, revised melting points being given for cadmium dimethyl and aluminium trimethyl. The heats of formation, deduced by the application of additional thermal data, have been listed with all those so far determined for the metal alkyls, and the energies of dissociation and bond energies of the metal-carbon links estimated. This has entailed a recalculation of the heats of sublimation of aluminium and tin. From a comparison of the values obtained for the dissociation energies with evidence from spectroscopic and kinetic studies, a definite necessity for taking into account the energies required to promote the various elements to the states of maximum valency is apparent.

Introduction

The purpose of this investigation was to determine the heats of formation of several metal alkyls and, from these, to derive information about the bond energies of the respective metal-carbon links. Very little material has been published hitherto concerning the strengths of covalent metal bonds. This is rather surprising, for, in addition to the cases where stable gaseous hydrides are known, many metals form suitable compounds with organic radicals worthy of study. Published values for the heats of formation of the metal alkyls exist only in the cases of zinc diethyl (Guntz 1887), mercury dimethyl and diethyl (Berthelot 1899), five other mercury alkyls, tin tetraethyl and three of its homologues (Jones, Evans, Gulwell & Griffiths 1935). To these are now added values for zinc dimethyl, zinc diethyl, zinc di-*n*-propyl, zinc di-*n*-butyl, cadmium dimethyl, boron trimethyl and aluminium trimethyl, all of which have been obtained through their heats of combustion.

Apparatus

The bomb calorimeter employed for measuring the heats of combustion of the metal alkyls was of the ordinary type commonly used for organic compounds. The bomb itself was constructed of stainless steel and polished on the inside. The internal surface of the lid was lined with platinum for added protection. The assembled bomb weighed 3604 g. and had an internal capacity of 287 ml. The calorimeter was constructed mainly of copper, weighed 1233 g. when empty, and required about 2600 g. of water to cover the bomb. As far as possible, the apparatus was adapted to comply with the recommendations of Dickinson (1915). Both calorimeter and jacket were fitted with electrically driven rotary stirrers. The Beckmann thermometer employed had been previously standardized at the National Physical Laboratory, Teddington, and could be read to 0·001° C. Additional thermometers enabled the temperature of the water in the jacket to be read to 0·05° C, and that of the air immediately above the ebonite cover to 0·1° C.

Determination of constants

The following abbreviations will be used in the succeeding pages:

t	time in minutes.
θ	temperature of the calorimeter at any instant.
θ_0	temperature of the jacket.
θ_s	temperature of the surroundings immediately above the apparatus.
r	rate of rise in temperature due to heat transfer.
s	rate of rise in temperature due to stirring.
K	cooling constant, equivalent to $r/(\theta_0-\theta)$.
k, k_s	cooling constant to take account of the difference between θ_0 and θ_s, so that $r=k(\theta_0-\theta)+k_s(\theta_s-\theta_0)$.
A	total cooling correction.
S	total correction for stirring.
subscripts 1, 2	qualifying symbols referring to arbitrary points in time during the equilibrium conditions occurring respectively before and after combustion.
subscript m	qualifying symbol referring to a fixed point in time during combustion of significance only in that it simplifies the evaluation of A.

(*a*) *Heat of stirring*

The rate of stirring chosen as the most suitable was 300 r.p.m., and this was maintained constant for all experiments. From the rate of change of θ under adiabatic conditions, the value found for s was 0·00113° C/min.

(*b*) *Cooling constants*

The expression for cooling, if the calorimeter were entirely surrounded by the jacket, would be of the form

$$r=K(\theta_0-\theta),$$

where K is a constant specific for the apparatus. For the 'open-top' type of calorimeter, the rate of cooling can be represented by

$$r=k(\theta_0-\theta)+k_s(\theta_s-\theta_0),$$

where k and k_s are two new constants, and k_s is experimentally much smaller than k. The values of k and k_s were determined by measuring the rate of change of θ for varying values of θ and θ_s, r being obtained from the experimental rate by subtracting s. The value of θ_0 chosen for these determinations was the same as that adopted for the subsequent heat of combustion experiments, namely about 19° C. Altogether, eight series of determinations were carried out, each involving from six to twelve separate determinations, making a total number of 78. Since

$$\frac{r}{\theta_0-\theta}=k+k_s\frac{\theta_s-\theta_0}{\theta_0-\theta},$$

by plotting $r/(\theta_0-\theta)$ against $(\theta_s-\theta_0)/(\theta_0-\theta)$ it was possible to determine k and k_s from the straight line which best satisfied the points. The values so obtained were respectively 0·00190 and 0·00053° C/min. per degree difference.

(c) *Heat capacity*

The weight of water to be included in the standard calorimetric system was so chosen that

$$\text{weight of calorimeter} + \text{water} = 3800 \text{ g.},$$

and the heat capacity always reduced to this standard. The heat capacity of the standard system was measured by using pure benzoic acid as a reference substance. For every combustion experiment, both during the calibration and subsequently, an excess pressure of 25 atm. (26 atm. absolute) was employed, and 0·1 ml. of water placed inside the bomb before combustion. Similarly, the quantity of material burnt was always that required to give a temperature rise of about 4° C, the range employed being approximately 15 to 19° C. The heat evolved by the combustion of 1 g. mass of benzoic acid in the bomb process for certain specified conditions is, according to the most recent work of Jessup (1946), 26,429·4 international joules, that is, 6317·8 cal. This figure, when corrected by the formula of Jessup (1942*b*) to 17° C, and the other specifications already mentioned for the bomb process employed here becomes 6320·2 cal./g. mass, which is equivalent to 6325 cal./g. weighed in air against brass weights. Two different samples of benzoic acid with a reputed purity of 99·9% or better were used, and the figure adopted was 6322 ± 3 cal./g. weighed in air.

The technique of Dickinson (1915) for computing the experimental temperature-time relations has been shown effectively to eliminate errors due to thermal lag (Jaeger & von Steinwehr 1906; White 1928; Jessup 1942*a*). For the case where $r=K(\theta_0-\theta)$, the correction for heat transfer is given by

$$A=K(\theta_1-\theta_0)(t_m-t_1)+K(\theta_2-\theta_0)(t_2-t_m),$$

with the condition that

$$\int_{t_1}^{t_m}(\theta-\theta_1)\,dt=-\int_{t_m}^{t_2}(\theta-\theta_2)\,dt.$$

Now these latter quantities may be represented as areas on a single graph. The condition, therefore, is that the value of t_m is so chosen that these areas are made equal.

For the present apparatus, where

$$r=k(\theta_0-\theta)+k_s(\theta_s-\theta_0),$$

it can be shown, with the same stipulation regarding t_m, that

$$A=k(\theta_1-\theta_0)(t_m-t_1)+k(\theta_2-\theta_0)(t_2-t_m)-k_s(\theta_s-\theta_0)(t_2-t_1).$$

In practice, the position of t_m for all experiments in which combustion completed itself rapidly was found to lie at an instant when between 63 and 65% of the total temperature rise had taken place.

For each calibration experiment, an accurately weighed pellet (about 2 g.) of pure dry benzoic acid was burnt in a platinum crucible, and the ignition effected by firing electrically a known weight of thin, analytically pure, iron wire. From the length of wire left after combustion, it was possible to calculate the weight of iron burnt. In order to lessen the likelihood of error due to 'sticking' of the mercury thread in the Beckmann thermometer, θ_1 and θ_2 were taken from the equilibrium rates of change of θ respectively before and after combustion, rather than from the actual thermometer readings at t_1 and t_2. The mean values of θ_0 and θ_s during each experiment were employed in calculating A.

Correction was not made for the traces of nitric acid produced during combustion, since it was unpractical to estimate the very small quantities involved in the presence of a large excess of metallic oxide. For all experiments, the amount of nitric acid formed was minimized by flushing the bomb thoroughly with oxygen before filling. That formed during the benzoic acid combustions was determined by titrating the bomb washings with N/100 sodium hydroxide solution, using methyl orange as indicator. The amount of nitric acid found was nearly constant at 0·005 g. This corresponds to an error in the heat capacity of 0·01 %, an insignificant quantity. Although in the subsequent heat of combustion determinations the nitric acid can react with the basic metal oxides, on the assumption that the same amount of nitric acid is formed, the errors introduced into the heats of combustion of the metal alkyls are in all cases negligible.

In all, ten different heat-capacity determinations were carried out, five with each of two different samples of benzoic acid. Sample 1 was from British Drug Houses, sample 2 being an 'A.R.' product. The results of the determinations, reduced to the standard calorimetric system, are listed in table 1.

Table 1

experiment no.	sample no.	heat capacity (g.)	experiment no.	sample no.	heat capacity (g.)
1	1	3063·7	6	2	3066·1
2	1	3062·6	7	2	3062·8
3	1	3061·2	8	2	3065·6
4	2	3065·4	9	1	3058·1
5	2	3062·2	10	1	3064·4

For sample 1, considered separately, the mean value is 3062·0 g., the maximum deviation from the mean being 0·13 %, and the mean deviation from the mean, 0·06 %. For sample 2, the maximum deviation from the mean of 3064·4 g. is 0·07 %, and the mean deviation 0·05 %. These figures indicate the reliability of the measurements. The difference of 0·08 % in the mean values provided by the two samples is probably not wholly attributable to experimental error. The average deviation from the over-all mean, 3063·2 g., is 0·06 %.

Measurement of heats of combustion

Although in theory it should have been possible to obtain mean values for the heats of combustion with probable errors of about 0·1 %, the accuracy was considerably less than this in the case of the metal alkyls for two reasons. In the first place, the realization within a small enclosure of the complete combustion of a spontaneously inflammable liquid forming solid combustion products is a process beset with too many technical difficulties to be normally possible. For example, in the case of zinc diethyl no less than fifty separate experiments were carried out with nearly twenty variations in technique, but combustion always fell short of 100 %. The second factor increasing uncertainty is that the products of combustion are frequently difficult to define by reason of the slow reactions which take place between them, it not being possible to determine subsequently the precise amount of such reactions having occurred before the time t_2. In practice, an uncertainty of several tenths of 1 % had always to be associated with the heats of combustion obtained experimentally.

The metal alkyls used were carefully purified, the final purification being carried out by repeated fractional condensation in high vacuum. Since the metal alkyls either attack vacuum grease or dissolve in it to a troublesome extent, a special high-vacuum fractionating apparatus was constructed in which the taps were replaced by mercury ventiles. This type of apparatus was found very suitable for the purification of all the metal alkyls except cadmium dimethyl. The purified compounds were stored at the temperature of liquid nitrogen and shielded from direct light.

For the combustion experiments, samples of the purified liquids were distilled *in vacuo* into specially constructed ampoules of soda or pyrex glass and sealed off. The ampoules, which were drawn down to a narrow constriction near one end, had previously been tested by subjecting them to an external pressure somewhat greater than 25 atm. The procedure was to seal each ampoule on to a 5 mm. ground-glass cone which fitted into a socket attached to the vacuum apparatus. After the ampoule had been filled and sealed off, the increase in weight of the cone and ampoule weighed together provided the weight of substance taken, correction being made for the weight of air diplaced by the small evacuated space above the liquid in the ampoule.

A magnesium collar made from a known weight of clean ribbon was employed to open the ampoule inside the bomb. The magnesium, ignited by the same iron wire used in the calibration experiments, served to melt the glass at some point and permit combustion to commence. The platinum crucible was in general found unsuitable for these experiments, since the temperature attained locally during combustion was often sufficient to fuse the crucible in places. Instead, a porcelain crucible with a perforated base, or a specially constructed crucible of perforated alumina, was found preferable. It was necessary to use a fresh crucible for each experiment. Corrections were made for the change in heat capacity due to the crucible and ampoule.

The technique developed for burning the metal alkyls inside the bomb demanded some sort of control over the rate of combustion. If combustion occurred too rapidly, premature cooling of the burning gas by the walls and lid of the bomb led to the deposition of patches of soot on the interior of the bomb. On the other hand, if combustion did not take place rapidly enough, the crucible and its contents did not become hot enough to effect an adequate melting of the glass walls of the ampoule with the result that incompletely oxidized matter was left inside the remnants of the ampoule. Other factors which could lead to incomplete oxidation were explosion of the ampoule at the moment of opening, or the disintegration of the crucible during combustion. But the most persistent cause of uncertainty was the presence of glass from the ampoule which, on fusing, tended to envelope unoxidized material, and the fused remnants of the ampoule were frequently blackened through the presence of finely divided metal. For this reason, an accurate estimation of the amount of metal remaining unburnt at the end of an experiment was not normally possible, an exception being cadmium which collected together in globules and did not disperse in the molten glass.

Because of the numerous difficulties involved, it was frequently necessary to conduct a large number of experiments and obtain an estimate of the true value from the more successful determinations. This procedure was often laborious and time-consuming, but it was always possible to obtain occasional results which were not more than a few tenths of 1% low through incomplete combustion. For those experiments in which combustion exceeded 99% thermally, it was found possible, as experience was gained, to make an approximate visual estimate of the number of tenths of 1% by which the results would fall short of that for complete oxidation. Thus, for example, if in two separate experiments the total amount of unoxidized matter remaining after the second were one-third the quantity of that left at the end of the first, and if the heat of combustion calculated in the second case were the greater by 0·4%, then the indication is that the two results are respectively 0·6 and 0·2% below the value for complete combustion. With very few exceptions, the quantity of soot remaining and the deficiency in the heat of combustion were fairly closely proportional, so that the individual results when thus corrected mostly agreed to within one- or two-tenths of 1% of the mean value. The rather approximate nature of the correction is to be freely admitted, it having already been emphasized that the results cannot be stated with the degree of precision obtainable for substances containing only carbon, hydrogen and oxygen. In this way errors have been reduced to a minimum. It should be noted that in the experimental results which follow, the allowances made for possible errors are in all cases generous ones.

In general, the methyl compounds were found easier to burn satisfactorily than the higher alkyls, which demanded a different technique. For the methyl compounds, cylindrical ampoules were employed about 1 cm. in diameter, and with an internal capacity of about 3 ml. Except in the case of boron trimethyl, these ampoules were the thinnest possible that would withstand the pressure inside the bomb and constructed of soda glass. The crucibles used were of porcelain and of the Gooch type, since the perforated bottoms permitted a better supply of oxygen. When the ampoule was opened a little above the surface of the liquid, combustion was found to occur quietly and steadily, the heat liberated melting the walls of the ampoule as combustion proceeded downwards. In this manner a measure of control over the rate of combustion was obtained. In the case of boron trimethyl a somewhat thicker ampoule was required in order that it could be weighed with safety at room temperature. With this compound rather better results were obtained with ampoules constructed of pyrex glass.

To prevent liquid alkyl from being splashed on to the bomb walls with the opening of the ampoule, a small piece of thin asbestos matting was placed across the top of the crucible. The matting was prepared from a suspension of clean asbestos fibre, being subsequently treated with an oxidizing flame. Another improvement was to raise the ampoule about 1 cm. from the bottom of the crucible by a solid glass projection provided with three small feet enabling it to stand upright in the crucible. This reduced the likelihood of unoxidized matter becoming trapped. It was further found advisable to prevent the ampoule from being upset by securing it into position by platinum wire. In this way, contact between the burning liquid and the crucible was reduced to a minimum.

For zinc diethyl and the higher alkyls, however, the foregoing method was found to be totally unsuitable. Even with the thinnest ampoule that would withstand the pressure, the combustion of the liquid could not be made to effect an adequate melting of the glass walls. The reason for this probably lay in the greater proportion of gaseous products formed, these hindering combustion in the confined space and preventing the temperature from becoming high enough to melt the glass. Many variations in technique were tried, but it was finally found necessary to open the ampoule well below the surface of the liquid. This caused fresh complications, the chief of which were inconveniently rapid combustion, a greater tendency for the fused glass to trap unoxidized matter, and frequent disintegration of the crucible. The latter difficulty was overcome by employing specially constructed crucibles of fused alumina. These crucibles were 1 to 2 mm. thick and made with a few 1 mm. perforations in the sides as well as numerous perforations in the base. In some experiments the crucible was divided into an upper and lower compartment by an alumina partition through which the neck of the ampoule projected into the lower compartment. A few additional and larger holes were drilled into the sides of the crucible near the base to permit a better supply of oxygen. Thus, by opening the crucible at the lowest point, an attempt was made to keep most of the glass in the upper compartment while the liquid was burnt in the lower, an attempt which was only partly successful. The procedure finally adopted was to use the whole crucible as the upper compartment and allow the liquid to run through a large hole in the base into a platinum crucible which rested on the bottom of the bomb. In this way, errors due to unoxidized matter becoming embedded in the glass were kept at a minimum. Apparently the higher alkyls have a lower temperature of combustion than the methyl compounds and did not seriously damage the platinum crucible. Various kinds of ampoules were tried, the type finally adopted being pear-shaped and about 1 mm. thick leading to a thin region at the point of sealing to facilitate reopening. The ampoules, when opened at the lowest point, showed a great tendency to shatter at the top, a phenomenon apparently caused by the sudden pressure from below violently forcing the liquid upwards into the evacuated space above the liquid. But by filling this space with argon at about 1 atm. before sealing off the ampoule, this difficulty was overcome. The experimental details and results for the individual compounds are most conveniently described separately.

(*a*) *Zinc dimethyl*

Pure zinc dimethyl was prepared by the prolonged action of excess zinc amalgam on purified mercury dimethyl in a sealed tube at 100° C (Frankland & Duppa 1864*a*, *b*). This method was to be preferred to the usual preparation from zinc-copper couple and methyl iodide (Renshaw & Greenlaw 1920), which yields a product contaminated with methyl iodide (Bamford, Levi & Newitt 1946), an impurity difficult to remove. The zinc dimethyl was purified by repeated fractional condensation *in vacuo* at $-90°$. In this way a very pure product was obtained.

The weight of zinc dimethyl required for a combustion experiment was about 2·5 g. In all, five determinations were carried out with this substance. The results are given in table 2. Experiments 1 and 2 did not furnish complete combustion.

Combustion was very nearly complete in the remaining experiments. A comparatively slight amount of splashing of the liquid on to the walls of the bomb had occurred in experiment 3, and in experiment 4 a small amount of soot was left on the walls of the crucible. The amount of soot remaining at the end of experiment 5 was quite negligible, this being the only combustion experiment on any of the metal alkyls in which virtually complete combustion was obtained. Since determinations 3 and 4 may well be 0·1 or

TABLE 2

experiment number	$ZnMe_2$ (g.)	total cal. (corr.)	cal. for $ZnMe_2$	cal./g.
1	1·9928	10,160	9,952	4,994
2	2·4467	12,382	12,167	4,973
3	2·4553	12,598	12,403	5,052
4	2·4649	12,635	12,444	5,048
5	2·4453	12,579	12,364	5,056

0·2 % low owing to incomplete combustion, the agreement between the last three determinations is seen to be very satisfactory.

The zinc oxide remaining at the end of the reaction was spread over the base and walls of the bomb as a fine powder. It has been shown by X-ray investigation that, when produced in the bomb, it assumes the form of hexagonal crystals (Becker & Roth 1933). Unfortunately, there was the possibility of a slow reaction between the zinc oxide and the carbon dioxide and water formed by the combustion. From the volume of carbon dioxide evolved by the solid product when treated with acid, it was estimated that approximately 5 to 8 % of the zinc oxide was converted to carbonate between t_1 and t_2. For zinc dimethyl, diethyl, di-*n*-propyl and di-*n*-butyl, respectively, the measured heats of combustion if all the zinc oxide were converted to carbonate would exceed the true values by 2·9, 1·7, 1·3 and 1·0 %. In the case of zinc dimethyl, therefore, the negative correction to be applied amounted to about 0·15 to 0·2 %. For the other zinc alkyls, decreasing proportions of zinc oxide and increasing final pressures of carbon dioxide maintained the required correction at practically the same percentage. The error due to the hydration of the zinc oxide was much less serious and probably negligible. According to de Forcrand (1902), the hydration is a slow process evolving 4·6 kcal. for the first mol. of water. Even if as much as 10 % of the oxide ended up as $ZnO.H_2O$, the error would be under 0·1 % in the case of the dimethyl, and still less for the other zinc alkyls. The proportion of hydrate was probably very much less than 10 %, especially considering that it would almost certainly be converted to carbonate more readily than the unhydrated oxide. The correction for hydration was therefore taken as negligible in comparison with that for carbonate formation.

Applying the correction for carbonate formation to the results of experiments 3, 4 and 5, and bearing in mind that experiments 3 and 4 are probably one- or two-tenths of 1 % low through incomplete combustion, the most probable figure for the heat of combustion of zinc dimethyl, to three significant figures, is 5050 cal./g. This refers to the general reaction

$$Zn(C_nH_{2n+1})_2\,[\textit{liquid}] + (3n+1)O_2 \rightarrow ZnO\,[\textit{hexagonal}] + 2nCO_2 + (2n+1)H_2O\,[\textit{liquid}],$$

carried out at constant volume under the conditions prescribed, where the zinc dimethyl has been weighed in air against brass weights. The total error should not exceed ±0·3 %.

(*b*) *Zinc diethyl*

The zinc diethyl was prepared from pure mercury diethyl by the procedure adopted for the preparation of zinc dimethyl, and purified by several fractional condensations *in vacuo* at −45° C.

The weight of substance taken for each determination was about 1·8 g. Because of the multiplicity of experimental difficulties no instance of perfectly complete combustion resulted, but in several experiments the combustion came sufficiently near completion to permit an estimation of the true figure with an uncertainty only slightly greater than in the case of zinc dimethyl. Of the fifty determinations completed, the more satisfactory are given in table 3.

TABLE 3

experiment number	$ZnEt_2$ (g.)	total cal. (corr.)	cal. for $ZnEt_2$	cal./g.
6	2·0113	13,206	13,061	6,494
8	1·9449	12,771	12,604	6,481
15	1·8144	11,991	11,796	6,501
21	1·8962	12,730	12,289	6,481
22	1·7644	11,989	11,436	6,482
23	1·7992	11,884	11,693	6,499
30	1·8262	12,155	11,835	6,481
31	1·8403	12,314	11,934	6,485
32	1·8243	12,261	11,876	6,510
39	1·8240	12,177	11,876	6,511
40	1·8176	12,157	11,797	6,490

Allowing for incomplete oxidation, the results generally tended to indicate a true figure around 6520 cal./g. In particular, experiments 32 and 39, the two determinations in which combustion was most nearly complete, were thought to be less than 0·2% low from this cause. Allowing for the formation of zinc carbonate, the figure 6510 cal./g. for the pure combustion process in the bomb is selected. With this must be associated an uncertainty of ±0·4%.

(c) *Zinc di-*n*-propyl*

The action of anhydrous zinc chloride on excess of the appropriate alkyl magnesium halide in ethereal solution was employed to prepare zinc di-*n*-propyl (Krause & von Grosse 1937). The zinc dipropyl was separated by fractional distillation under reduced pressure before transferring to the vacuum apparatus for final purification by repeated fractional condensation at −25° C. No difficulty was experienced in removing the last traces of ether.

The weight of zinc dipropyl burnt in each experiment was about 1·6 g. The results are tabulated in table 4, a systematic agreement, depending upon the amount of soot remaining, being observed in all cases except determination 1, which result was neglected as erroneous since the combustion was manifestly very much less complete than the result would indicate. Of the remaining values, experiments 6 and 10 were thought to be approximately four-tenths of 1% low through incomplete combustion, with determina-

TABLE 4

experiment number	$ZnPr_2$ (g.)	total cal. (corr.)	cal. for $ZnPr_2$	cal./g.
1	1·5174	11,511	11,104	7,318
2	1·5556	11,709	11,293	7,260
3	1·5805	11,888	11,550	7,308
4	1·5858	11,938	11,592	7,310
5	1·5749	11,860	11,456	7,274
6	1·6074	12,219	11,763	7,318
7	1·5998	12,063	11,607	7,255
8	1·5910	11,855	11,410	7,172
9	1·5180	11,508	11,095	7,309
10	1·3936	10,602	10,193	7,314

tions 3, 4 and 9 scarcely less complete. Allowing for the formation of zinc carbonate, the best representative figure for the pure combustion reaction in the bomb becomes 7330 cal./g. with an uncertainty of less than ±0·5 %.

(*d*) *Zinc di*-n-*butyl*

The preparation of zinc dibutyl was similar to that of the dipropyl, the isolated product being purified by repeated fractional condensation *in vacuo* at −15° C.

Each determination required about 1·5 g. of the substance. The trouble caused by incomplete combustion was considerably less than with the diethyl and dipropyl, presumably because of the smaller proportion of zinc present. The experimental results are given in table 5. Experiments 5 and 6 were thought to be less than 0·2 % low through imperfect combustion, and experiments 1 and 4 about 0·3 % low. The results are seen to be in excellent agreement. The correction for carbonate formation being about 0·15 %, the figure selected for combustion in the bomb process is 7930 cal./g. ±0·4 %.

TABLE 5

experiment number	$ZnBu_2$ (g.)	total cal. (corr.)	cal. for $ZnBu_2$	cal./g.
1	1·5069	12,325	11,935	7,922
2	1·4739	12,049	11,660	7,911
3	1·4682	12,010	11,578	7,886
4	1·4617	11,982	11,580	7,922
5	1·4920	12,236	11,830	7,929
6	1·5549	12,746	12,328	7,928

(*e*) *Cadmium dimethyl*

The cadmium dimethyl used was prepared by the action of anhydrous cadmium chloride on methyl magnesium iodide (Gilman & Nelson 1936), using the technique employed for zinc di-*n*-propyl.

This substance could not be purified in contact with mercury. It was found that the mercury in the ventiles was affected and 'tailed' on the glass walls, and that an impurity was produced slightly more volatile than the cadmium dimethyl, but no perceptible amount of gas. The indication is that cadmium dimethyl vapour reacts slowly with mercury at room temperature to produce the more volatile mercury dimethyl. This phenomenon was quite unexpected, but in a mercury-free vacuum apparatus in which glass taps replaced the ventiles, the cadmium dimethyl was purified at once without difficulty by fractional condensation at −40° C. The final product melted at −2·4° C, that is, about 2° C higher than the values quoted in the literature (Krause & von Grosse 1937; Bamford *et al.* 1946). Fortunately, cadmium dimethyl is one of the metal alkyls which does not react appreciably with vacuum grease. As a precautionary measure, the apparatus was so constructed that the final distillation into the ampoule could be effected without passing the vapour through a tap.

The measurement of the heat of combustion of cadmium dimethyl presented some unique problems. The mercury alkyls on combustion leave metallic mercury (Berthelot 1899; Jones *et al.* 1935), the zinc alkyls zinc oxide, whereas cadmium dimethyl was found to leave a mixture of metal and oxide. This necessitated determining gravimetrically the cadmium remaining unoxidized at the end of each experiment. The unburnt cadmium mostly remained as small metallic beads at the bottom of the crucible. In the first experiment these were confused with pieces of fused platinum wire and lost while washing with nitric acid, which revealed their true nature. Thus determination 1 was low and had to be rejected. Some cadmium was also left mixed with carbon in the form of soot on the inside of the bomb, and it was found convenient to estimate this separately. The procedure was to remove the soot quantitatively from the walls of the bomb with the aid of a cut-down feather and dissolve away the red-brown cadmium oxide in very dilute (N/20) hydrochloric acid, this showing no signs of reacting with the metallic cadmium. The mixture of cadmium and carbon remaining, which was usually contaminated with small pieces of glass from the ampoule, was washed, transferred to a porous glass crucible, dried and weighed. The cadmium was determined by dissolving in cold nitric acid and noting the loss in weight. The carbon was determined by boiling with a mixture of 2 parts of concentrated sulphuric acid and 1 part of concentrated nitric acid until it dissolved. To the loss in weight a small correction had to be applied for the action of the boiling acid on the glass crucible, the rate of loss in weight being determined separately.

The heat of combustion of graphite (Prosen, Jessup & Rossini 1944), when corrected for weighing in air and burning under constant volume, is 7834 cal./g. However, we are here concerned with soot, which is a form of carbon with a heat of combustion 279 cal./g. above that of graphite (Papp 1941). Accordingly, the figure employed for correcting the experimental values for unburnt carbon was 8113 cal./g. That employed for cadmium was 551 cal./g. at constant volume, being obtained from the measurements of Becker & Roth (1933).

About 3·6 g. of cadmium dimethyl were required for each experiment. The results are given in table 6. Although the ampoule did not open satisfactorily in experiment 3, and a large amount of cadmium and a small amount of carbon were recovered as a black powder from inside the ampoule to be determined in the usual way, the corrected result agrees satisfactorily with the others. The extreme values differ by 1·6 %, an unexpectedly large amount and one difficult to account for fully. In this instance, every result should be given equal weight since corrections have been applied for the unoxidized residues. The mean value is 3315 cal./g. with a mean deviation of 0·50 %. There is a certain small probability, however, that the results are low rather than high. Small amounts of unoxidized matter fused into the remnants of the ampoule may, in spite of precautions, have escaped determination. Also, the deposit of soot on the walls of the bomb may have been accompanied by the formation of small amounts of carbon monoxide. The true value,

TABLE 6

experiment number	$CdMe_2$ (g.)	total cal. (corr.)	Cd recovered (g.)	C recovered (g.)	cal. for $CdMe_2$ (corr.)	cal./g.
2	3·7113	12,417	0·2085	0·0176	12,337	3,324
3	3·4952	10,778	1·6920	0·0269	11,632	3,328
4	3·6782	11,889	0·9503	nil	12,101	3,290
5	3·7045	12,297	0·2142	0·0160	12,228	3,301
6	3·6654	12,086	0·8393	0·0020	12,255	3,343
7	3·7064	12,391	0·2738	0·0035	12,247	3,304

therefore, probably lies somewhat higher than the mean and in the range 3315 to 3345 cal./g. The brown cadmium oxide remaining at the end of each experiment was not found to exhibit visible signs of contamination by the white carbonate or hydroxide, neither was any effervescence observed on treatment with dilute acid. For very similar conditions of formation, X-ray analysis has identified the crystalline form to be cubic (Becker & Roth 1933). The most probable figure for the reaction

$$\mathrm{Cd(CH_3)_2}\,[\textit{liquid}] + 4\mathrm{O_2} \rightarrow \mathrm{CdO}\,[\textit{cubic}] + 2\mathrm{CO_2} + 3\mathrm{H_2O}\,[\textit{liquid}]$$

in the bomb is 3330 cal./g. The uncertainty should not exceed ±0·6 %, the 'probable' error, as usually expressed, being appreciably smaller.

(*f*) *Boron trimethyl*

For the preparation of boron trimethyl, the action of trimethyl borate on methyl aluminium sesquiiodide* was employed, a reaction which does not involve the presence of ether:

$$\mathrm{(CH_3)_3Al_2I_3} + \mathrm{B(OCH_3)_3} \rightarrow \mathrm{B(CH_3)_3} + \mathrm{Al_2(OCH_3)_3I_3}.$$

The trimethyl borate was prepared and separated according to the method of Webster & Dennis (1933). The aluminium sesquiiodide was prepared by refluxing methyl iodide with granulated aluminium and a little anhydrous aluminium chloride (von Grosse & Mavity 1940). The gaseous boron trimethyl as evolved was passed through a trap at −15° C to remove methyl iodide vapour and condensed in a second trap at −100° C. As thus prepared the boron trimethyl was nearly pure, although a small amount of a slightly less volatile impurity solid below −100° C proved rather difficult to remove during the subsequent fractional condensation in vacuum apparatus at −140° C. The fractionation was repeated until the head and tail fractions possessed identical vapour pressures.

About 0·95 g. of substance was taken for each determination. The experimental results are given in table 7. Because of the great volatility of boron trimethyl, it was found exceedingly difficult to control the rate of combustion. In determinations 1, 2, 5, 9 and 11 the ampoule failed to open satisfactorily. The most satisfactory measurement was determination 8, which was considered to be two- to four-tenths of 1 % low through incomplete combustion. Determination 6 was thought to be about 0·6 % low. From these

TABLE 7

experiment number	$\mathrm{BMe_3}$ (g.)	total cal. (corr.)	cal. for $\mathrm{BMe_3}$	cal./g.
1	0·8259	10,495	10,220	12,374
2	0·9611	11,590	11,277	11,733
3	0·9560	12,208	11,876	12,423
4	0·8939	11,672	11,298	12,639
5	0·9555	11,190	10,848	11,353
6	0·9523	12,365	11,997	12,598
7	1·0354	13,478	13,102	12,654
8	0·9786	12,808	12,454	12,726
9	0·9615	11,979	11,601	12,066
10	0·9676	12,679	12,287	12,698
11	0·9009	10,978	10,606	11,773

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* We are indebted to an N.D.R.C. communication for this method.

results, the figure 12,770 cal./g. ± 0·4 % is selected as the best representative value for the bomb process. In this case, the end product is crystalline boric acid, part of which is dissolved in the water present (Roth & Börger 1937).

(g) *Aluminium trimethyl*

The action of excess coarse aluminium powder on pure mercury dimethyl was employed to prepare aluminium trimethyl in a pure state (Buckton & Odling 1865*a*, *b*). The product was purified by several fractional condensations *in vacuo* at −30° C. The melting point of the purified compound was 15·4° C. The value given elsewhere is 15° C (Schlesinger, Sanderson & Burg 1940; Bamford *et al.* 1946; Pitzer & Gutowsky 1946).

Each combustion determination required about 1·1 g. of aluminium trimethyl. The results are expressed in table 8. Experiments 4 and 5 were the only determinations to indicate a thermal deficit of more than 1 %. The results consistently pointed to a true value of 10,550 cal./g. ± 0·3 %. In particular, determination 8 was thought to be two-tenths, and determination 2 five-tenths of 1 % low. In this case there are apparently no complications caused by the formation of carbonate or hydroxide. The aluminium oxide remaining at the end of the experiments gave no effervescence with dilute sulphuric acid, neither did it dissolve appreciably. Aluminium oxide formed during combustion inside the bomb has elsewhere been identified by X-ray analysis as the α form or corundum (Snyder & Seltz 1945). The figure quoted refers, therefore, to the reaction

Table 8

experiment number	$AlMe_3$ (g.)	total cal. (corr.)	cal. for $AlMe_3$	cal./g.
1	1·1275	11,994	11,799	10,465
2	1·1188	11,969	11,755	10,507
3	1·1289	12,002	11,801	10,454
4	1·1279	11,958	11,597	10,282
5	1·0286	10,912	10,698	10,401
6	1·0770	11,616	11,260	10,455
7	1·0934	11,806	11,446	10,468
8	1·1014	11,823	11,596	10,528

$$Al(CH_3)_3\,[\textit{liquid}] + 6O_2 \rightarrow \tfrac{1}{2}Al_2O_3\,[\textit{corundum}] + 3CO_2 + 4\tfrac{1}{2}H_2O\,[\textit{liquid}].$$

Calculation of the heats of formation

For calculating the heats of formation of the metal alkyls, the experimental figures for the heats of combustion have still to be corrected for the following factors in order to bring them to the conventional conditions of temperature and pressure:

(i) reducing the weighings to *vacuo*,
(ii) converting to constant pressure,
(iii) reducing the pressure to 1 atm.,
(iv) raising the temperature to 25° C.

Correction (iv) requires specific heat data for the liquids concerned. Since, apart from one measurement of the specific heat of gaseous zinc dimethyl (Trautz 1917), no heat-capacity data have been published for the metal alkyls, correction (iv) cannot be applied, but it would be expected to be negligible for the small temperature change (8° C) involved. Correction (iii), computed by the method of Washburn (1933), is quite negligible, being of the order of a few thousandths of 1 % for the metal alkyls. The other minor corrections listed by Washburn and not so far applied are also negligible. Corrections (i) and (ii) are not negligible. The former requires the densities of the liquid alkyls at room temperature. Reliable figures for these are available except in the case of boron trimethyl, for which the density was separately measured and found to be 0·523 at 18° C.

In the case of boron trimethyl, a further correction has to be applied to the measured heat of combustion, since the product of combustion is not boric oxide but boric acid, part of which is dissolved in the water present. The heats of reaction for the two processes

$$B_2O_3\,[\textit{amorphous}] + 3H_2O \rightarrow 2H_3BO_3\,[\textit{crystalline}]$$

and

$$B_2O_3\,[\textit{amorphous}] + (3+x)H_2O \rightarrow 2H_3BO_3\,[\textit{aqueous}]$$

are 18·15 and 7·8 kcal./mol. respectively (Roth 1946), having been selected from the measurements of Roth, Börger & Bertram (1937) and the amended figures of von Stackelberg, Quatram & Dressel (1937). Now 1 mol. of boron trimethyl on combustion produces $\frac{1}{2}$ mol. of boric oxide and $4\frac{1}{2}$ mol. of water, only $1\frac{1}{2}$ mol. of which becomes combined chemically in the formation of boric acid, this dissolving to some extent in the remaining 3 mol. of water. From the solubility of boric acid at 19° C it can be calculated that the amount of boric oxide ending up in solution is 0·020 mol., that is, 4 % of the total. On this basis, an additional correction of −8·87 kcal./mol. is required to adjust the experimental figure to conform with the reaction

$$B(CH_3)_3\,[\textit{liquid}] + 6O_2 \rightarrow \tfrac{1}{2}B_2O_3\,[\textit{amorphous}] + 3CO_2 + 4\tfrac{1}{2}H_2O\,[\textit{liquid}].$$

The experimental molecular heats of combustion are listed in column 2 of table 9, which also includes the figures of Berthelot (1899) and Jones *et al.* (1935) for the mercury and tin

TABLE 9

substance	heat of combustion (kcal./mol.)		heat of formation (kcal./mol.)	
	experimental	corrected	liquid	gas (monomer)
$Zn(CH_3)_2$*	$482_{\cdot0}$	$482_{\cdot8}$	$-6_{\cdot5}$	$-13_{\cdot3}$
$Zn(C_2H_5)_2$*	$804_{\cdot0}$	$805_{\cdot1}$	$-4_{\cdot1}$	$-12_{\cdot9}$
$Zn(C_3H_7{}^{\alpha})_2$*	$1110_{\cdot9}$	$1112_{\cdot1}$	$+13_{\cdot6}$	$+3_{\cdot9}$
$Zn(C_4H_9{}^{\alpha})_2$*	$1424_{\cdot2}$	$1425_{\cdot6}$	$+24_{\cdot9}$	$+14_{\cdot6}$
$Cd(CH_3)_2$*	$474_{\cdot5}$	$475_{\cdot4}$	$-18_{\cdot9}$	$-27_{\cdot8}$
$Hg(CH_3)_2$	$431_{\cdot9}$	$432_{\cdot7}$	$-39_{\cdot6}$	$-47_{\cdot5}$
$Hg(C_2H_5)_2$	$737_{\cdot6}$	$738_{\cdot8}$	$-21_{\cdot0}$	$-31_{\cdot1}$
$Hg(C_3H_7{}^{\alpha})_2$	1036	$1037_{\cdot6}$	$+4_{\cdot9}$	$-6_{\cdot7}$
$Hg(C_3H_7{}^{\beta})_2$	1050	$1051_{\cdot5}$	$-9_{\cdot0}$	—
$Hg(C_4H_9{}^{\alpha})_2$	1342	$1343_{\cdot9}$	$+23_{\cdot4}$	$+9_{\cdot7}$
$Hg(C_4H_9{}^{\beta})_2$	1341	$1342_{\cdot9}$	$+24_{\cdot4}$	—
$Hg(C_5H_{11}{}^{\beta})_2$	1653	$1655_{\cdot2}$	$+36_{\cdot8}$	—
$B(CH_3)_3$*	$714_{\cdot1}$	$705_{\cdot4}$	$+52_{\cdot8}$	$+47_{\cdot6}$
$Al(CH_3)_3$*	$760_{\cdot3}$	$760_{\cdot9}$	$+28_{\cdot2}$	$+13_{\cdot3}$
$Sn(C_2H_5)_4$	1521	$1523_{\cdot1}$	$+50_{\cdot6}$	$+38_{\cdot1}$
$Sn(C_3H_7{}^{\alpha})_4$	2163	$2165_{\cdot6}$	$+57_{\cdot6}$	$+43_{\cdot1}$
$Sn(C_4H_9{}^{\alpha})_4$	2773	$2776_{\cdot0}$	$+96_{\cdot6}$	—
$Sn(C_5H_{11}{}^{\alpha})_4$	3384	$3387_{\cdot4}$	$+134_{\cdot7}$	—

* Substances for which heats of combustion are here published for the first time.

alkyls. When corrected for the factors already mentioned, the figures in column 3 are obtained. It is assumed that the figures of Jones *et al.* refer to combustion at constant volume since these authors choose Berthelot's constant-volume figures for comparison with their own. In the case of the mercury and tin alkyls, the figures refer to the general reactions:

$$\mathrm{Hg(C}_n\mathrm{H}_{2n+1})_2\,[\textit{liquid}]+(3n+\tfrac{1}{2})\mathrm{O}_2\rightarrow \mathrm{Hg}\,[\textit{liquid}]+2n\mathrm{CO}_2+(2n+1)\mathrm{H_2O}\,[\textit{liquid}];$$

$$\mathrm{Sn(C}_n\mathrm{H}_{2n+1})_4\,[\textit{liquid}]+(6n+2)\mathrm{O}_2\rightarrow \mathrm{SnO_2}\,[\mathrm{III}]+4n\mathrm{CO}_2+(4n+2)\mathrm{H_2O}\,[\textit{liquid}].$$

The calculation of the heats of formation of the metal alkyls requires the heats of formation of liquid water and gaseous carbon dioxide, which are 68,317·4 (Wagman, Kilpatrick, Taylor, Pitzer & Rossini 1945) and 94,051·8 (Prosen *et al.* 1944) cal./mol. respectively at 25° C. The heats of formation of the relevant oxides of the metals concerned (except mercury) are also required.

The molecular heats of formation of ZnO [*hexagonal*] and CdO [*cubic*] are 83·2 and 62·2 kcal. respectively (Becker & Roth 1933). These are the most probable figures obtained from the results provided by various methods. That direct measurement in the bomb furnishes the slightly higher value 83·4 kcal. for zinc oxide (Becker & Roth 1933; Roth, Wirths & Berendt 1942) may be due to formation of small amounts of zinc carbonate produced by interaction with the carbon dioxide from the paraffin used to aid combustion.

The values for the molecular heat of formation of B_2O_3 [*amorphous*] given by Roth & Börger (1937) and Todd & Miller (1946) are 349 and 335·8 kcal. respectively. Recently Roth (1946) has applied corrections to these figures which apparently reduce the discrepancy to almost negligible proportions. A large discrepancy still exists, however, since a further adjustment must be applied to the figures of Todd & Miller, who, in spite of the fact that the amount of water liberated in their experiments was sufficient to dissolve only a small fraction of the boric acid produced, erroneously based their corrections on total solution. The corrected value according to the experimental data of Todd & Miller is 328·5 kcal. This differs from the amended value of Roth & Börger (340·2 kcal.) by 3·5 %, an unsatisfactory state of affairs. Unfortunately the former figure rests on only two determinations compared with six for the latter. In the latter figure, however, Roth (1946) introduces an element of uncertainty by assuming that 50 % of the boric oxide remained in the crucible where it did not become hydrated, whereas Todd & Miller mixed the boron with benzoic acid before combustion and found that no boric oxide remained in the crucible.* The average of the eight determinations is 337·3 kcal./mol., which at present may be regarded as the 'most probable' value.

The value employed for the molecular heat of formation of Al_2O_3 [*corundum*] is 399·04 kcal. due to Snyder & Seltz (1945). The independent estimate, 398 kcal., of Roth *et al.* (1942) provides very good confirmation. The figure accepted for SnO_2 [III] is 138·1 kcal. (Bichowsky & Rossini 1936).

The heats of formation of the metal alkyls are listed for the liquid state in column 4 of table 9. By way of comparison, the experimental results of Guntz (1887), when combined with modern thermal data, provide the mean value −0·5 kcal./mol. for the heat of formation of liquid zinc diethyl.

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* Private communication from B. J. Todd.

Except in the case of aluminium trimethyl, the heats of formation of the gaseous metal alkyls can be calculated from the respective values for the liquids by subtracting the heats of vaporization. These have been estimated, wherever possible, from vapour-pressure data. In those cases where the calculations could be made only for a temperature other than that required, namely 25° C, the error introduced by ignoring this will not exceed a few tenths of 1 kcal. Much of the published data on the vapour pressures of the metal alkyls are unreliable and in wide disagreement. This is particularly true in the case of measurements made within a closed system, as many of these compounds are not very stable, particularly at elevated temperatures, and are sensitive towards light. For this reason, vapour-pressure measurements obtained by continual distillation under reduced pressure are to be preferred where available.

It was necessary to make fresh measurements of the boiling points under reduced pressure in the cases of zinc di-*n*-propyl and cadmium dimethyl. Combining these with the normal boiling points determined by Cahours (1873*b*) and Krause (1917) furnishes 9·7 and 8·9 kcal. for the respective molecular heats of vaporization. Cahours' value for zinc dipropyl is to be preferred to the very different and discordant values published elsewhere, since Cahours is the only investigator to have employed a sample prepared from mercury dipropyl, a method which yields a pure product in contrast to the preparation from zinc-copper couple and propyl iodide. It is further at the mean temperature of the boiling points of zinc diethyl and di-*n*-butyl.

The most satisfactory vapour-pressure data for zinc dimethyl, zinc diethyl, mercury dimethyl and mercury diethyl are expressed in the equations of Thompson & Linnett (1936*a*), which yield 6·8, 8·8, 7·9 and 10·1 kcal. respectively for the molecular heats of vaporization. The value for zinc diethyl is in excellent agreement with that from the results of Hein & Schramm (1930). The equations of Bamford *et al.* (1946) for zinc di-*n*-butyl and Jones *et al.* (1935) for tin tetra-*n*-propyl furnish 10·3 and 14·5 kcal./mol. respectively for the heats of vaporization.

For boron trimethyl, the measurements of Stock & Zeidler (1921) below the boiling point at −20° C are very well represented by the linear relationship

$$\log_{10} p_{\text{mm.}} = -1176{\cdot}5/T + 7{\cdot}5382.$$

Assuming that this relationship holds on extrapolation to 25° C, the figure derived for the heat of vaporization is 5·2 kcal./mol.

For mercury di-*n*-propyl and di-*n*-butyl the values 11·6 and 13·7 kcal. respectively are calculated for the molecular heats of vaporization from the single readings of Cahours (1873*a*), Marvel & Gould (1922), Goddard (1923), Jones *et al.* (1935), Tiffeneau (1921) and Gilman & Brown (1929). The value for tin tetraethyl is 12·5 kcal. calculated from the points of Grüttner & Krause (1917), Garner & Sugden (1929) and Jones *et al.* (1935).

In the case of aluminium trimethyl, allowance has to be made for the fact that the vapour is associated. Laubengayer & Gilliam (1941) give 9·6 kcal./mol. for the heat of vaporization over the range 23 to 70° C, where the vapour is apparently dimeric, and 20·2 kcal. for the energy of dissociation into two molecules of the monomer. This figure refers to the temperature range 100 to 156° C, but will scarcely differ at room temperature. Although Yeddanapalli & Schubert (1946) found evidence to indicate that the vapour is at least tetrameric at room temperature, the latest experimental work (Pitzer & Gutowsky 1946) indicates that the vapour is only dimeric. The heat of formation of the monomeric vapour may be calculated as follows:

	kcal.
$Al\,[solid] + 3C\,[graphite] + 4\tfrac{1}{2}H_2 \rightarrow Al(CH_3)_3\,[liquid]$	$+28{\cdot}2$
$Al(CH_3)_3\,[liquid] \rightarrow \tfrac{1}{2}Al_2(CH_3)_6\,[gas]$	$-\ 4{\cdot}8$
$\tfrac{1}{2}Al_2(CH_3)_6\,[gas] \rightarrow Al(CH_3)_3\,[gas]$	$-10{\cdot}1$
$Al\,[solid] + 3C\,[graphite] + 4\tfrac{1}{2}H_2 \rightarrow Al(CH_3)_3\,[gas]$	$+13{\cdot}3$

The heats of formation of the gaseous metal alkyls are listed in column 5 of table 9. It is seen that the lower members of the series are endothermic in the case of the metals of group II of the Periodic Table, but exothermic for boron, aluminium and tin. The increments in the heats of formation of the members of the zinc alkyl series are not constant, the dimethyl proving to be more stable thermochemically than might be expected from the trend in the heats of formation of the other members. In the normal paraffin series a similar state of affairs is observed for the lowest member (Prosen & Rossini 1945). For all organic series, the heats of formation at 25° C rapidly assume a constant increment of $+4{\cdot}926$ kcal. per CH_2 group as the series is ascended (Prosen, Johnson & Rossini 1946), although irregularities are invariably observed for the lower members. The ultimate difference to be expected between the heats of formation of two adjacent members of the series is thus 9·85 kcal. for the zinc or mercury alkyls, and 19·7 kcal. for the tin alkyls. Within the limits of accuracy of the experiments, this difference is observed for the zinc alkyls with the expected exception of zinc dimethyl. It is surprising to note that the increments for the mercury di-*n*-alkyls are persistently very much larger than the corresponding figures in the zinc alkyl series. How far this is due to experimental error on the part of the respective investigators cannot be estimated.

Heats of atomization of the elements

In order to calculate the bond energies and dissociation energies, values for the heats of atomization of the elements concerned are required. Whereas the figures for the metals of group II of the Periodic Table can be expressed with a reasonably high degree of accuracy, this is certainly not true of the other metals involved. The heats of sublimation of aluminium and tin have been recalculated here from the rather scanty thermal data to be found in the literature.

(*a*) *Hydrogen*

The heat of atomization of hydrogen is equal to one-half of $D(H_2)$. The latter is 103·2 kcal. at 0° K (Herzberg 1939), which is equivalent to 104·1 kcal. at 25° C.

(*b*) *Carbon*

The heat of sublimation of carbon has already received a detailed treatment by us (Long & Norrish 1946*a*, *b*, *c*). Here we are concerned only with L_2, the heat of atomization into the lowest atomic state corresponding to tetravalence (^5S). This we concluded to be of the order 190 kcal./g.-atom.

(*c*) *Zinc and cadmium*

The heats of sublimation per g.-atom at 25° C given in the reviews of Maier (1926), Sherman (1932), Kelly (1935) and Ditchburn & Gilmour (1941) are 31·35, 31·59, 31·19 and 30·90 kcal. respectively for zinc, and 26·68, 27·21, 26·75 and 27·27 kcal. for cadmium. The values selected as the 'best' are 31·1 and 27·0 kcal. respectively. These figures are probably within 0·2 kcal. of the true values. In the case of zinc, the value selected receives excellent support from that calculated from the depression and elevation of crystal levels (Satô 1937).

(*d*) *Mercury*

The vapour pressure of mercury is the most accurately known for any metal, and has been reviewed by Ditchburn & Gilmour (1941). The five points they quote for the range 246 to 354° K provide the value 14·75 kcal./g.-atom for the heat of vaporization of mercury at 25° C. A new method employed by Thomas & Olmer (1942) furnishes the closely confirmatory figure 14·92 at 10° C. Mercury vapour contains a small proportion of diatomic molecules. Allowing for this fact, the heat of vaporization into free atoms at 25° C is calculated at the National Bureau of Standards, Washington, to be 14·66 kcal./g.-atom.*

(*e*) *Boron*

Reliable vapour-pressure data for elementary boron are almost entirely lacking. This element melts in the range 2000 to 2075° C (Ceuilleron 1944, 1945), and most published estimates place the boiling-point in the range 2200 to 2550° C. From the spectroscopic energy levels of the vapour and the heat capacity of crystalline boron, extrapolated to an estimated sublimation temperature of 2700° K, the heat of sublimation into free atoms in the ground state is calculated at the National Bureau of Standards to be 94 kcal./g.-atom at 0° K,* which corresponds to 95 kcal./g.-atom at 25° C.

(*f*) *Aluminium*

The review of Ditchburn & Gilmour (1941) provides the best representative equation for the vapour pressure of liquid aluminium over the temperature range 1476 to 2237° K, being based mainly on the work of Baur & Brunner (1934). From this it can be deduced by means of the Clausius-Clapeyron relation that the heat of vaporization of aluminium is 78·92 kcal./g.-atom in the neighbourhood of 1779° K, the harmonic mean of the absolute temperature limits to which the vapour-pressure equation refers.

The atomic heat of aluminium at 25° C is 5·817 (Giauque & Meads 1941). At higher temperatures, the figures suggested in the review of Treadwell & Terebesi (1933) have been accepted, except at 700° K and above, where the values chosen by these authors seem to be rather lower than the experimental data warrant, both Awbery & Griffiths (1926) and Seekamp (1931) indicating a sharper upward trend in the curve. The more recent values of Avramescu (1939), determined by a new electrical method, seem to be consistently too low. Treadwell & Terebesi assert that this is also true of the results published by Umino (1926). The melting point of aluminium is 660° C (Feldmann 1938; Taylor, Willey, Smith & Edwards 1938). From 25° C to the melting point we have selected for the atomic heat of solid aluminium the values given in table 10.

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* We are indebted to a private communication from F. D. Rossini for the figures for mercury and boron.

TABLE 10

temperature (° K)	atomic heat of aluminium	temperature (° K)	atomic heat of aluminium
298·2	5·82	700	6·90
300	5·83	800	7·31
400	6·24	900	7·95
500	6·46	933	8·18
600	6·66		

The heat required to raise 1 g.-atom of aluminium from 25° C to the melting point may be calculated from the figures in table 10 to be 4·32 kcal. The heat required to fuse the aluminium is 2·49 kcal. (Awbery 1938), and that required to raise the liquid to 1779° K about 6·05 kcal. The latter figure is the mean of 5·92 and 6·18, the figures obtained from the constant value of Kelly (1935) and the formula of Wüst, Meuthen & Durrer (1918) respectively for the heat capacity of liquid aluminium, it having been necessary to extrapolate beyond the temperature of experiment. The total heat calculated to bring the solid at 298·2° K to the liquid state at 1779° K is therefore 12·86 kcal. The heat required to raise the same amount of monatomic vapour through the same total temperature change is 7·35 kcal., it being assumed that the departure for aluminium vapour from the relation $C_p = \frac{5}{2}R$, which becomes noticeable towards 3000° K (Kelly 1935), is negligible for the temperature range under consideration. From the foregoing data, the heat of sublimation of aluminium at 25° C is found to be 84·4 kcal./g.-atom. This figure is to be preferred to the respective values 55 and 67·5 put forward by Sherman (1932) and Kelly (1935).

(*g*) *Tin*

The published data concerning the vapour pressure of liquid tin are for the most part very discordant. Probably the most reliable values are due to Baur & Brunner (1934), whose equation on extrapolation roughly agrees with the data of Greenwood (1909, 1910), Ruff & Bergdahl (1919) and Ruff & Mugdan (1921), but disagrees with most of the other published measurements. The equation gives 45·75 kcal. for the atomic heat of vaporization at 1808° K.

Solid tin exists near the melting point as the γ modification, but when cooled undergoes a transition at about 162° C (Jeffery 1927) to the β or tetragonal form. The heat of transition is negligibly small (Werner 1913). The most satisfactory data on the specific heat of tin appear to be that of Jaeger & Bottema (1932) when their values for the high-temperature modification have been recalculated for the correct transition point. The heat required to raise 1 g.-atom of tin from 25° C to the melting point at 232° C takes the value 1·45 kcal. Bichowsky & Rossini (1936) regard 1·69 kcal. as the most probable value for the heat of fusion.

For the liquid state, thermal data are scanty and discordant. Iitaka (1919) and Umino (1926) have both measured the specific heat up to 600° C. Each investigator reports a constant value, but the figures are at variance. That of Umino is low for liquid tin, but high for the solid, the results being seemingly unreliable as they are in the case of aluminium. On the other hand, Iitaka's measurements for solid tin agree very much better with those of Jaeger & Bottema. His value for the atomic heat of the liquid is 7·30, which agrees very much better with the expectations of d'Or & Degard (1934) that the specific heat of the liquid will be somewhat higher than that of the solid at the melting point, expectations that are based on measurements of the depression of the freezing point and theoretical considerations by Fischer (1927). Assuming this value remains constant at higher temperatures, and that the specific heat of the vapour may be taken as constant at $\frac{5}{2}R$, the foregoing data lead to 50·9 kcal. for the atomic heat of sublimation of tin at 25° C. The much larger values which from time to time have been put forward appear to have been derived from insufficient or unreliable vapour-pressure data.

STRENGTHS OF THE COVALENT METAL BONDS

The distinction between bond energies and dissociation energies, which have been emphasized previously (Long & Norrish 1946*c*), is also fundamental to the understanding of the true nature of the forces binding the metal and carbon atoms in the metal alkyls. No less important is the question of the electronic levels of the atoms involved. This applies not only to carbon, but also to the metals concerned, as in the ground states some or all of the bonding electrons are already paired.

It is possible to calculate values for the mean dissociation energies of the links between the alkyl (methyl or ethyl) radicals and the central metal atoms by combining the heats of formation of the compounds concerned (table 9) with other thermochemical data. These calculations are independent of the heat of atomization of carbon.

The calculation of bond energies, however, depends directly upon the value of L_2, and further, as for all polyatomic molecules possessing more than one kind of bond, involves certain assumptions regarding the true strengths of the remaining bonds within the molecules.

(*a*) *The zinc-carbon link*

From the energy absorbed in the removal of a hydrogen atom from the methane molecule (Andersen & Kistiakowsky 1943; Kistiakowsky & Van Artsdalen 1944) and the ethane molecule (Andersen & Van Artsdalen 1944) respectively, and the heats of formation of these molecules (Prosen & Rossini 1945), the energy required to remove the two alkyl groups from the zinc atom in the zinc alkyls may be calculated as follows:

	kcal.
$\mathrm{Zn}\ [solid] + 2\mathrm{C}\ [graphite] + 3\mathrm{H}_2 \rightarrow \mathrm{Zn(CH_3)_2}\ [gas]$	− 13·3
$\mathrm{Zn}\ (^1\mathrm{S}) \rightarrow \mathrm{Zn}\ [solid]$	+ 31·1
$2\mathrm{CH}_4 \rightarrow 2\mathrm{C}\ [graphite] + 4\mathrm{H}_2$	− 35·8
$\mathrm{H}_2 \rightarrow 2\mathrm{H}$	−104·1
$2\mathrm{CH}_3 + 2\mathrm{H} \rightarrow 2\mathrm{CH}_4$	+204
$\mathrm{Zn}\ (^1\mathrm{S}) + 2\mathrm{CH}_3 \rightarrow \mathrm{Zn(CH_3)_2}\ [gas]$	+ 81·9

The corresponding figure for zinc diethyl is 71·6 kcal. The mean dissociation energies of the zinc-carbon bonds in zinc dimethyl and zinc diethyl, where the zinc atoms are left in the ground (^{1}S) state, are therefore seen to be 41·0 and 35·8 kcal. respectively. The difference, which is outside the limits of experimental error, is not surprising since methyl radicals are usually found to be more tightly bound than ethyl radicals, and is in accordance with the fact that at low pressures zinc diethyl vapour oxidizes much more rapidly than does that of the dimethyl (Bamford & Newitt 1946*a*, *b*). The dissociation energies for zinc di-*n*-propyl and di-*n*-butyl could also be calculated if the energies required to remove the first α-hydrogen atoms from the propane and *n*-butane molecules were known. With reasonable asumptions regarding these latter quantities, the values for zinc dipropyl and dibutyl are the same as that for the diethyl within the limits of experimental error.

Now, in all cases, the energy required to remove the first alkyl radical from the molecule must be considerably higher than the mean energy of removal of both radicals. The free zinc atom in its ground (^{1}S) state has the electron configuration $4s^2$, that is, it possesses no unpaired electrons and can hence form no stable attractive states with alkyl radicals. We must regard the zinc alkyl molecules, therefore, as built up from excited zinc atoms for the same reason that they must also be regarded as being built up from excited (^{5}S) carbon atoms (Long & Norrish 1946*c*). This also applies to the $ZnCH_3$ and ZnC_2H_5 radicals. The lowest atomic state of zinc in which the outer electrons are unpaired is $4s4p$, $^3P_0^\circ$, which has an excitation energy of 92·3 kcal. (Hetzler, Boreman & Burns 1935). Employing this figure, the energy required for the process

$$ZnR_2\,[gas] \rightarrow Zn\ (^3P_0^\circ) + 2R$$

becomes 174·2 kcal. for zinc dimethyl and 163·9 kcal. for zinc diethyl. The energy required to remove one radical will be of the order of half the corresponding figure in either case, but will differ from half by the energy of reorganization of the ZnR radical. Thus, assuming the energy of reorganization of the $ZnCH_3$ and ZnC_2H_5 radicals are negligibly small, $D(CH_3—ZnCH_3)$ and $D(C_2H_5—ZnC_2H_5)$ are *c.* 87·1 and 82·0 kcal. respectively.

For calculating the sum of the bond energies in the zinc dimethyl molecule, the heat of atomization of zinc into the $^3P_0^\circ$ state must be employed, and likewise the heat of atomization of carbon into the ^{5}S state, since both elements are in a state of maximum valency. The former figure is 123·4 kcal. The latter figure we have already shown to be of the order of 190 kcal. (Long & Norrish 1946*c*). Thus we have the following series of thermochemical equations:

	kcal.
$Zn(CH_3)_2\,[gas] \rightarrow Zn\,[solid] + 2C\,[graphite] + 3H_2$	$+\ 13{\cdot}3$
$Zn\,[solid] \rightarrow Zn\ (^3P_0^\circ)$	$-123{\cdot}4$
$2C\,[graphite] \rightarrow 2C\ (^5S)$	-380
$3H_2 \rightarrow 6H$	$-312{\cdot}3$
$Zn\,(CH_3)_2\,[gas] \rightarrow Zn\ (^3P_0^\circ) + 2C\ (^5S) + 6H$	$-802{\cdot}4$

On the assumption that the C—H bonds in zinc dimethyl possess the same strength as in methane, where the bond energy is about 104 kcal. (Long & Norrish 1946*c*), the value provided for the Zn—C bond strength is 89 kcal. But E(C—H) in zinc dimethyl is very probably smaller than in methane for two reasons. First, replacement of a hydrogen atom in methane by a more electropositive atom or radical invariably weakens the remaining C—H bonds. This may be explained by an increase in polarity of these C—H bonds, which is to be associated with an increase in bond length and a decrease in bond energy and force constant (Walsh 1946, 1947). Secondly, the force constant is considerably smaller in the case of zinc dimethyl (Linnett 1945), which itself indicates a lower bond energy. Thus, the Zn—C bond is probably a few kcal. stronger than 89 kcal., which may be regarded as a lower limit for the bond energy. The value similarly calculated for the Zn—C bond energy in zinc diethyl is 86 kcal.

(*b*) *The cadmium-carbon link*

The energy required to rupture both of the Cd—C bonds simultaneously in the cadmium dimethyl molecule, at the same time allowing the cadmium atom to fall to the ground $5s^2$ (^{1}S) state, is calculated by the foregoing method to be 63·3 kcal., that is, 31·7 kcal. per bond. The lowest $5s5p$ configuration for cadmium is the $^3P^\circ_0$ level with an excitation energy of 86·1 kcal. (Bacher & Goudsmit 1932). Neglecting the energy of reorganization of the $CdCH_3$ radical, the value of $D(CH_3—CdCH_3)$ is found to be 74·7 kcal.

The heat of atomization of cadmium into the $^3P^\circ_0$ state, namely 113·1 kcal., combines to give a bond energy for the Cd—C link in cadmium dimethyl around 77 kcal. Again, since the C—H bond energy in this compound is probably less than in methane, this figure may be regarded as a lower limit.

(*c*) *The mercury-carbon link*

The mean energy of dissociation of the Hg—C links in mercury dimethyl and diethyl are 15·6 and 18·5 kcal. respectively. These figures replace those of Sidgwick & Springall (1945), who fail to take account of the excitation energy of the carbon atoms. The excitation energy of the $6s6p$, $^3P^\circ_0$ state of mercury, the lowest sp term, being 107·6 kcal. (Mrozowski 1938), the values of $D(CH_3—HgCH_3)$ and $D(C_2H_5—HgC_2H_5)$, neglecting the energies of reorganization of the $HgCH_3$ and HgC_2H_5 radicals, are 69·4 and 72·3 kcal. respectively. That the energy of dissociation for the ethyl compound is thus calculated to be greater than that for the methyl homologue in opposition to what Bamford & Newitt (1946*a*, *b*) have observed for the corresponding zinc and antimony alkyls, and to what we have observed for the zinc alkyls, is probably to be explained by errors in the figures of Berthelot (1899) for the heats of combustion of the mercury alkyls. Krause (1926) cites indications that mercury diethyl is less stable than the dimethyl.

The values obtained for the Hg—C bond energies are 72 and 76 kcal. for mercury dimethyl and diethyl respectively.

(*d*) *The boron-carbon link*

The energy required for the process

$$B(CH_3)_3 \rightarrow B\ (^2P^\circ) + 3CH_3$$

may be similarly calculated to be 239 kcal., involving a mean energy of removal of a methyl radical of about 80 kcal. Intercombinations for the quartet terms of boron have not been observed, but Edlén (1936), employing the law of irregular doublets, calculates that the ^{4}P state, the lowest-lying $2s2p^2$ level, has an excitation energy of about 28,800 cm.$^{-1}$ or 82 kcal., which brings the value of $D(CH_3—B(CH_3)_2)$ to 107 kcal., neglecting the energy of reorganization of the $B(CH_3)_2$ radical.

The value of E(B—C) in boron trimethyl, assuming that the C—H bonds have the same strength as in methane, is 109 kcal. The foregoing figures rest on an estimate of the heat of sublimation of boron to which, in view of the lack of experimental data, no high order of accuracy can be ascribed. The rather high value obtained for the energy of linkage of the B—C bond suggests that the figure adopted for the heat of atomization of boron is more probably high than low. However, since Roth & Börger (1937) consider that the lattice energy of boron lies between that of carbon and silicon and above that of aluminium, it is unlikely that the heat of sublimation of boron is lower than that of aluminium. Thus it is improbable that the figure 95 kcal. is more than about 10 kcal. above the true figure, which would imply that the value of E(B—C) is definitely higher than E(C—C) unless the C—H bonds in boron trimethyl are unexpectedly strong.

(*e*) *The aluminium-carbon link*

The energy calculated to effect the process

$$\mathrm{Al\,(CH_3)_3}\ [\textit{gaseous monomer}] \rightarrow \mathrm{Al\,(^2P^\circ) + 3CH_3}$$

is 193·9 kcal., or 64·6 kcal. per methyl group. Neglecting the energy of reorganization of the $Al(CH_3)_2$ radical, the energy required to remove the first CH_3 group is calculated to be 92·3 kcal., the figure 82·9 kcal. being employed for the excitation energy of the $^4P_{\frac{1}{2}}$ state (Paschen 1932) of aluminium.

The Al—C bond energy in monomeric aluminium trimethyl is calculated from its heat of atomization to be 94 kcal., assuming the C—H bonds to have the same strength as in methane.

(*f*) *The tin-carbon link*

The energy that would be absorbed by the change

$$\mathrm{Sn(C_2H_5)_4}\ [\textit{gas}] \rightarrow \mathrm{Sn\ (^3P_0) + 4C_2H_5}$$

is 195·9 kcal., amounting to 49 kcal. per Sn—C link ruptured. Unfortunately, the amount of energy required to raise the tin atom from the $5s^25p^2$ to the lowest $5s5p^3$ configuration is not known with certainty. That it is fairly large is seen from the fact that for Sn^+ the change $5s^25p$, $^2P^\circ_{\frac{1}{2}} \rightarrow 5s5p^2$, $^4P_{\frac{1}{2}}$ involves no less than 44,509 cm.$^{-1}$ (McCormick & Sawyer 1938). Whereas the figure we require is expected to be smaller, it will approach this order of magnitude. Meggers (1940), from an examination of the emission spectrum of Sn, has fixed two levels which he considers are probably attributable to sp^3 terms. The lower of these is situated 39,625·5 cm.$^{-1}$ or 113·2 kcal. above the ground $^3P_0$ state, and, being of the right order of magnitude, is probably the level which is required. Adopting this figure tentatively, the value of $D(C_2H_5—Sn(C_2H_5)_3)$ is 77·3 kcal., provided the energy of reorganization of the $Sn(C_2H_5)_3$ residue is negligible.

By assuming that the C—C and C—H bond energies are the same as in ethane, the value of the Sn—C bond energy in tin tetraethyl is calculated from the molecular heat of atomization to be 81 kcal.

Discussion

The values of the energies of dissociation and bond energies calculated in the last section are tabulated in table 11. The figures in column 5 for the energy required to strip all the alkyl radicals from the central atom, leaving it in its ground state, are independent of all assumptions, their accuracies depending solely on the accuracy of the thermochemical data involved. They will therefore be quite close to the true values in the case of the zinc and cadmium alkyls. For reasons already mentioned, the heat of combustion data of Berthelot (1899) for mercury dimethyl or mercury diethyl (or both) appear to be inaccurate. It is seemingly unlikely and against experimental evidence that the methyl compound should be less stable than its ethyl analogue. For the alkyls of boron, aluminium and tin, additional uncertainties are introduced through lack of precise knowledge concerning the heats of sublimation of these very involatile elements. This is especially true of boron.

TABLE 11

molecule	heat of atomization of metal (kcal.)	excitation energy of metal atom (kcal.)	energy of removal of first alkyl radical (kcal.)	total energy of removal of all alkyl radicals (kcal.)	metal—C bond energy (kcal.)
$Zn(CH_3)_2$	31·1	92·3	$87._1$	$81._9$	89
$Zn(C_2H_5)_2$	31·1	92·3	$82._0$	$71._6$	86
$Cd(CH_3)_2$	27·0	86·1	$74._7$	$63._3$	77
$Hg(CH_3)_2$	14·66	107·6	$69._4$	$31._3$	72
$Hg(C_2H_5)_2$	14·66	107·6	$72._3$	$37._0$	76
$B(CH_3)_3$	95	82	107	239	109
$Al(CH_3)_3$	$84._4$	82·9	$92._3$	$193._9$	94
$Sn(C_2H_5)_4$	$50._9$	113·2*	$77._3$	$195._9$	81

* This figure is not certain.

As already explained, the values given in the fourth column of table 11 for the dissociation energies of the first metal-carbon bonds of the various metal alkyl molecules rest on the assumption that the energies of reorganization of the remaining molecular fragments containing the metal atoms can be neglected, that is, that the effective sums of the energies of the remaining bonds in these radicals do not change appreciably in each case. For the Sn—C link, in addition, there is some uncertainty in the energy required to bring tin to the tetravalent state.

Likewise, the values suggested in the last column of table 11 for the bond energies of the metal—C links are, as is always the case for bond energies in molecules containing more than one type of linkage, subject to approximations. Here the assumption involved is that the C—H bonds in the methyl compounds, for example, have the same strength as in methane. Particularly in the case of the more electropositive metals, however, the C—H bonds are probably weaker than in methane, so that the values indicated for the strengths of the covalent metal bonds will tend to be on the low side.

Considering the values listed in table 11 as a whole, several points are worthy of especial mention. Essentially, the covalent metal bonds are rather stronger relatively than might have been expected, or indeed, have hitherto been supposed. The Al—C bond, for example, is just about as strong as the C—C bond, and the Zn—C bond approaches the C—C bond in strength. The B—C bond, in particular, appears to be unexpectedly strong, and appreciably stronger than the C—C bond. It is well established that the B—F bond, for example, is considerably stronger than the C—F bond, a fact which is easily accounted for in terms of electronic structure. In the case of the B—C bond, the extra stabilization relative to the C—C bond is smaller. It is not so simply explainable in terms of the vacant orbital of the sp^2 boron atom, since the carbon atom possesses no lone pair of valence electrons. Rather, the different type of hybridization of the boron atom with the resultant increase of *s* character in the bonds suggests itself as an important factor. This factor will also be operative for aluminium bonds and still more for those of the metals in group II of the Periodic Table.

That the covalent bonds decrease in strength with increasing atomic weight of the elements in groups II*b* and III is in no way surprising, and in fact to be expected from the general behaviour observed for the bonds of the elements in other groups and subgroups. A further point of interest for the alkyls of the metals in group II*b* is that it requires more energy to rupture one of the metal—C links than to break both of them, assuming that the metal atom drops to the ground level. This fact may have a considerable influence on the mode of decomposition of zinc, cadmium and mercury alkyls, and a study of the rates and mechanisms of pyrolysis of these compounds would be well worth undertaking. Such information as is already available is very meagre. Cunningham & Taylor (1938) have studied the products of pyrolysis of mercury dimethyl above 290° C and found that they are mainly methane with a smaller amount of ethane plus a considerable quantity of a solid which, it is suggested, might be a polymer of methylene. The primary act is clearly the production of methyl radicals, but the experiments do not decide which of the processes

$$\mathrm{Hg(CH_3)_2 \rightarrow CH_3 + HgCH_3} \quad \text{or} \quad \mathrm{Hg(CH_3)_2 \rightarrow 2CH_3 + Hg}$$

is the initial step. Further study and a determination of the energy of activation might make a decision possible. Cunningham & Taylor also studied the photolysis of mercury dimethyl and found the main product to be ethane, thus confirming the observations of Linnett & Thompson (1937). The simplest explanation was that the original act of photodecomposition could be attributed to

$$\mathrm{Hg(CH_3)_2} + h\nu \rightarrow \mathrm{Hg + C_2H_6},$$

but Thompson & Linnett (1937), by further experiments in the presence of nitric oxide, demonstrated that the initial process is the production of methyl radicals. Since nearly two molecules of nitric oxide disappeared for every molecule of mercury dimethyl decomposed, very little if any ethane is formed in the first step. The production of methyl radicals from the photodecomposition of mercury dimethyl has been further demonstrated by Smith & Taylor (1939). None of the experiments show whether one or two radicals are produced by the actual act of absorption. In any case, the $\mathrm{HgCH_3}$ radical would have only a very short life and could decompose with the liberation of energy.

In a similar manner, the photolysis of mercury diethyl and zinc diethyl has been shown to be a radical-producing process, the final product in each case being a complex mixture, mainly butane and ethane (Moore & Taylor 1940).

Thompson & Linnett have also studied the ultra-violet absorption spectra of a number of the metal alkyls (Thompson 1934, 1935; Thompson & Linnett 1936*b*), and found that each exhibits a broad continuum, the long wave-length limit of which varies considerably with changing conditions of temperature and pressure. In some cases the continua overlap diffuse band systems at shorter wave-lengths. The ultra-violet spectra and photodissociation of certain of the zinc, mercury and tin alkyls have also received attention elsewhere

(Terenin 1934; Terenin & Prilezhaeva 1935; Asundi, Rao & Samuel 1935; Riccoboni 1941). The farthest recorded extensions of the continua towards the longer wave-lengths are repeated in table 12, together with the energies corresponding to these absorption limits. All the figures stated refer to the vapours, except that for tin tetraethyl which was obtained from a solution in hexane. These limits are only approximate, and would presumably extend to longer wave-lengths at higher pressures. There are no figures for the alkyls of boron or aluminium.

Table 12

substance	observed limit of continuum (A)	energy (kcal.)
$Zn(CH_3)_2$	2800	102
$Zn(C_2H_5)_2$	2800	102
$Cd(CH_3)_2$	2600	110
$Hg(CH_3)_2$	2800	102
$Hg(C_2H_5)_2$	2760	104
$Sn(C_2H_5)_4$	2420	118

Since the photodecomposition of the metal alkyls by light of wave-lengths corresponding to the continua is a process which produces free radicals, there is no reason to doubt that a metal-carbon bond is the link ruptured with the primary act of absorption. No pronounced maxima are in general exhibited by the continua, but, in the case of mercury dimethyl, Prilezhaeva & Terenin (1935) have shown that the most efficient wave-length for producing methyl radicals is 2000 to 2100 Å. These continua have been attributed to transitions to repulsive states, the excess energy appearing as kinetic energy of the products of photodecomposition. Thus the actual dissociation energy of the first metal—C bond in each case will be considerably less than the corresponding amount of energy indicated in column 3 of table 12. Our thermochemical measurements are seen to be in qualitative agreement with this interpretation of the continua in the spectra of the metal alkyls.

For a quantitative comparison, the dissociation energy of the metal—C link can be estimated spectroscopically only if the nature of the potential curves of the repulsive states to which transition occurs are known, so that the repulsive energy at the relevant internuclear distance can be estimated. An accurate evaluation of this repulsive energy is very difficult, but the breadth of the continua and the considerable shift of the limits towards longer wave-lengths with increasing temperature or pressure indicate that the repulsive curves are steep. By a study of the amounts of shift observed in the limits for mercury dimethyl and mercury diethyl, Asundi *et al.* (1935) have estimated that the energy of dissociation of the Hg—C link is roughly 60 kcal. This figure suggests that one methyl radical rather than two is removed in the primary step, and is to be compared with the thermochemical value of about 70 kcal. Considering the uncertainties involved, agreement is about as good as might be expected. A similar value for mercury dimethyl (50 to 60 kcal.) has been suggested by Terenin & Prilezhaeva (1935).

In the case of tin tetraethyl, Riccoboni (1941) calculates the dissociation energy of the first Sn—C link to be 109 kcal. Presuming photodecomposition to be similar to that of the mercury and zinc diethyls in the vapour phase (Moore & Taylor 1940), where ethane and ethylene are among the main products and produced in about equal proportions, it would follow that the ethyl radicals possess enough energy on formation to effect the reaction

$$2C_2H_5 \rightarrow C_2H_4+C_2H_6,$$

for which Rice & Herzfeld (1939) have suggested an activation energy of 8 kcal. Deducting this figure from the energy calculated for the limit of continuous absorption, that is, 117 kcal. (with the older conversion factors), Riccoboni obtains the figure 109 kcal. for the rupture of the Sn—C link. Clearly, this method of calculation could in any case supply only an upper limit, and the discrepancy between this figure and the thermochemical value is easily attributable to additional translational and vibrational energy, not only of the ethyl radical liberated, but also of the larger fragment of the ruptured molecule.

Published information about the pyrolysis of the metal alkyls is very scanty. A detailed study of the modes of degradation and the rates of thermal decomposition would afford interesting comparisons with the values here estimated for the dissociation energies of the metal—C links. At the present time, this comparison is only possible in the cases of the Al—C and Sn—C links, the energies of activation of the decomposition processes of aluminium trimethyl and tin tetramethyl having been recently determined.

Yeddanapalli & Schubert (1946) found that methane was the main gaseous product obtained from the pyrolysis of aluminium trimethyl between 298 and 334° C. Unidentified solid matter, probably consisting of a mixture of aluminium, aluminium carbide and polymeric material was also produced. The order of reaction was found to be $\frac{3}{2}$ with an apparent activation energy of about 45 kcal. The chain mechanism suggested to account for the reaction order will have an observed energy of activation equal to $E_2+\frac{1}{2}E_1$, where E_1 and E_2 are the respective activation energies of the steps:

$$Al(CH_3)_3 \rightarrow CH_3+Al(CH_3)_2,$$

$$Al(CH_3)_3+CH_3 \rightarrow CH_4+Al(CH_3)_2CH_2.$$

E_2 is ascribed the probable value of 15 kcal. or less, by analogy with similar processes. E_1, according to our thermochemical measurements, should be rather more than 90 kcal. In consequence, if the suggested pyrolysis mechanism is correct, the apparent activation energy should be about 60 kcal., which is not in good agreement with experiment. However, the reaction mechanism is not completely clear, and that it may need modification is also suggested by two other facts. First, the addition of hydrogen decreases the rate of pyrolysis and also decreases the apparent activation energy, the opposite effects to those expected. Secondly, in several of the experiments, the ratio of methane formed to aluminium trimethyl consumed was found to be considerably greater than that theoretically possible on the basis of a dimeric vapour. In consequence, a tetrameric vapour was suggested, but further study by Yeddanapalli & Schubert, as reported in a private communication to Pitzer & Gutowsky (1946), has shown that the vapour is only dimeric at room temperature. Since compounds such as $Al(CH_2)Br$ are known to exist, the additional methane may perhaps be accounted for by the formation of $Al(CH_2)CH_3$, this subsequently being measured as unchanged aluminium trimethyl. Possibly relevant to this point is the fact that Yeddanapalli & Schubert themselves accidentally prepared a new organic compound of aluminium boiling at 49 to 51° and more spontaneously inflammable than aluminium trimethyl. The alternative suggestion that this might be an organic compound of both aluminium and mercury does not appear to be very satisfactory in view of the fact that the boiling-point is far below that of mercury dimethyl. Clearly, the pyrolysis of aluminium trimethyl needs further investigation. In particular, the effect of nitric oxide on the rate of decomposition would be worth studying, as this might throw light on the chain process involved, which is still obscure.

The thermal decompostion of tin tetramethyl, on the other hand, is not a chain process. It is not inhibited by the presence of nitric oxide, and the reaction is of the first order except at low pressures. The main products are tin, carbon and methane, with smaller amounts of ethylene and hydrogen. From a study of the rates of pyrolysis at 440 to 493° C, Waring & Horton (1945) have determined the activation energy to be 82·4±1·2 kcal. This they consider to be too large to refer to the process

$$\mathrm{Sn(CH_3)_4 \rightarrow CH_3 + Sn(CH_3)_3},$$

a conclusion which is probably attributable to a comparison of the observed activation energy with the strength of the C—C link as formerly calculated by ignoring the excitation energy of the carbon atoms. They conclude, consequently, that the decomposition is mainly one of rearrangement, and tentatively favour one of the following modes of decomposition:

$$\mathrm{Sn(CH_3)_4} \begin{array}{l} \nearrow \mathrm{Sn + 2C_2H_4 + 2H_2} \\ \rightarrow \mathrm{Sn + C_2H_4 + 2CH_4} \\ \searrow \mathrm{Sn + C + 3CH_4}. \end{array}$$

Alternatively, if the reaction is one involving the production of radicals, then the following initial steps are suggested:

$$\mathrm{Sn(CH_3)_4} \begin{array}{l} \nearrow \mathrm{Sn + C_2H_4 + H_2 + 2CH_3} \\ \searrow \mathrm{Sn + 4CH_3}. \end{array}$$

Now none of these processes are likely: indeed, the two radical processes are energetically impossible at a single step and would absorb much more than 82·4 kcal. This is also true of the first and third of the rearrangement processes suggested, whereas the second seems to be excluded as the sole spontaneous decomposition process, since it does not produce a sufficiently large proportion of methane. Further, if the step

$$\mathrm{Sn(CH_3)_4 \rightarrow CH_3 + Sn(CH_3)_3}$$

requires less energy than 82·4 kcal., it is not at all apparent why it should not occur. On the contrary, we consider it to be by far the most reasonable assumption for the nature of the primary act, and one which is in accord with experiment. The $\mathrm{Sn(CH_3)_3}$ residue would be relatively unstable and liberate more methyl radicals, energy being provided by the drop in valency of the tin atom, as suggested by Riccoboni (1941) to account for the products of photodecomposition of tin tetraethyl.

The energy required to remove an ethyl radical from the tin tetraethyl molecule has been estimated thermochemically to be in the neighbourhood of 77·3 kcal. (table 11). In view of the fact that methyl radicals are usually more tightly bound than ethyl radicals, and that the pyrolysis experiments refer to a higher temperature, agreement with the figure 82·4 kcal. obtained from the rates of pyrolysis of tin tetramethyl is not far short of perfect, and well inside the limits of error.

In conclusion, the values obtained thermochemically for the dissociation energies of metal-carbon bonds are in general agreement with the rather meagre evidence from other sources. This agreement would not have been obtained if, in deducing the thermochemical values from the heats of formation, the excitation energies of the atoms involved had been neglected. In every case the excitation energy has been assumed equal to the minimum energy of promotion of an *s* electron from the ground state of the atom concerned. If, as has sometimes been suggested, mixtures of atomic states rather than single states should be employed in calculations of this kind, then the evidence discussed here clearly indicates that the excitation energy to be included is equivalent to at least the major part of this promotional energy.

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