80. *A Thermochemical Evaluation of Bond Strengths in Some Carbon Compounds. Part II.* Bond Strengths based on the Reaction* $CH_3I + HI \longrightarrow CH_4 + I_2$.

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Methods previously described for constant-pressure calorimetry for studying heat changes in Grignard reactions have been modified by use of carefully selected solvents having vapour pressures lower than that of ethyl ether, and by design of the reaction vessel so as to shorten the time required for attainment of thermal equilibrium.

Heat changes in the reactions

$$CH_3{\cdot}MgI + I_2 \longrightarrow CH_3I + MgI_2;\ Q_1 = -111{\cdot}91 \pm 0{\cdot}75 \text{ kcal./mole}$$

and

$$CH_3{\cdot}MgI + HI \longrightarrow CH_{4\,gas} + MgI_2;\ Q_2 = -125{\cdot}12 \pm 0{\cdot}61 \text{ kcal./mole}$$

(all in solution in *p*-xylene except $CH_{4\,gas}$)

give important thermochemical quantities which include the reaction (at standard pressure and 18°)

$$CH_3I + HI \longrightarrow I_2 + CH_4;\ Q_3 = -11{\cdot}04 \pm 1{\cdot}33 \text{ kcal./mole}$$

On this basis various bond energies can be calculated including a new value for $D(CH_3{-}I) = 54{\cdot}65 \pm 1{\cdot}70$ kcal. and $D(CH_3{-}H) - D(CH_3{-}I) = 45{\cdot}35 \pm 1{\cdot}37$ kcal./mole.

As described in Part I,* the use of a fairly simple constant-pressure calorimeter and carefully selected Grignard reactions permits the evaluation of certain bond energies not readily accessible in other ways.

The versatile possibilities of Grignard calorimetry made it desirable to check the basic procedure independently, before examining a greater variety of bond energies. In addition to the reactions described in Part I, the chemistry and calorimetry of the reaction

$$CH_3{\cdot}MgI + HI \longrightarrow CH_4 + MgI_2;\ Q_2 = -125{\cdot}12 \pm 0{\cdot}61 \text{ kcal./mole}$$

have now been studied. On account of the reaction of ethyl ether with hydrogen iodide and with free radicals, and also in order to minimise corrections for the vapour pressure of the solvent, the Grignard reactions were carried out substantially in *p*-xylene. The calorimeter was improved by constructing the reaction vessel of quartz which permits a much faster heat exchange than does glass, and by using a metal " adiabatic " mantle in place of a water-bath.

The calculated dissociation energy $D(CH_3{-}I) = 54{\cdot}65 \pm 1{\cdot}70$ kcal. overlaps the value obtained in Part I by use of other reactions and other methods of evaluation.

Other thermochemical results are referred to below.

Experimental

Preparation of the Grignard Solutions.—Except where otherwise specified, general methods of preparation and of protection against moisture, oxygen and light were as reported in Part I. To obtain the Grignard compound in xylene, 1 g. of pure dry vacuum-distilled magnesium was covered with 30 ml. of specially purified ether. After dropwise addition of 5 ml. of methyl iodide, reaction was completed by 15 minutes' refluxing. 300 Ml. of purified *p*-xylene were then added, and the ether together, with a little xylene was removed by distillation at 60°/13 mm. until no more ether distilled off. The *p*-xylene was purified by fractional freezing and final refluxing with sodium wire *in vacuo* for 3 hours. Analysis showed that the resulting xylene solutions contained approx. 1 mole of ethyl ether per mole of magnesium compound. For

* Part I, *J.*, 1948, 1161.

reasons described below, approximately 0·07 mole of dry anhydrous magnesium iodide was added to the stock solution per mole of methylmagnesium iodide.

We are indebted to Imperial Chemical Industries Limited, Billingham Division, for the very valuable help in supplying pure *p*-xylene. Other solvents tried and found less satisfactory for various reasons included *n*-hexane, anisole, dibutyl ether, dinonyl ether, acetaldehyde diethyl acetal, phenetole, and purified " technical " xylene.

Preparation of Solutions of Reagents in Xylene.—After trial of alternative methods, hydrogen iodide was prepared (Fig. 1*a*) by heating dry iodine (30 g.) in a round flask (500-ml. capacity) with decalin (300 ml.), freshly distilled to free it from peroxides, water, etc. The hydrogen iodide evolved was carried by a slow stream of oxygen-free nitrogen up the condenser, which retained most of any unchanged iodine, decalin, etc., and after passing through a tube packed with cleaned glass wool (to arrest iodine and decalin mist) was condensed in a wide U-trap cooled with solid carbon dioxide–alcohol. After no more reaction occurred in the decalin, as observed from the " clearing " of colour, the generator was removed and the crude solid hydrogen

FIG. 1*a*.

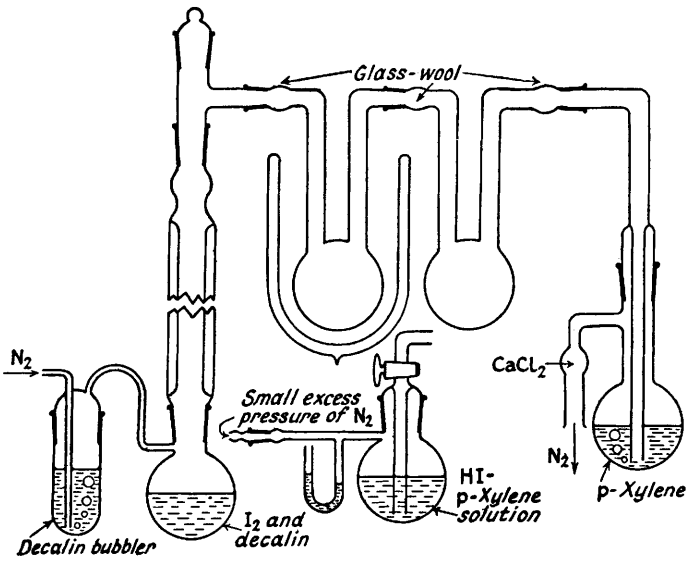


FIG. 1*b*.

iodide was redistilled into a second wide U-trap, in a slow current of nitrogen. Finally, the contents of the second trap, which were quite colourless, were allowed to warm to room temperature and were carried over by the nitrogen into about 300 ml. of pure dry *p*-xylene. The resulting solution was transferred for storage under slight excess pressure of nitrogen to a blackened vessel as illustrated in Fig. 1*b*.

In view of the photochemical decomposition of hydrogen iodide bright light was avoided throughout the preparation and storage. Before use of the solutions, minute traces of iodine which gave a weak sherry colour were removed by contact with a droplet of mercury. This stock solution (approx. 0·02N) was titrated at intervals, a pipette similar to that described in Part I being used. With all the precautions described, titrations reproducible within $\pm 0{\cdot}13\%$ could be obtained over a period of weeks.

Solutions of dry iodine in *p*-xylene were prepared by shaking and their titre also remained constant within an experimental error of $\pm 0{\cdot}1\%$ for several weeks.

Stoicheiometry of the Reactions.—

$$(a)\quad \underset{\text{in } p\text{-xylene}}{CH_3{\cdot}MgI,Et_2O} + \underset{\text{in } p\text{-xylene}}{HI} \longrightarrow \underset{\text{gas}}{CH_4} + \underset{\text{in } p\text{-xylene}}{MgI_2,Et_2O} \qquad (2)$$

The standard solution (20 ml.) of methylmagnesium iodide in xylene was transferred to the reaction vessel and three successive quantities of hydrogen iodide in *p*-xylene were pipetted in. The residual methylmagnesium iodide was then evaluated by Gilman's method.

In a typical experiment, the direct conversion of methylmagnesium iodide due to $0{\cdot}593 \times 10^{-3}$ mole of hydrogen iodide corresponded with $0{\cdot}591 \times 10^{-3}$ equivalent. This and similar tests showed that reaction (2) above, could be treated as quantitative under the conditions used for calorimetry. Before these tests had been carried out it had been feared that some of the hydrogen iodide might be carried off by the methane, but apparently owing to the excess of Grignard compound and the rapid reaction this possibility can be neglected.

FIG. 2. *Constant-pressure calorimeter.*

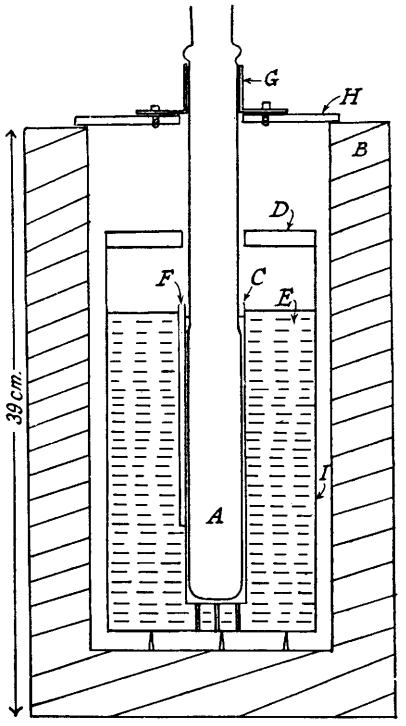
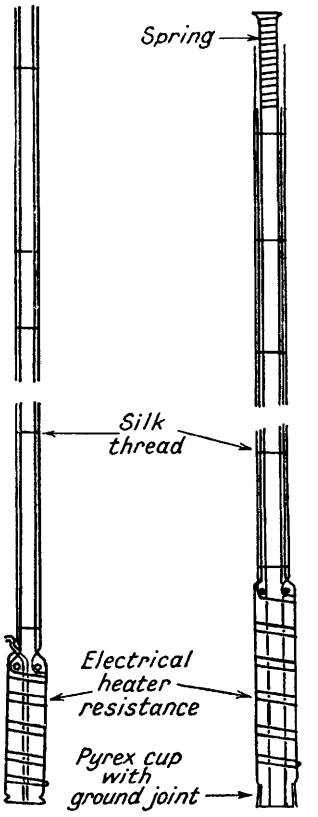


FIG. 3*a*. FIG. 3*b*.



Direct tests using combusion methods confirmed that methane was quantitatively evolved as a gas in accordance with equation (2).

$$(b)\quad CH_3{\cdot}MgI,Et_2O + I_2 \longrightarrow CH_3I + MgI_2,Et_2O \quad . \; . \; . \quad (1)$$
(all in *p*-xylene)

Tests based on those described in Part I showed that in the presence of excess of magnesium iodide added beforehand, as above, an amount of methylmagnesium iodide corresponding with $0{\cdot}537 \times 10^{-3}$ mole reacted with the disappearance of $0{\cdot}540 \times 10^{-3}$ mole of iodine. Under these conditions the alternative reaction (cf. Part I)

$$2CH_3{\cdot}MgI,Et_2O + I_2 \longrightarrow C_2H_6 + 2MgI_2,Et_2O$$

had a negligible influence on the calorimetry.

To make sure that no substantial attack on the solvent occurred in any of the these reactions, the methyl iodide formed in reaction (1) was determined by Zeisel's method after decomposition of the unchanged methylmagnesium iodide with dilute sulphuric acid: $0{\cdot}538 \times 10^{-3}$ mole of methyl iodide was recovered, which agreed within experimental error with the amount of methylmagnesium iodide used. In reaction (1) the magnesium iodide formed was retained

as a clear solution, presumably owing to the residual ethyl ether present. For accurate calorimetry this avoidance of solid phases whose heat content can depend on the state of division, etc., is an important feature.

The Constant-pressure Calorimeter.—To accelerate heat exchange a copper calorimeter (*C*, Fig. 2) (approx. mass 17·4 g.) was fitted with minimum clearance of about 1 mm. over the reaction vessel (*A*) which was made of quartz in view of its thermal conductivity being ten times that of Pyrex glass. A thin layer of silver was plated on to the quartz up to the shoulder. Paraffin (approx. 10 ml.) filled the space between the copper and the quartz to the shoulder of the reaction vessel. The adiabatic mantle (*B*) consisted of a cast aluminium block (approx. 27·3 kg.), and was fitted to reaction vessel by a brass lid (*H*) and an adiabatic collar (*G*); its temperature was kept by electrical heating within about $\pm 0{\cdot}04°$ of that of the calorimeter; a differential thermocouple and hand-controlled heating were used. By means of tests it was found that rather better estimations of heat exchange curves between the calorimeter and its surroundings with smaller root-mean-square deviations were obtained by filling part of the air space with carefully dried light magnesium carbonate (*E*). For convenience, this was packed in immediate contact with the calorimeter, in an intermediate copper pot (*I*) with a lid (*D*).

The temperature of the copper calorimeter was read to 0·004° by means of a single copper–constantan thermojunction, fitted into a pocket (*F*), and a galvanometer, lamp, and scale. Electrical heating for purposes of calibration was by means of a length of 40-gauge platinum–iridium wire (resistance $50{\cdot}887 \pm 0{\cdot}017$ ohms) wound direct on the reaction pipette (Fig. 3*a*). This wire remained bright and resistance measurements showed that it was unaffected by immersion in solutions of Grignard reagents.

Any heat flow down the walls of the quartz tube which connects the reaction vessel with the outside was minimised by keeping the closely fitting brass adiabatic collar at the same temperature as the brass lid and the aluminium adiabatic mantle.

For determining heats of solution of solid iodine in *p*-xylene at the appropriate concentration it was found more convenient to replace the pipette by the spring-loaded delivery vessel, (Fig. 3*b*). The solid was placed in the Pyrex cup which was ground into the upper container, so as to prevent ingress of the liquid around it, until the plunger was depressed. Alternate depression and raising of this plunger a few times led to rapid mixing and dissolution of the solid.

Heat of Vaporisation of Hydrogen Iodide from p-*Xylene Solution.*—This quantity, which is required in connection with one of the thermochemical cycles discussed below, was evaluated by direct determination of the equilibrium concentration of hydrogen iodide vapour above the solution, at three different temperatures. Bubblers were used to saturate a stream of dry oxygen-free nitrogen with the vapours at the temperature of the experiment. By duplicating these bubblers in series it was verified that saturation was effectively reached by means of two bubblers. The vapours in known volumes of gas were absorbed in standard alkali, and the concentration of hydrogen iodide was evaluated.

Heat of Vaporisation of Methyl Iodide from the Grignard Solutions.—A procedure corresponding to that for hydrogen iodide was used, with alcoholic silver nitrate as the analytical reagent. The remaining procedures and precautions were essentially as recorded in Part I.

Estimation of Residual Ether in p-*Xylene Solution.*—A solution (approx. 180 ml.) of methylmagnesium iodide in *p*-xylene, prepared as described above, was decomposed with *ca.* N-sulphuric acid (about 20 ml.; the requisite amount). The water and ether were separated from the resultant mixture by distillation. A few drops of *p*-xylene which distilled at the same time were separated, extracted with water, and rejected. The aqueous distillate and washings contained all the residual ether that may have been in the original solution. A method developed by the authors (to be published) for the determination of ether in aqueous solutions, based on the quantitative conversion of ether into acetic acid by acid potassium dichromate, was used. The residual ether in the *p*-xylene solution corresponded with approximately 1 mole per mole of the Grignard compound. This is probably held by co-ordination forces.

Accuracy of Electrical Calibration.—An input of electrical energy equivalent to $19{\cdot}10 \pm 0{\cdot}07$ cal. during $3\frac{1}{2}$ minutes gave a rise of $8{\cdot}03 \pm 0{\cdot}05$ arbitrary divisions on our scale. The energy was supplied from two 2-v accumulators in series through a platinum–iridium wire of approx. 40 gauge and with a resistance of $50{\cdot}887 \pm 0{\cdot}017$ ohm. The current from the accumulators had previously been passed through a similar resistance until a steady voltage was obtained. The chemical temperature–time curve was then matched electrically. The current through the heater wire was measured by means of the potential drop measurable to $\pm 0{\cdot}0001$ v across a standard resistance of 1 ohm in series with it.

Results and Discussion

The following heats of reaction were calculated from these observations (1 calorie = $4{\cdot}1833 \times 10^7$ ergs) :

$$\underset{0{\cdot}079\text{m}}{CH_3{\cdot}MgI,Et_2O} + \underset{0{\cdot}0192\text{m}}{I_2} \longrightarrow \underset{0{\cdot}00654\text{m}}{CH_3I} + \underset{0{\cdot}00654\text{m}}{MgI_2,Et_2O};\ Q_1 = -111{\cdot}91 \pm 0{\cdot}75 \text{ kcal./mole} \quad (1)$$

(all in *p*-xylene)

The probable mean error is calculated from the standard mean deviation of ten independent experiments.

$$\underset{\substack{0{\cdot}079\text{m}\\ \text{in}\\ p\text{-xylene}}}{CH_3{\cdot}MgI,Et_2O} + \underset{\substack{0{\cdot}0209\text{m}\\ \text{in}\\ p\text{-xylene}}}{HI} \longrightarrow \underset{\substack{\text{gas} +\\ p\text{-xylene}\\ \text{vapour}}}{CH_4} + \underset{\substack{0{\cdot}00711\text{m}\\ \text{in}\\ p\text{-xylene}}}{MgI_2,Et_2O};\ Q_2 = -125{\cdot}12 \pm 0{\cdot}61 \text{ kcal./mole} \quad (2)$$

Combination of (1) and (2), effects of small differences in molalities being neglected, gives equations for the cyclic process

$$\underset{\substack{0{\cdot}00654\text{m}\\ \text{in}\\ p\text{-xylene}}}{CH_3I} + \underset{\substack{0{\cdot}0209\text{m}\\ \text{in}\\ p\text{-xylene}}}{HI} \xrightarrow{Q_4} \underset{\substack{\text{gas} +\\ p\text{-xylene}\\ \text{vapour}}}{CH_4} + \underset{\substack{0{\cdot}0192\text{m}\\ \text{in}\\ p\text{-xylene}}}{I_2};\ Q_4 = -13{\cdot}21 \pm 0{\cdot}96 \text{ kcal./mole} \quad . \quad . \quad (3)$$

$$\downarrow q_1 \qquad \downarrow q_2 \qquad \downarrow q_3 \qquad \downarrow q_4$$

$$CH_3I_{gas} + HI_{gas} \xrightarrow{Q_3} CH_{4\,gas} + I_{2\,gas};\ Q_3 = -11{\cdot}04 \pm 1{\cdot}33 \text{ kcal./mole} \quad (4)$$

The gaseous reaction (4) can be calculated by evaluating the heat terms indicated in the cycle :

$$Q_3 = -13{\cdot}21 - (q_1 + q_2 + q_3 + q_4) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In equation (5) the subsidiary thermal quantities were evaluated as described in the following paragraphs.

(i) In spite of the comparatively high dilution of the magnesium compounds, experiments showed that the differential heats of solution departed to a measurable extent from integral heats of solution. q_1 was therefore determined from directly measured partial pressures of methyl iodide over the solutions corresponding to the end-concentrations of the calorimetric reactions, at different temperatures. Concentrations found over the solution represented in equation (1) were, in 10^{-4} mole/l., 0·38 at 298° K, 0·317 at 293° K, and 0·298 at 291° K. This gives $q_1 = +6{\cdot}73 \pm 0{\cdot}52$ kcal./mole.

(ii) $HI_{p\text{-xylene}} \longrightarrow HI_{gas}$; $q_2 = 3{\cdot}03 \pm 0{\cdot}16$ kcal./mole. This was calculated by means of the Clausius–Clapeyron equation for the partial molal concentrations in the vapour over the solution. These were found to be $[HI] = 1{\cdot}976 \times 10^{-4}$ mole/l. at −1·2° C, $2{\cdot}120 \times 10^{-4}$ at 4·8° C, and $[HI] = 2{\cdot}480 \times 10^{-4}$ at 13·9° C, from which the partial pressures were calculated.

(iii) $CH_{4\,(gas\,+\,p\text{-xylene})} \longrightarrow CH_{4\,gas} + p$-xylene (liquid); $q_3 = -0{\cdot}12 \pm 0{\cdot}1$ kcal./mole. On the assumption that the methane was saturated with *p*-xylene, the partial pressure of methane at the temperature of the experiment was 751·13 mm. If pure methane is separated from the mixture by means of a semipermeable membrane at this pressure and is then compressed to 1 atmosphere, the work per mole done on the system is $293\boldsymbol{R} \log_e 760/751{\cdot}13 = 0{\cdot}0066$ kcal./mole. The heat liberated when the *p*-xylene is condensed back to liquid is $(8{\cdot}87/751{\cdot}13) \times 10{\cdot}11 = 0{\cdot}12$ kcal./mole, the heat of vaporisation for *p*-xylene being taken as 10·11 kcal. at 25° C (Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803).

The overall correction q_3 is quite small. It becomes much more serious when more volatile solvents are used, such as ethyl ether or *n*-hexane. It may be noted that this

correction lapses when the products of reaction all remain in solution, as is the case in many possible applications of Grignard calorimetry.

(iv) $q_4 = (\Delta H_3 + \Delta H_4) = -11{\cdot}81 \pm 0{\cdot}75$ kcal., where, for $I_{2\ gas} \longrightarrow I_{2\ crystals}$, $\Delta H_3 = -14{\cdot}91$ kcal. (Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Rheinhold Publ. Corp., 1936) and, for $I_{2\ crystals}$ + *p*-xylene $\longrightarrow$ I_2(0·0192m in *p*-xylene), $\Delta H_4 = +3{\cdot}10 \pm 0{\cdot}75$ kcal. (our experiments). Insertion of these values into equation (5) gives:

$$Q_3 = -11{\cdot}04 \pm 1{\cdot}33 \text{ kcal./mole}$$

This new result may be used in conjunction with known bond dissociation energies. For example, equation (4) is interchangeable with

$$D(CH_3\text{–}I) + D(H\text{–}I) \longrightarrow D(I\text{–}I) + D(CH_3\text{–}H);\ Q_3 = -11{\cdot}04 \pm 1{\cdot}33 \text{ kcal./mole}$$

Combining this with the accurately known values (at 291° K) for $D(H\text{–}I) = 71{\cdot}58 \pm 0{\cdot}2$ kcal. and for $D(I\text{–}I) = 36{\cdot}27 \pm 0{\cdot}2$ kcal. (Bichowsky and Rossini, *op. cit.*) gives the *bond substitution* I *for* H *in methane*

$$D(CH_3\text{–}H) - D(CH_3\text{–}I) = 45{\cdot}35 \pm 1{\cdot}37 \text{ kcal.} \quad . \quad . \quad . \quad . \quad (6)$$

In view of the uncertainties of bond dissociations energies, this form of stating the result seems preferable at the present time. However, if our result (6) is combined with the known value

$$D(CH_3\text{–}H) = 101 \pm 1 \text{ kcal.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(Szwarc, *Chem. Reviews*, 1950, **47**, 75), this gives

$$D(CH_3\text{–}I) = 54{\cdot}65 \pm 1{\cdot}7 \text{ kcal.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Allowance for the temperature coefficient of $D(CH_3\text{–}H)$ (cf. Kistiakowsky and Van Artsdalen, *J. Chem. Physics*, 1944, **12**, 478) seems premature in view of the uncertainty limits. Probable mean errors in individual results above are estimated on the basis of ten or more independent experiments. The probable mean error in equation (8) combines all the errors in the individual data according to standard procedure, and is an assessment of the overall reliability. It should not be confused with the mean deviation in a single type of experiment as quoted, *e.g.*, by Carson, Hartley, and Skinner (*Proc. Roy. Soc.*, 1949, *A*, **195**, 500).

The new value in (8) may be compared with previously published results.

(*a*) The value quoted by Mackle and Ubbelohde (Part I, *loc. cit.*). In Part I the heat value for the process $I_{2\,c} \longrightarrow I_{2\ gas}$ was taken as $18{\cdot}9 \pm 0{\cdot}25$ kcal. This was arrived at from the sum of F, the heat of fusion, and V, the heat of vaporisation of iodine as quoted by Bichowsky and Rossini (*op. cit.*, p. 25). In fact, V, as used by these authors, is a misprint for V_s (see Bichowsky and Rossini, *op. cit.*, p. 15). On this basis the correct value for the above process is 14·91 kcal. This has the effect of making $\frac{1}{2}q_2$, which is the relevant term in equation (19) of Part I, equal to 6·65 kcal. instead of 8·6 kcal., as hitherto employed. The final value for $D(CH_3\text{–}I)$ given in Part I is now modified to $52{\cdot}8 \pm 1{\cdot}4$ kcal.

(*b*) The value recorded by Carson, Hartley, and Skinner (*loc. cit.*) should be corrected to $54{\cdot}00 \pm 0{\cdot}5$ kcal on account of the modified $D(CH_3\text{–}H)$ value given in (7) above.

Both the results of Part I and of Carson, Hartley, and Skinner involve systematic uncertainties in a direction which tends to bring the calculations into closer overlap with those obtained by the present method. The chief systematic uncertainty in Part I is the value assumed for $D(CH_3\text{–}CH_3)$ (84·3 kcal./mole). If the upper probable limit (cf. Szwarc, *loc. cit.*) of 87 kcal./mole is used, this would make $D(CH_3\text{–}I) = 54{\cdot}2 \pm 1{\cdot}4$, calculated according to the procedures of Part I (see equation 19, p. 1169).

The chief systematic uncertainty in the procedure of Carson, Hartley, and Skinner lies in the calorimetric production of what may be imperfectly crystalline cadmium iodide from organic solvents (cf. also Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1950, **46**, 1022). The lattice energy of cadmium iodide is about 190 kcal. An increased

heat content of 1% of this lattice energy, which is by no means unlikely in strained or otherwise imperfect crystals such as might be produced from organic solvents by precipitation, may be used to illustrate possible effects. Allowance for crystals imperfect to this extent would *increase* $D(CH_3–I)$ recorded by these authors to around 55·00 kcal., when the value $D(CH_3–H)$ is taken as 101 kcal. This overlaps our present value.

Attempts were also made to develop the methods of Part I by using ethereal solutions and solutions of hydrogen iodide in *n*-hexane (Mackle, Maniece, and Ubbelohde, unpublished observations). Vapour-pressure and other corrections left a rather large measure of uncertainty. The value of $D(CH_3–I)$ calculated from these unpublished observations was 57·6 $\pm$ 3·2 kcal., which gives quite independent support to our more accurate results now reported.

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