A Thermochemical Evaluation of Bond Strengths in Some Carbon Compounds. Part III. Bond Strengths based on the Reactions: (a)* $Ph{\cdot}CH_2I + HI \longrightarrow Ph{\cdot}CH_3 + I_2$ *and (b)* $PhI + HI \longrightarrow PhH + I_2$.

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[Reprint Order No. 5656.]

Methods described in Part II * have been used to determine heat changes in the reactions :

(A) (1) $Ph{\cdot}CH_2{\cdot}MgCl + I_2 \longrightarrow Ph{\cdot}CH_2I + MgICl;\ Q_1 = -105{\cdot}9 \pm 0{\cdot}8$ kcal./mole.

(2) $Ph{\cdot}CH_2{\cdot}MgCl + HI \longrightarrow Ph{\cdot}CH_3 + MgICl;\ Q_2 = -113{\cdot}7 \pm 0{\cdot}7$ kcal./mole.

(all in *p*-xylene solution)

(B) (3) $\underbrace{PhMgBr + 505{\cdot}2\ C_7H_8O} + \underbrace{I_2 + 182{\cdot}7\ C_7H_{16}} \longrightarrow$

$PhI + MgIBr + 505{\cdot}2\ C_7H_8O + 182{\cdot}7\ C_7H_{16};\ Q_3 = 123{\cdot}9 \pm 1{\cdot}0$ kcal./mole.†

(4) $\underbrace{PhMgBr + 505{\cdot}2\ C_7H_8O} + \underbrace{HI + 182{\cdot}7\ C_7H_{16}} \longrightarrow$

$PhH + MgIBr + 505{\cdot}2\ C_7H_8O + 182{\cdot}7\ C_7H_{16};\ Q_4 = 114{\cdot}3 \pm 0{\cdot}8$ kcal./mole.†

(Grignard reagent in anisole, C_7H_8O; iodine and hydrogen iodide in solution in *n*-heptane)

Known heats of reaction being used, these reactions give rise to the important thermochemical quantities (at standard pressure and 25°) :

(6) $Ph{\cdot}CH_2I_g + HI_g \longrightarrow I_{2,g} + Ph{\cdot}CH_{3,g};\ -Q_6 = +1{\cdot}0 \pm 1{\cdot}3$ kcal./mole

and (10) $PhI_g + HI_g \longrightarrow I_{2,g} + PhH;\ -Q_{10} = -5{\cdot}2 \pm 1{\cdot}4$ kcal./mole.

On this basis various bond strengths can be calculated, including new values for :

$$D(Ph{\cdot}CH_2\text{–}H) - D(Ph{\cdot}CH_2\text{–}I) = 34{\cdot}3 \pm 1{\cdot}3 \text{ kcal./mole}$$
$$D(Ph{\cdot}CH_2\text{–}I) = 43{\cdot}2 \pm 1{\cdot}8 \text{ kcal./mole}$$
$$D(Ph\text{–}H) - D(Ph\text{–}I) = 40{\cdot}5 \pm 1{\cdot}6 \text{ kcal./mole}$$

and
$$D(Ph - I) = 60{\cdot}9 \pm 1{\cdot}8 \text{ kcal./mole}$$

Differences between the corresponding disruption energies for the phenyl and the benzyl compounds are compared with those for methyl iodide and are discussed in terms of the electronic structures. (Here the Q and q symbols are identical with ΔH.)

FOR development of the physical chemistry of aromatic systems, there are still only few data on bond disruption energies from which quantitative information can be derived about inductive and mesomeric effects in the ground states of the molecules. Grignard-reaction calorimetry seemed likely to open up an extensive range of interesting bond data on aromatic systems, and has therefore been investigated as described below. The chief difficulty in this method of measuring disruption energies in important aromatic compounds was found to lie in the chemistry of the Grignard reactions. It proved unexpectedly difficult to establish conditions where useful stoicheiometric reactions took place. Whilst the general reason for these difficulties appears to be the long life of some of the free radicals produced as reaction intermediates, the present paper gives details only for the solvents and concentration ranges which gave reactions usable in chemical calorimetry. Methods described below give new bond data for a significant pair of aromatic compounds, and open up the field for further developments. The significance of the wide range of reactions discovered in which the stoicheiometry is different is being further studied.

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* Part II, *J.*, 1952, 415.

† These values include a large heat-absorption term resulting from the mixing of anisole and heptane in the amounts indicated in the equations. This term cancels out in the subsequent thermochemical equations.

EXPERIMENTAL

Preparation of Solutions of Reagents.—Solutions of the Grignard reagents, of hydrogen iodide, and of iodine were prepared as in Part II (*loc. cit.*). Benzyl chloride was used instead of the bromides and iodides employed hitherto, because it was found to give more favourable preparations for the present purpose. Commercial benzyl chloride and phenyl bromide were purified by refluxing them *in vacuo* over fresh calcium turnings and then distilling them at reduced pressure. Benzylmagnesium chloride was prepared in pure diethyl ether and diluted with pure *p*-xylene so that the resulting 0·08M-Grignard solution contained approximately 1% v/v of diethyl ether.

Phenylmagnesium bromide was prepared in a similar manner but was diluted with pure anisole instead of *p*-xylene. The resultant 0·08M-solution of Grignard reagent contained a similar proportion of ether. For reactions involving phenylmagnesium bromide *n*-heptane was used as solvent for the iodine and hydrogen iodide. This solvent was purified by prolonged storage over fuming sulphuric acid to remove unsaturated materials, then shaken with 10% potassium hydroxide solution to remove traces of acid, dried by prolonged storage over potassium hydroxide pellets, and refluxed over sodium wire, over which it was fractionally distilled; the fraction of b. p. 97—97·5° was used.

Stoicheiometry of the Reactions.—Tables 1 and 2 give typical examples of the reactions of iodine and hydrogen iodide with phenylmagnesium bromide and benzylmagnesium chloride.

TABLE 1. *Mean of ten iodine reactions.*

	I_2 solution (M)	Grignard solution (M)	Grignard reagent orig. (mmole)	reacted (mmole)	I_2 reacted (mmole)
$Ph{\cdot}CH_2{\cdot}MgCl$	0·02	0·087	1·740	0·256	0·252
PhMgBr	0·036	0·069	1·379	0·359	0·362

TABLE 2. *Mean of ten hydrogen iodide reactions.*

	HI solution (M)	Grignard solution (M)	Grignard reagent orig. (mmole)	reacted (mmole)	HI reacted (mmole)
$Ph{\cdot}CH_2{\cdot}MgCl$	0·018	0·087	0·740	0·514	0·510
PhMgBr	0·036	0·069	1·379	0·353	0·357

The reactions of iodine and hydrogen iodide with benzylmagnesium chloride proceeded smoothly in *p*-xylene (cf. Part II) and resulted in quantitative conversion of benzylmagnesium chloride into benzyl iodide and toluene respectively, according to the equations :

$$(a)\quad Ph{\cdot}CH_2{\cdot}MgCl + I_2 \longrightarrow Ph{\cdot}CH_2I + MgICl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$(b)\quad Ph{\cdot}CH_2{\cdot}MgCl + HI \longrightarrow Ph{\cdot}CH_3 + MgICl \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

(all in *p*-xylene)

On the other hand the reactions involving phenylmagnesium bromide did not give quantitative stoicheiometry in *p*-xylene. Therefore the stoicheiometry of these reactions was investigated in a series of pure and mixed solvents, including diethyl ether, ethyl tetrahydropyran-2-yl ether, diphenyl ether containing diphenyl, anisole, and an anisole–heptane mixture. The general trend of reactions in *p*-xylene supported the working hypothesis that the mechanism of the desired reaction was ionic. In the case of phenylmagnesium bromide a solvent more polar than *p*-xylene was indicated in order to suppress free-radical reactions. Finally, anisole containing about 1% of diethyl ether was chosen as solvent for the Grignard reagent. Ethers are unsuitable as solvents for hydrogen iodide, when there is prolonged contact. To balance the thermal cycles, *n*-heptane was used for both iodine and hydrogen iodide. Under these conditions the reactions followed the equations :

$$(a)\quad \underset{\text{(anisole)}}{PhMgBr} + \underset{\text{(heptane)}}{I_2} \longrightarrow \underset{\text{(anisole–heptane)}}{PhI + MgIBr} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$(b)\quad \underset{\text{(anisole)}}{PhMgBr} + \underset{\text{(heptane)}}{HI} \longrightarrow \underset{\text{(anisole–heptane)}}{PhH + MgIBr} \quad . \; . \; . \; . \; . \; . \quad (4)$$

Typical examples of the stoicheiometry in these solvents are quoted in the above Tables.

Various subsidiary thermal quantities were required to complete the thermochemical cycles below. Some of these were obtained from the literature but the following were determined experimentally :

Heat of vaporisation of HI *from* n-*heptane solution.* This was evaluated by direct determination of the equilibrium concentrations of hydrogen iodide vapour above the solution at four different temperatures (for method see Part II).

Heat of vaporisation of benzyl iodide from the Grignard solutions. A procedure corresponding to that for hydrogen iodide was adopted, with alcoholic silver nitrate as the analytical reagent.

The Constant-pressure Calorimeter.—For the measurement of the heat changes in the reactions involving benzylmagnesium chloride the constant-pressure calorimeter described in Part II was used. However, a modified form of this calorimeter was employed for the reactions of phenylmagnesium bromide. The main modifications were a reduction of about 30% in the size of the constant-temperature jacket, and a closer control of temperature at 25° ± 0·001° in the jacket by means of a toluene regulator with a " Sunvic " proportionating head. The toluene (130 ml.) was contained in two glass bulbs diametrically opposed in the block. The remaining procedures and precautions, including the calibration of the calorimeter, were essentially as recorded in Part II.

RESULTS

The following heats of reaction were calculated from the observations for the reactions involving benzylmagnesium chloride (1 calorie = 4·1833 × 10^7 ergs. N.B. : throughout this paper, as in Parts I and II, the Q and q symbols are identical with ΔH, *not* $-\Delta H$).

$$\underset{0{\cdot}087\text{M}}{\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}} + \underset{0{\cdot}018\text{M}}{\text{HI}} \longrightarrow \underset{0{\cdot}00578\text{M}}{\text{Ph}\cdot\text{CH}_3} + \underset{0{\cdot}00578\text{M}}{\text{MgICl}};\ Q_2 = -113{\cdot}7 \pm 0{\cdot}7 \text{ kcal./mole} \quad . \quad (2)$$

$$\underset{0{\cdot}087\text{M}}{\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}} + \underset{0{\cdot}02\text{M}}{\text{I}_2} \longrightarrow \underset{0{\cdot}0065\text{M}}{\text{Ph}\cdot\text{CH}_2\text{I}} + \underset{0{\cdot}0065\text{M}}{\text{MgICl}};\ Q_1 = -105{\cdot}9 \pm 0{\cdot}8 \text{ kcal./mole} \quad . \quad (1)$$

Combination of equations (1) and (2), neglecting small differences in molality, gives :

$$\underset{0{\cdot}018\text{M}}{\text{HI}} + \underset{0{\cdot}0065\text{M}}{\text{Ph}\cdot\text{CH}_2\text{I}} \longrightarrow \underset{0{\cdot}00578\text{M}}{\text{Ph}\cdot\text{CH}_3} + \underset{0{\cdot}02\text{M}}{\text{I}_2};\ Q_5 = -7{\cdot}8 \pm 1{\cdot}1 \text{ kcal./mole} \quad . \quad . \quad . \quad (5)$$

(all in *p*-xylene)

The heat of a similar reaction in the gaseous phase can be arrived at from the cyclic process :

$$\begin{tikzcd}
\underset{0{\cdot}0065\text{M}}{\text{Ph}\cdot\text{CH}_2\text{I}} & + & \underset{0{\cdot}018\text{M}}{\text{HI}} \arrow[r, "Q_5"] & \underset{0{\cdot}00578\text{M}}{\text{Ph}\cdot\text{CH}_3} \arrow[d, "q_3"'] & + & \underset{0{\cdot}02\text{M}}{\text{I}_2} \arrow[d, "q_4"'] & ;\ Q_5 = -7{\cdot}8 \pm 1{\cdot}1 \text{ kcal./mole} \quad . \quad . \quad (5) \\
\text{Ph}\cdot\text{CH}_2\text{I}_\text{g} \arrow[u, "q_1"] & + & \text{HI}_\text{g} \arrow[u, "q_2"] & \text{Ph}\cdot\text{CH}_{3.\text{g}} \arrow[l, "Q_6"'] & + & \text{I}_{2.\text{g}} & ;\ Q_6 = -1{\cdot}0 \pm 1{\cdot}3 \text{ kcal./mole} \quad . \quad . \quad (6)
\end{tikzcd}$$

The heat of the gaseous reaction (6) can be calculated from the heat terms indicated in the cycle :

$$Q_6 = -Q_5 - (q_1 + q_2 + q_3 + q_4) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In equation (7) the subsidiary thermal quantities were evaluated as described in the following paragraphs :

(i) q_1 was determined from directly measured partial pressures of benzyl iodide over the solutions corresponding to the end-concentrations of the calorimetric reactions, at different temperatures. Partial pressures found over the solution represented in equation (1) were 0·255 mm. at 298° K, 0·287 mm. at 303° K, and 0·419 mm. at 308° K. From the slope of the plot of log p against $1/T$ it is calculated that $q_1 = -8{\cdot}9 \pm 0{\cdot}5$ kcal./mole.

(ii) $\text{HI}_\text{g} \longrightarrow \text{HI}_{p\text{-xylene sol.}}$: $q_2 = -3{\cdot}0 \pm 0{\cdot}2$ kcal./mole. For the determination of this quantity see Part II.

(iii) $q_3 = (\Delta H_1 + \Delta H_2) = 9{\cdot}1 \pm 0{\cdot}5$ kcal./mole, where, for $\text{Ph}\cdot\text{CH}_{3\,p\text{-xylene sol.}} \longrightarrow \text{Ph}\cdot\text{CH}_{3\,\text{liquid}}$, ΔH_1 = zero (determined experimentally) ; and the heat of vaporisation, $\text{Ph}\cdot\text{CH}_{3\,\text{liquid}} \longrightarrow \text{Ph}\cdot\text{CH}_{3\,\text{gas}}$, $\Delta H_2 = 9{\cdot}1 \pm 0{\cdot}5$ kcal./mole (Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803).

(iv) $q_4 = +11{\cdot}6 \pm 0{\cdot}7$ kcal./mole (see Part II).

Solubilities (S; g./100 g. of solution) of crystalline iodine in *p*-xylene were redetermined: 15·43 at 292·92° K; 16·50 at 296·86° K; 17·55 at 300·04° K. From the plot of log S against $1/T$ a new value of the heat of solution (ΔH_4 of Part II) was found:

$$I_{2,\,\text{cryst.}} + p\text{-xylene} \longrightarrow I_{2,\,p\text{-xylene sol.}} + 3{\cdot}3 \pm 0{\cdot}2 \text{ kcal./mole.}$$

For the reactions involving phenylmagnesium bromide the following heats of reaction were calculated from the observations:

$$\underbrace{\text{PhMgBr} + 505{\cdot}2\,C_7H_8O} + \underbrace{\text{HI} + 182{\cdot}7\,C_7H_{16}} \longrightarrow$$

$$\text{PhH} + \text{MgIBr} + 505{\cdot}2\,C_7H_8O + 182{\cdot}7\,C_7H_{16};\quad Q_3 = 114{\cdot}3 \pm 0{\cdot}8 \text{ kcal./mole} \quad . \quad (3)$$

$$\underbrace{\text{PhMgBr} + 505{\cdot}2\,C_7H_8O} + \underbrace{I_2 + 182{\cdot}7\,C_7H_{16}} \longrightarrow$$

$$\text{PhI} + \text{MgIBr} + 505{\cdot}2\,C_7H_8O + 182{\cdot}7\,C_7H_{16};\quad Q_4 = 123{\cdot}9 \pm 1{\cdot}0 \text{ kcal./mole} \quad . \quad . \quad . \quad (4)$$

[mean probable error in individual results from five independent experiments in both (3) and (4)]

Combination of equations (3) and (4) gives:

$$\begin{array}{c}\text{HI}\\ 0{\cdot}036\text{M}\\ \text{in heptane}\\ \\ \end{array} + \begin{array}{c}\text{PhI}\\ 0{\cdot}012\text{M}\\ \text{in anisole}\\ \text{–heptane}\end{array} \longrightarrow \begin{array}{c}\text{PhH}\\ 0{\cdot}012\text{M}\\ \text{in anisole}\\ \text{–heptane}\end{array} + \begin{array}{c}I_2\\ 0{\cdot}036\text{M}\\ \text{in heptane}\\ \\ \end{array};\ Q_9 = -9{\cdot}6 \pm 1{\cdot}4 \text{ kcal./mole} \quad (9)$$

The heat of a similar reaction in the gaseous phase can be arrived at from the cyclic process:

$$\begin{tikzcd}
\begin{array}{c}\text{PhI}\\ 0{\cdot}012\text{M}\\ \text{in anisole}\\ \text{–heptane}\end{array} \arrow[r, phantom, "+"] & \begin{array}{c}\text{HI}\\ 0{\cdot}036\text{M}\\ \text{in heptane}\\ \\ \end{array} \arrow[r, "Q_9"] & \begin{array}{c}\text{PhH}\\ 0{\cdot}012\text{M}\\ \text{in anisole}\\ \text{–heptane}\end{array} \arrow[r, phantom, "+"] \arrow[d, "q_7"] & \begin{array}{c}I_2\\ 0{\cdot}036\text{M}\\ \text{in heptane}\\ \\ \end{array} \arrow[d, "q_8"] & ;\ Q_9 = -9{\cdot}6 \pm 1{\cdot}4 \text{ kcal./mole} \\
\text{PhI}_{\text{gas}} \arrow[u, "q_5"'] \arrow[r, phantom, "+"] & \text{HI}_{\text{gas}} \arrow[u, "q_6"'] & \text{PhH}_{\text{gas}} \arrow[l, "Q_{10}"'] \arrow[r, phantom, "+"] & I_{2\,\text{gas}} & ;\ Q_{10} = +5{\cdot}2 \pm 1{\cdot}4 \text{ kcal./mole}
\end{tikzcd}$$

The heat of the gaseous reaction (10) (page 115) can be calculated from the heat terms indicated in the cycle:

$$Q_{10} = -Q_9 - (q_5 + q_6 + q_7 + q_8) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In equation 11 the subsidiary thermal quantities were evaluated as described in the following paragraphs:

(i) $q_5 = (\Delta H_3 + \Delta H_4) = -9{\cdot}5 \pm 0{\cdot}2$ kcal./mole, where, for $\text{PhI}_g \longrightarrow \text{PhI}_l$, $\Delta H_3 = -9{\cdot}5 \pm 0{\cdot}2$ kcal./mole. (Zil'berman-Granovskaya and Shugsam, *J. Phys. Chem. U.S.S.R.*, 1940, **14**, 1004); and, for $\text{PhI}_l \longrightarrow \text{PhI}_{\text{products of reaction (4)}}$, ΔH_4 = zero (determined experimentally).

(ii) $q_6 = -3{\cdot}4 \pm 0{\cdot}2$ kcal./mole. This quantity was determined by the method described in Part II. The values for the partial pressure (mm.) of hydrogen iodide over heptane at the specified temperatures are: 19·75 at 294·95° K, 20·63 at 296·85° K, 21·04 at 299·06° K, 22·27 at 301·30° K. From the slope of the line obtained when the log of the partial pressure of hydrogen iodide was plotted against $1/T$, the heat term q_6 was calculated.

(iii) $q_7 = (\Delta H_5 + \Delta H_6) = +8{\cdot}3 \pm 0{\cdot}2$ kcal./mole, where, for $\text{PhH}_{\text{products of reaction (3)}} \longrightarrow \text{PhH}_l$, ΔH_5 = zero (determined directly in the calorimeter); and, for $\text{PhH}_{\text{liquid}} \longrightarrow \text{PhH}_{\text{gas}}$. $\Delta H_6 = +8{\cdot}3 \pm 0{\cdot}2$ kcal./mole (Timmermans, "Physico-Chemical Constants of Pure Organic Substances," Elsevier, Amsterdam, 1951).

(iv) $q_8 = \Delta H_7 + \Delta H_8 = +9{\cdot}0 \pm 0{\cdot}3$ kcal./mole, where for $I_{2,\,\text{heptane}} \longrightarrow I_{2,\,\text{cryst.}}$, $\Delta H_7 = -5{\cdot}9 \pm 0{\cdot}2$ kcal./mole (Semb, *J. Amer. Pharm. Assoc.*, 1935, **24**, 547); and for $I_{2,\,\text{cryst.}} \longrightarrow I_{2,\,\text{gas}}$, $\Delta H_8 = +14{\cdot}9 \pm 0{\cdot}2$ kcal./mole (Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Rheinhold Publ. Corpn., New York, 1936). Insertion of these values into equation (11) gives $Q_{10} = 5{\cdot}2 \pm 1{\cdot}4$ kcal./mole.

The heat of mixing of anisole and *n*-heptane in the proportions present during the reactions (3) and (4) was determined directly in the calorimeter. Although this value was not required for the calculations involved in the thermochemical cycle above it was considered advisable to know this term as its magnitude affected appreciably the measured heats of reactions (3) and (4). It was found that, for $505{\cdot}2\,C_7H_8O + 182{\cdot}7\,C_7H_{16} \longrightarrow$ Mixture, $\Delta H_9 = 192{\cdot}6 \pm 1{\cdot}4$ kcal./mole.

DISCUSSION

The value $Q_6 = -1{\cdot}15 \pm 1{\cdot}29$ kcal. may be used in conjunction with known bond-dissociation energies. For example, equation (6) can be transformed into

$$D(\mathrm{Ph{\cdot}CH_2{-}I}) + D(\mathrm{H{-}I}) \longrightarrow D(\mathrm{Ph{\cdot}CH_2{-}H}) + D(\mathrm{I{-}I});\ -Q_6 = +1{\cdot}0 \pm 1{\cdot}3\ \text{kcal./mole}$$

Combining this with the accurately known values (at 291° K) for $D(\mathrm{H{-}I}) = 71{\cdot}6 \pm 0{\cdot}2$ kcal. and for $D(\mathrm{I{-}I}) = 36{\cdot}3 \pm 0{\cdot}2$ kcal. (Bichowsky and Rossini, *op. cit.*) gives the bond substitution energy I for H in toluene:

$$D(\mathrm{Ph{\cdot}CH_2{-}H}) - D(\mathrm{Ph{\cdot}CH_2{-}I}) = 34{\cdot}3 \pm 1{\cdot}3\ \text{kcal./mole} \quad . \; . \; . \; . \; . \; . \quad (8)$$

In view of the uncertainties of bond-dissociation energies, stating the result in this form seems preferable at the present time. However, if the result (8) is combined with the known value $D(\mathrm{Ph{\cdot}CH_2{-}H}) = 77{\cdot}5 \pm 1{\cdot}3$ kcal./mole (Szwarc, *J. Chem. Phys.*, 1948, **16**, 128) this gives $D(\mathrm{Ph{\cdot}CH_2{-}I}) = 43{\cdot}2 \pm 1{\cdot}8$ kcal./mole, which is in good agreement with Butler and Polanyi's value (43·7 kcal./mole) (*Trans. Faraday Soc.*, 1943, **39**, 19). The results of Blades, Blades, and Steacie (*Canad. J. Chem.*, 1954, **32**, 298) throw some doubt on the significance of the value quoted by Szwarc, but Schissler and Stevenson's electron-impact data (*J. Chem. Phys.*, 1954, **22**, 151) give a value for $D(\mathrm{Ph{\cdot}CH_2{-}H})$ in good agreement with the value quoted by Szwarc.

The value $Q_{10} = 5{\cdot}2 \pm 1{\cdot}4$ kcal./mole may be used in conjunction with known bond-dissociation energies. For example, equation (10) can be transformed into

$$D(\mathrm{Ph{-}I}) + D(\mathrm{H{-}I}) \longrightarrow D(\mathrm{Ph{-}H}) + D(\mathrm{I{-}I});\ -Q_{10} = -5{\cdot}2 \pm 1{\cdot}4\ \text{kcal.}$$

Combining this with the accurately known values at 298° K for $D(\mathrm{H{-}I})$ and $D(\mathrm{I{-}I})$ quoted above, gives the bond substitution energy I for H in benzene:

$$D(\mathrm{Ph{-}H}) - D(\mathrm{Ph{-}I}) = 40{\cdot}5 \pm 1{\cdot}6\ \text{kcal./mole} \quad . \; . \; . \; . \; . \; . \quad (12)$$

Stated in this form the result seems preferable for the reason mentioned above and particularly because of the uncertainty of the present value for $D(\mathrm{Ph{-}H})$. However, if this result (12) is combined with one of the recently quoted values $D(\mathrm{Ph{-}H}) = 101{\cdot}4$ kcal. (Ladacki and Szwarc, *Proc. Roy. Soc.*, 1953, *A*, **219**, 341) we obtain $D(\mathrm{Ph{-}I}) = 60{\cdot}9 \pm 1{\cdot}8$ kcal./mole.

From the new results together with some well-known heats of formation (see, *e.g.*, Timmermans, *op. cit.*), important C–C bond-dissociation energies as well as interesting heats of formation have been calculated. These are summarised in Table 3.

TABLE 3.

R	$Q_f(\mathrm{RI_{gas}})$ (kcal./mole)	$Q_f(\mathrm{R_{gas}})$ (kcal./mole)	D(C–C) in R–R (kcal./mole)	D(R–I) (kcal./mole)
$\mathrm{CH_3}$	− 1·86	−31·03	82·3	54·6
$\mathrm{Ph{\cdot}CH_2}$	−18·77	−36·63	45·4	43·2
Ph	−33·78	−69·14	97·8	60·9

All the results in Table 3 depend on the D(C–H) values used in calculating D(C–I). The C–H bond-dissociation energies employed were:

$D(\mathrm{CH_3{-}H}) = 101$ kcal./mole (Szwarc, *Chem. Reviews*, 1950, **47**, 157)
$D(\mathrm{Ph{-}H}) = 101{\cdot}4$ kcal./mole (Ladacki and Szwarc, *Proc. Roy. Soc.*, 1953, *A*, **219**, 341)
$D(\mathrm{Ph{\cdot}CH_2{-}H}) = 77{\cdot}5$ kcal./mole (Szwarc, *J. Chem. Phys.*, 1948, **16**, 128)

For $D(\mathrm{Ph{\cdot}CH_2{-}H})$ Szwarc's result has been used but this is markedly different from that obtained by VanArtsdalen (89·5 kcal./mole); Schissler and Stevenson (*J. Chem. Phys.*, 1954, **22**, 151), however, recently reported the value $D(\mathrm{Ph{\cdot}CH_2{-}H}) = 77 \pm 3$ kcal./mole from electron-impact studies, in agreement with Szwarc's figure. Values derived from Grignard calorimetry may be compared with a selection of similar data obtained recently (see Table 4).

The values in Table 4 are generally in good agreement with those of Table 3, especially those in the third and the fourth column. The high value for Q_f ($Ph{\cdot}CH_{2\,gas}$) reported by VanArtsdalen is dependent on the $D(Ph{\cdot}CH_2{-}H)$ value used. Since this is 12 kcal./mole higher than Szwarc's value, the deviation from the other result quoted follows. Bond lengths are discussed below.

TABLE 4.

R	$Q_f(RI_{gas})$ (kcal./mole)	$Q_f(R_{gas})$ (kcal./mole)	D(C–C) in R–R (kcal./mole)	R–I bond length (Å)
CH_3	−2·8,[a] −4·3[b]	−32·1[d]	84·4[d]	2·13 (spec.),[f] 2·28 (E.D.)[f]
$Ph{\cdot}CH_2$	−26·4[c]	−37·4,[d] −49·4[e]	46·8[d]	
Ph	−38·35[b]	−69·7[b]	102·4[d]	2·02 (E.D.)[g]

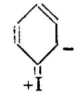
[a] Carson, Hartley, and Skinner, *Proc. Roy. Soc.*, 1949, *A*, **195**, 500. [b] Carson, Carson, and Wilmshurst, *Nature*, 1952, **170**, 320. [c] Gellner and Skinner, *J.*, 1949, 1145. [d] Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **45**, 339. [e] Anderson, Scheraga, and VanArtsdalen, *J. Chem. Phys.*, 1953, **21**, 1258. [f] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46. [g] Hugill, Coop, and Sutton, *Trans. Faraday Soc.*, 1938, **34**, 1529.

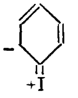
Bond-dissociation Energies.—The marked sequence

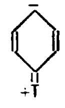
$$\begin{array}{ccccc} D(Ph{-}I) & > & D(CH_3{-}I) & > & D(Ph{\cdot}CH_2{-}I) \\ \text{Diff.} & -6{\cdot}3 & & -11{\cdot}4 & \text{kcal./mole} \end{array}$$

is clear evidence for the non-additivity of bond dissociation energies. Evidence of this kind appears to have been first discussed by Baughan, Evans, and Polanyi (*Trans. Faraday Soc.*, 1941, **37**, 377).

The principal factors that increase the C–I disruption energy in iodobenzene, compared with that of $CH_3{-}I$, seem to be associated with increased interaction between the electrons of the iodine atom and those of the aromatic group. Previous published evidence for such increased interaction can be derived from the greater difficulty of hydrolysis for iodobenzene than for methyl iodide and from the formation of iodonium and iodoxy-compounds. Such evidence from reactivity differences might, however, refer to activated states of the molecule. The quantitative evidence obtained from evaluation of bond strengths refers to the molecules in the ground state and is substantiated by bond-length data. The decrease in the C–I bond length from methyl iodide to iodobenzene (Table 4) is indicative of increased electronic interaction. [Results from electron diffraction (2·02 and 2·28 Å) are more immediately comparable.] The calculated "double-bond character" of the phenyl–iodine linkage (~0·14) (Smyth, *J. Amer. Chem. Soc.*, 1941, **63**, 57) is of the same order as that derived from dipole-moment measurements. The value Ph–I = 1·4 D contrasted with $CH_3{-}I$ = 1·6 D may be explained in terms of contributions from the annexed structures to the resonance hybrid of iodobenzene resulting in less negative iodine.







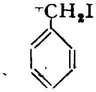
The decreased disruption energy of $Ph{\cdot}CH_2{-}I$ compared with that of $CH_3{-}I$ is probably mainly due to the large resonance energy of the benzyl radical compared with that of the methyl radical. A quantitative notion of the magnitude of the relative contributions from resonance energies of the radicals follows from arguments developed by Szwarc (*J. Chem. Phys.*, 1950, **18**, 1660). Assuming the resonance energy of the methyl radical to be zero, he proposes that any difference between disruption energies $D(CH_3{-}H)$ and $D(R{-}H)$ is to be attributed to the increased stabilisation of the radical R after disruption of the C–H bond.

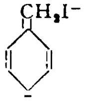
TABLE 5.

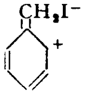
Compound	CH_4	PhMe	C_6H_6
D(R–H)	101	77·5	101
Exptl. resonance energies for R	0	23·5	0

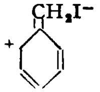
On this basis the " experimental resonance energies " presented in Table 5 have been derived.

Neither bond length nor dipole moment data appear to be available for benzyl iodide. For benzyl chloride Parts (*Z. physikal. Chem.*, 1931, **12**, *B*, 323) points out that replacement of hydrogen in methyl chloride by phenyl increases the moment above that calculated by vectorial addition of the partial moments for the tetrahedral valency angle of 109° 29′ in the central carbon atom. This may be attributed to first-order conjugation, the origin of which is clearly seen by consideration of the influence of the annexed canonical forms









on the resonance hybrid of benzyl iodide. These considerations lead to prediction of a stronger bond in benzyl iodide than in methyl iodide, for which only the forms CH_3–I and CH_3^+–I^- are important. From the values for the bond-dissociation energies reported here, the magnitude of any such bond-strengthening appears to be small in comparison with the weakening of the bond due to radical-resonance stabilisation.

The authors thank The Queen's University of Belfast for a Studentship (to R. J. N.) and the Ministry of Education for Northern Ireland for a Maintenance Grant (to W. S. G.).

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[*Received, August 25th,* 1954.]