584. *A Thermochemical Evaluation of Bond Strengths in Some Carbon Compounds. Part IV.* Bond-strength Differences based on the Reaction :* $RI + HI \longrightarrow RH + I_2$, *where* R = p-*Methoxyphenyl and* cyclo*Hexyl.*

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By using developments of methods described previously, bond-strength differences $D(R-H) - D(R-I)$ have been determined for the compounds where R = *p*-methoxyphenyl and *cyclo*hexyl. The differences are practically identical for these two radicals. They are compared with values for compounds where R = phenyl, benzyl, and methyl, in order to establish how far the electronic character of R affects the carbon–iodine bond.

ONE of the means of testing theories of valency is to compare the influence of neighbouring groups on bond-disruption energies. For example, by comparing disruption energies for the bond C–I in $R^1R^2R^3C-I$ where various groups, R^1, R^2, R^3, are linked to the carbon atom, it is possible to draw significant conclusions about the electronic character of this bond. These conclusions are especially interesting when at least one of the groups R is aromatic. Though there is much semiquantitative information about the correlation between aromatic character and the properties of neighbouring bonds, most of it is based on considerations of reactivity. Studies of bond-disruption energies which refer to the ground states of the molecules can help to place theories of aromatic character on a firm quantitative basis.

To meet this need, it has proved possible to develop methods of calorimetry based on the reactions of Grignard compounds, by careful control of the stoicheiometry through accurately maintained reaction conditions. Frequently, however, the corresponding disruption energies for the molecule $R^1R^2R^3C-H$ are not known with comparable accuracy. At present, therefore, it seems best to discuss the conclusions for valency theories in terms of the difference of disruption energies for the processes $R^1R^2R^3C\text{-}{\mid}\text{-}H$ and $R^1R^2R^3C\text{-}{\mid}\text{-}I$. As detailed below, the new results described in the present paper now permit comparisons of disruption energies over the series : MeI, CH_2PhI, $C_6H_{11}I$ (C_6H_{11} = *cyclo*hexyl, here and below), PhI, and *p*-$MeO{\cdot}C_6H_4I$, relative to the corresponding hydrogen compounds as standards. The conclusions are discussed in terms of the influence of electronic interaction of neighbours on primary valencies. Summarised bond-disruption energies are given in Table 1, which shows how they depend on the character of the neighbouring atoms.

TABLE 1. *Derived bond-disruption energies.*

R	Me	CH_2Ph	Ph	*p*-$MeO{\cdot}C_6H_4$	C_6H_{11}
D(R–I) (kcal./mole)	$54{\cdot}_7 \pm 1{\cdot}7$	$43{\cdot}_2 \pm 1{\cdot}8$	$60{\cdot}_9 \pm 1{\cdot}8$	$59{\cdot}_2$ (± 2)	52 (± 3)
Footnote	*a*	*b*	*b*	*c*	*d*

a, Part II, *J.*, 1952, 415. *b*, Part III, *J.*, 1955, 115. *c*, Present paper; based on the assumption that $D(p\text{-}MeO{\cdot}C_6H_4-H) = D(Ph-H)$. *d*, Present paper; based on the assumption that $D(C_6H_{11}-H) = D(Pr^i-H) = 94 \pm 2$ kcal./mole.

In the present work, reactions of Grignard reagents with iodine and with hydrogen iodide, under conditions of carefully controlled stoicheiometry, have been employed to determine the following heats of reaction (in the gas phase at standard pressure and 25°) :

$$p\text{-}MeO{\cdot}C_6H_4I + HI \longrightarrow p\text{-}MeO{\cdot}C_6H_5 + I_2;\ \Delta H = -6{\cdot}9 \pm 1{\cdot}2\ \text{kcal./mole}$$
$$C_6H_{11}I + HI \longrightarrow C_6H_{12} + I_2;\ \Delta H = -6{\cdot}8 \pm 1{\cdot}0\ \text{kcal./mole}$$

These thermochemical quantities are combined with $D(I_2) = 36{\cdot}06 \pm 0{\cdot}01$ and D(H–I) = $71{\cdot}37 \pm 0{\cdot}02$ kcal./mole to obtain bond strengths as in the above Table. The resulting values agree with the known chemical character of the iodides and present a quantitative basis for further investigations.

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* Part III, *J.*, 1955, 115.

Attempts to apply the present thermochemical method to the determination of C–I bond strengths in the higher alkyl iodides have been unsuccessful, because undesirable side reactions could not be eliminated. Interesting phenomena observed during the examination of the reaction of several Grignard reagents with iodine and with hydrogen iodide are the subject of further study.

EXPERIMENTAL

Preparation of Reagents.—An ethereal solution of the requisite bromide was added under reflux to turnings of triply distilled magnesium in an atmosphere of dry, oxygen-free nitrogen. The resulting solution of the Grignard reagent was diluted with anisole, and the excess of diethyl ether was removed under reduced pressure. In general, the organomagnesium bromides were most satisfactory for this work; the iodides tended to take part in undesirable side reactions, while with the chlorides there was precipitation of relatively insoluble magnesium chloride iodide which gave rise to thermochemical difficulties. Anhydrous hydrogen iodide was prepared by reaction of iodine with decalin; the gas was then bubbled into heptane, in nitrogen as carrier, until a solution of the desired strength had been obtained. A more detailed description of these preparations is given in Part II;[1] for the present work the solution of hydrogen iodide was stored at 0°. When required, this solution was passed through a spiral, immersed in a thermostat kept at the temperature of the calorimeter block (25°). Before use, *p*-methoxyphenyl bromide, b. p. 70·5—71·0°/~1 mm., and *cyclo*hexyl bromide, b. p. 35·3—36·0°/~3 mm., were dried (Na_2SO_4) and distilled at reduced pressure. *p*-Methoxyphenyl iodide was prepared from *p*-anisidine by thermal decomposition of the diazonium iodide; the product, purified by several recrystallizations from aqueous ethanol and then by distillation at reduced pressure, melted at 49·6—50·2° under standard conditions (lit.,[2-4] 51°, 50—52°, 51—52°). *cyclo*Hexyl iodide, prepared by the addition of hydrogen iodine to *cyclo*hexene[5] and purified by distillation at reduced pressure, had n_D^{20} 1·549 (lit.,[5,6] 1·551, 1·547). Heptane and anisole, used as solvents, were purified as in Part III.[7]

Mean Heat of Vaporization of p-*Methoxyphenyl Iodide and of* cyclo*Hexyl Iodide.*—Vapour pressures were determined by the isoteniscopic method of Smith and Menzies.[8] The experimental results are recorded in Tables 2 and 3. With *p*-methoxyphenyl iodide, an insignificant amount of decomposition occurred at the higher temperatures; with *cyclo*hexyl iodide, however, the extent of the decomposition, while still small, was perhaps not insignificant. Thus, at the completion of the run, 20·0 ml. of the halide contained 0·0038 millimole of iodine; while the vapour pressure exerted by the iodine is negligible, that exerted by the hydrocarbon residue (assumed to be volatile) is not. The plots of log pressure against the reciprocal of the absolute temperature are straight lines for both halides, there being a slight tendency to curvature at the higher temperatures for the aromatic compound. The mean latent heats of vaporization, calculated from the slopes of the graphs at the lower temperatures, are *p*-methoxyphenyl iodide 12·7 ± 0·1, *cyclo*hexyl iodide 10·3 ± 0·2 kcal./mole. The uncertainty in the latter value has been derived by combining the experimental error with the error due to the decomposition on the worst possible view, namely, that the hydrocarbon residue was present entirely in the gas phase.

TABLE 2. *Vapour pressures of* p-*methoxyphenyl iodide.*

Temp. (± 0·2°)	128·2°	158·1°	178·3°	189·9°	198·6°	206·6°
Pressure (± 0·3 mm.)	20·4	63·8	123·1	175·2	224·9	281·1

TABLE 3. *Vapour pressures of* cyclo*hexyl iodide.*

Temp. (± 0·2°)	85·3°	101·1°	116·6°	135·0°
Pressure (± 0·3 mm.)	28·5	53·0	90·3	165·9

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[1] Nichol and Ubbelohde, *J.*, 1952, 415.
[2] Matheson and McCombie, *J.*, 1931, 1103.
[3] Kondo, Ikeda, and Taga, *Ann. Rep. I.T.S.U.U. Lab.*, 1952, **3**, 65.
[4] Reverdin, *Ber.*, 1896, **29**, 1000.
[5] Stone and Shechter, *Org. Synth.*, 1951, **31**, 66.
[6] Vogel, *J.*, 1948, 1809.
[7] Graham, Nichol, and Ubbelohde, *J.*, 1955, 115.
[8] Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412.

Constant-pressure Calorimeter.—The instrument used to measure the heats of the Grignard reactions was basically the same as that described in Part III,[7] and the techniques of calorimetry were largely those described in Part II.[1]

CALORIMETRIC RESULTS

The experimental results for *p*-methoxyphenyl iodide and *cyclo*hexyl iodide are reported separately; the derivation of the thermochemical equations common to both sets of data is conveniently given first.

These are as follows :

$$\underset{\substack{\text{in}\\ \text{anisole}}}{\mathrm{RMgBr}} + \underset{\substack{\text{in}\\ \text{heptane}}}{\mathrm{I_2}} \longrightarrow \underbrace{\mathrm{RI} + \mathrm{MgBrI}}_{\text{in anisole–heptane}} \ldots\ldots \Delta H_A \quad \ldots \quad (A)$$

$$\underset{\substack{\text{in}\\ \text{anisole}}}{\mathrm{RMgBr}} + \underset{\substack{\text{in}\\ \text{heptane}}}{\mathrm{HI}} \longrightarrow \underbrace{\mathrm{RH} + \mathrm{MgBrI}}_{\text{in anisole–heptane}} \ldots\ldots \Delta H_B \quad \ldots \quad (B)$$

Subtracting reaction (*B*) from (*A*), which is permissible without further corrections if the concentrations are the same in both equations, and rearrangement give :

$$\underset{\substack{\text{in}\\ \text{heptane}}}{\mathrm{I_2}} + \underset{\substack{\text{in anisole–}\\ \text{heptane}}}{\mathrm{RH}} \longrightarrow \underbrace{\mathrm{RI} + \mathrm{HI}}_{\text{in anisole–heptane}} \ldots\ldots \Delta H_A - \Delta H_B \quad \ldots \quad (1)$$

From equation (1), the following cycle can be established :

$$\begin{tikzcd}
\underset{\substack{\text{in anisole–}\\ \text{heptane}}}{\mathrm{RI}} & + & \underset{\text{in heptane}}{\mathrm{HI}} \arrow[r] & \underset{\substack{\text{in anisole–}\\ \text{heptane}}}{\mathrm{RH}} \arrow[d, "\Delta H_3"] & + & \underset{\substack{\text{in}\\ \text{heptane}}}{\mathrm{I_2}} \arrow[d, "\Delta H_4"] & \ldots\ldots \Delta H_B - \Delta H_A \quad \ldots \quad (1a) \\
\mathrm{RI_{gas}} \arrow[u, "\Delta H_1"] & + & \mathrm{HI_{gas}} \arrow[u, "\Delta H_2"] \arrow[r] & \mathrm{RH_{gas}} & + & \mathrm{I_{2gas}} & \ldots\ldots \Delta H_R \quad \ldots \quad (2)
\end{tikzcd}$$

Applying Hess's law to the cycle, we have :

$$\Delta H_R = \Delta H_B - \Delta H_A + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \quad \ldots \quad (3)$$

Since equation (2) refers to the gas phase, we can, neglecting corrections for imperfect gases, also write :

$$\Delta H_R = D(\mathrm{R{-}I}) + D(\mathrm{H{-}I}) - D(\mathrm{R{-}H}) - D(\mathrm{I_2}) \quad \ldots \quad (4)$$

Substitution in equation (3) and rearrangement give :

$$D(\mathrm{R{-}H}) - D(\mathrm{R{-}I}) = \Delta H_A - \Delta H_B + D(\mathrm{H{-}I}) - D(\mathrm{I_2}) - (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4) \,. \quad (5)$$

The values of some of the terms in equation (5) are known and may be substituted to effect some simplification, *viz.* :

$$D(\mathrm{I_2}) = 36{\cdot}06 \pm 0{\cdot}01 \text{ kcal./mole (ref. 9)}$$

$$D(\mathrm{H{-}I}) = 71{\cdot}37 \pm 0{\cdot}02 \text{ kcal./mole (ref. 9)}$$

$$\Delta H_2 = -3{\cdot}4 \pm 0{\cdot}2 \text{ kcal./mole (ref. 7)}$$

$$\Delta H_4 = 9{\cdot}0 \pm 0{\cdot}2 \text{ kcal./mole (ref. 7)}$$

It has been verified calorimetrically[7] that the heats of solution of the halide and of the hydrocarbon in anisole–heptane mixture are negligibly small. Hence,

$$\Delta H_1 = -\Delta H_e(\mathrm{RI}) \text{ and } \Delta H_3 = \Delta H_e(\mathrm{RH})$$

where the ΔH_e terms denote the latent heats of vaporization of the species indicated. Substituting these quantities into equation (5) gives :

$$D(\mathrm{R{-}H}) - D(\mathrm{R{-}I}) = 29{\cdot}7 \pm 0{\cdot}3 + (\Delta H_A - \Delta H_B) + \Delta H_e(\mathrm{RI}) - \Delta H_e(\mathrm{RH}) \,. \quad (6)$$

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[9] Herzberg, " Spectra of Diatomic Molecules," Van Nostrand Co., Inc., New York, 2nd Edn., 1950.

p-*Methoxyphenyl Iodide*.—The solution of *p*-methoxyphenylmagnesium bromide in anisole used for the reactions contained 4·4% by volume of diethyl ether which prevented the precipitation of magnesium halide formed in the reactions. The concentration of the Grignard solution was 0·0783M.

(1) *The* $(\Delta H_A - \Delta H_B)$ *term*. (*a*) The reaction with iodine. (i) Stoicheiometry. The iodine–heptane solution used was 0·0400M. The mean value of the reaction ratio (moles of RMgBr reacted) : (moles of I_2 reacted), determined for ten reactions, was 1·000 ± 0·003, indicating 100% of reaction (*A*).

(ii) Calorimetry. Ten determinations of the heat of reaction of 0·3743 millimole of iodine with 1·567 millimoles of the Grignard reagent were made. The mean of the results can be represented $(\delta H_{a,\,m}) = 39{\cdot}57 \pm 0{\cdot}20$ cal. where the symbol refers to the heat change for a reaction of *m* millimoles of iodine.

As noted below, the $(\delta H_{a,\,m})$ term and the $(\delta H_{b,\,n})$ term each contain a large positive term due to the heat of mixing of heptane with anisole; these cancel in the final outcome.

(*b*) The reaction with hydrogen iodide. (i) Stoicheiometry. The mean reaction ratio, (moles of RMgBr reacted) : (moles of HI reacted), for ten determinations was 0·972 ± 0·004. This is slightly low. The uncertainty introduced by possible side reactions is considered below.

(ii) Calorimetry. It has not proved possible to prevent a continuous decrease in strength of the hydrogen iodide solutions after preparation. Storage at 0°, however, greatly retarded the deterioration, so that the concentration of the solution changed by only about 5% in 30 hr., the time required for ten determinations of the heat of reaction. Results of the thermochemical measurements are presented in Table 4.

TABLE 4.

No. of detn.	HI reacted (*n* millimole)	$(\delta H_{b,\,n})$ (cals.)	Reaction ratio	No. of detn.	HI reacted (*n* millimole)	$(\delta H_{b,\,n})$ (cals.)	Reaction ratio
1	0·3865	35·00	0·964	6	0·3726	35·61	0·975
2	0·3777	35·24	0·974	7	0·3726	35·89	0·974
3	0·3762	35·76	0·969	8	0·3704	36·12	0·974
4	0·3755	35·91	0·973	9	0·3682	36·08	0·977
5	0·3748	35·91	0·968				

$(\delta H_{b,\,n})$ was plotted as a linear function of *n* so as to determine the value corresponding to $n = m = 0{\cdot}3743$ millimole; this was found by interpolation to be 35·8 ± 0·3 cal. It can be seen from Table 4 that the heat of reaction is not correlated in any way with fluctuations in the reaction ratio. This absence of correlation indicates that the heat term for the side reaction responsible for the slightly low reaction ratio is not appreciably different from that of the main reaction. From a consideration of possible competing reactions, it is found that the uncertainty in $(\delta H_{b,\,n})$ must be increased by about 0·1 kcal./mole to allow for the unidentified side reactions, giving :

$$(\delta \bar{H}_{b,\,n}) = 35{\cdot}8 \pm 0{\cdot}4 \text{ cal. when } n = 0{\cdot}3743 \text{ millimole}$$

The heats of reaction of iodine and of hydrogen iodide solutions with the Grignard reagent have thus been evaluated for identical conditions (*viz.*, $n = m$), and $\Delta H_A - \Delta H_B = m^{-1}[(\delta \bar{H}_{a,\,m}) - (\delta \bar{H}_{b,\,n})]$; heat of mixing and dilution terms which are in themselves quite large cancel in the subtraction. This gives :

$$\Delta H_A - \Delta H_B = 10{\cdot}2 \pm 1{\cdot}2 \text{ kcal./mole}$$

(2) *The* $\Delta H_e(\mathrm{RI})$ *term*. As described above, we can write :

$$\Delta H_e(p\text{-MeO}{\cdot}C_6H_4I) = 12{\cdot}7 \pm 0{\cdot}1 \text{ kcal./mole}$$

(3) *The* $\Delta H_e(\mathrm{RH})$ *term*. The mean latent heat of vaporization of anisole has been calculated from the vapour pressure–temperature data of Dreisbach and Shrader :[10]

$$\Delta H_e(p\text{-MeO}{\cdot}C_6H_5) = 10{\cdot}4 \pm 0{\cdot}1 \text{ kcal./mole}$$

Substituting these values in equation (6) gives :

$$D[(p\text{-MeO}{\cdot}C_6H_4)\text{–}H] - D[(p\text{-MeO}{\cdot}C_6H_4)\text{–}I] = 42{\cdot}2 \pm 1{\cdot}2 \text{ kcal./mole}$$

cyclo*Hexyl Iodide*.—The solution of *cyclo*hexylmagnesium bromide contained 5·5% by volume of diethyl ether; its concentration was 0·0615M.

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[10] Dreisbach and Shrader, *Ind. Eng. Chem.*, 1949, **41**, 2879.

(1) *The* $\Delta H_A - \Delta H_B$ *term.* (*a*) The reaction with iodine. (i) Stoicheiometry. The iodine–heptane solution was 0·0358M. The mean value of the reaction ratio for eight reactions was 1·007 ± 0·006. The uncertainty in the heat of reaction arising from this slightly high value for the reaction ratio can be shown to be negligibly small on the assumption that it is due to competition from the Wurtz coupling reaction :

$$2RMgBr + I_2 \longrightarrow R{-}R + 2MgBrI$$

which has a reaction ratio of 2·0.

(ii) Calorimetry. Eight determinations of the heat of reaction of 0·3350 millimole of iodine with 1·230 millimoles of the Grignard reagent were made :

$$(\overline{\delta H_{a,m}}) = 33{\cdot}77 \pm 0{\cdot}22 \text{ cal. where } m = 0{\cdot}3350 \pm 0{\cdot}0003 \text{ millimole}$$

(*b*) The reaction with hydrogen iodide. (i) Stoicheiometry. The mean reaction ratio for nine reactions was 0·996 ± 0·003. The uncertainty in the determination of the heat of reaction arising from this very slightly low value for the reaction ratio is negligibly small relative to the experimental error.

(ii) Calorimetry. The results of nine heat measurements are in Table 5.

TABLE 5.

No. of detn.	HI reacted (n millimole)	($\delta H_{b,n}$) (cal.)	Reaction ratio
1	0·3394	33·92	0·997
2	0·3406	33·72	0·996
3	0·3394	33·72	0·998
4	0·3387	33·70	0·992
5	0·3394	34·50	0·994
6	0·3394	33·83	1·000
7	0·3358	34·45	0·998
8	0·3347	34·37	0·990
9	0·3324	34·77	0·997

($\delta H_{b,n}$) was plotted as a linear function of n and from the graph it is evident that determination (5) is in considerable error. The interpolated value of ($\delta H_{b,n}$) corresponding to $n = m =$ 0·3350 millimole is 34·42 ± 0·20 cal.

As before, we write :

$$\Delta H_A - \Delta H_B = m^{-1}[(\overline{\delta H_{a,m}}) - (\overline{\delta H_{b,m}})],\ n = m$$

Hence

$$\Delta H_A - \Delta H_B = 10{\cdot}0 \pm 0{\cdot}9 \text{ kcal./mole}$$

(2) *The* ΔH_e(RI) *term.* As described above, we can write :

$$\Delta H_e\ (C_6H_{11}I) = 10{\cdot}3 \pm 0{\cdot}2 \text{ kcal./mole}$$

(3) *The* ΔH_e(RH) *term.* The latent heat of vaporization of *cyclo*hexane has been determined calorimetrically by Osborne and Ginnings :[11]

$$\Delta H_e\ (\textit{cyclo}\text{hexane}) = 7{\cdot}896 \text{ kcal./mole}$$

Substituting into equation (6) gives

$$D(\textit{cyclo}\text{hexane}) - D(C_6H_{11}{-}I) = 42{\cdot}1 \pm 1{\cdot}0 \text{ kcal./mole}$$

DISCUSSION

In the present state of knowledge, the most direct results based on experiment refer to differences of bond-disruption energies, as given in Table 6.

TABLE 6. *Differences of bond-disruption energies.*

R	Me	CH_2Ph	*p*-MeO·C_6H_4	C_6H_{11}	Ph
D(R–H) − D(R–I) (kcal./mole)	$45{\cdot}_5 \pm 1{\cdot}4$	$34{\cdot}_3 \pm 1{\cdot}3$	$42{\cdot}_2 \pm 1{\cdot}2$	$42{\cdot}_1 \pm 1{\cdot}2$	$40{\cdot}_5 \pm 1{\cdot}6$
Footnote	*a*	*b*	*c*	*c*	*b*

a, Part II, *J.*, 1952, 415. *b*, Part III, *J.*, 1955, 115. *c*, Present paper.

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[11] Osborne and Ginnings, *J. Res. Nat. Bur. Stand.*, 1947, **39**, 453.

The sequence suggested for some of these difference terms, *viz.*, Me $>$ *p*-MeO·C_6H_4 $\geqslant$ C_6H_{11} $>$ Ph, shows at most a 10% range in the energy of binding. It is noteworthy that the difference for *cyclo*hexyl is rather less than for methyl. This additional energy to be associated with the C–I bond in *cyclo*hexyl iodide partially offsets the relatively high stability of the *cyclo*hexyl radical (cf. the low disruption energy for secondary C–H). A value for $D(C_6H_{11}\text{–}I)$ results which is not very different from that of $D(\text{Me–I})$. This stability of the C–I bond in *cyclo*hexyl iodide can probably be associated with the increased polarity of the bond (cf. $\overset{\longmapsto}{\mathrm{CH_3I}} = 1{\cdot}6$ D; $\overset{\longmapsto}{\mathrm{C_6H_{11}I}} = 2{\cdot}0$ D), the ionic contribution from R^+I^- being more important in *cyclo*hexyl iodide; precise knowledge of the C–I bond lengths might throw additional light on this suggestion. However, the behaviour of the *cyclo*hexyl group is somewhat unexpected in other ways,[12] and possible hybridisation peculiarities of the alicyclic system should be kept in mind.

With regard to the difference for phenyl and *p*-methoxyphenyl, the present work shows that, in the ground states, any difference arising from replacement of H by OMe does not exceed about 2 kcal./mole. The experimental error is too large to establish fully the trend of values actually observed, but the increased donation of electrons to the ring by the methoxy-group could account for the values found. Whilst the experimental uncertainties are still somewhat disappointingly large, the results now quoted set limits and point the way to further quantitative developments of theories of bond strengths for aromatic molecules in the ground state. The finding that the C–I bond dissociation energies in phenyl iodide and in *p*-methoxyphenyl iodide are the same within the spread of the errors conforms with the conclusion from kinetic studies that substituted phenyl bromides have more or less constant C–Br dissociation energies.[13]

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[*Received, February 6th*, 1956.]

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[12] Slough and Ubbelohde, *J.*, 1955, 108.

[13] Szwarc and Williams, *Proc. Roy. Soc.*, 1953, *A*, **219**, 353.