244. *Dissociation Energies of Carbon–Halogen Bonds. The Bond Strengths Allyl–X and Benzyl–X.*

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Measurements of the heats of reaction of allyl bromide, allyl iodide, benzyl bromide, and benzyl iodide with silver nitrate in aqueous-alcoholic solution have been made. The results have been interpreted, by assuming a simplified reaction scheme, to provide rough values for the heats of formation (Q_f) of the allyl and benzyl halides. By combination of these experimental Q_f values with the D(C–H) bond dissociation energies in toluene and propylene, we derive D(R–I) bond dissociation energies as follows :

$$D(\text{allyl–I}) = 34{\cdot}4 \text{ kcals.} \quad D(\text{benzyl–I}) = 36{\cdot}5 \text{ kcals.}$$
$$D(\text{allyl–Br}) = 45{\cdot}5 \text{ kcals.} \quad D(\text{benzyl–Br}) = 48{\cdot}5 \text{ kcals.}$$

These values are considered to be uncertain within ± 3 kcals.

Recent determinations by Szwarc (*J. Chem. Physics*, 1948, **16**, 128; *ibid.*, 1949, **17**, 284) of the bond dissociation energies of the C–H bonds, $C_6H_5{\cdot}CH_2$–H and allyl–H, in toluene and propylene, taken in conjunction with the heats of formation, $Q_f(C_6H_5{\cdot}CH_3)$ and $Q_f(CH_2{:}CH{\cdot}CH_3)$, provide values for the heats of formation (from elements in their standard states) of the benzyl and the allyl radicals. These are (see Roberts and Skinner, *Trans. Faraday Soc.*, 1949, **46**, 339) : $Q_f(\text{benzyl}) = -37{\cdot}4$ and $Q_f(\text{allyl}) = -30{\cdot}9$ kcals. mole^{-1}.

The bond dissociation energies D(R–X) are simply related to the heats of formation Q_f(R) and Q_f(X) by the equation

$$D(\text{R–X}) = Q_f(\text{RX}) - Q_f(\text{R}) - Q_f(\text{X}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In cases where X = Cl, Br, or I, the terms in Q_f(X) are known with high accuracy (Rossini, " Selected Tables of Chemical Thermodynamic Properties," U.S. Bureau of Standards, 1947, Tables 10-1, 11-1, 12-1). Accordingly, we may use equation (1) to estimate the bond dissociation energies of the C–halogen bonds in the benzyl and allyl halides if the heats of formation of these compounds are known.

Thomsen's measurements (" Thermochemische Untersuchungen," Vol. IV, Barth, Leipzig) of the heats of combustion of allyl chloride and allyl bromide correspond to $Q_f(\text{allyl–Cl}) = -0{\cdot}6$ and $Q_f(\text{allyl–Br}) = -11{\cdot}2$ kcals. mole^{-1} (unless otherwise specified, all Q_f values in this paper refer to *gaseous* states). From the heat of combustion of liquid allyl iodide, as measured by Berthelot (*Ann. Chim. Phys.*, 1900, **21**, 296), one may derive $Q_f(\text{allyl–I}) \sim -33{\cdot}5$ kcals., but it is our view that this value is seriously in error. Relatively little is known of the heats of formation of the benzyl halides. Schmidlin's data (*ibid.*, 1906, **7**, 195) on the heat of combustion of benzyl chloride are insufficient to make a reliable estimate of Q_f(benzyl–Cl).

It is desirable that new and accurate measurements of the heats of combustion of allyl and benzyl halides should be made. Meanwhile, we are able to report the results of some measurements of the *heats of hydrolysis* of the allyl and benzyl halides, from which we can derive values for Q_f(allyl–X) and Q_f(benzyl–X). We make no claim for high accuracy in the new values reported here, for reasons given later. Nevertheless, the values we have found are consistent among themselves, and in our view, are correct within the limits of ± 3 kcals.

Thermochemical Method.—Both the iodides and the bromides, benzyl–X and allyl–X, react easily and relatively quickly with silver nitrate in aqueous-alcoholic solution at room temperature. The main reaction taking place may be represented by

$$\text{RX} + \text{AgNO}_3 + \text{H}_2\text{O} \longrightarrow \text{ROH} + \text{AgX} + \text{HNO}_3 \quad . \quad . \quad . \quad . \quad (2)$$

In our thermochemical method, we have *assumed* that (2) is the only reaction. This is strictly indefensible, but from the thermochemical point of view the assumption is unlikely to lead to serious error (see p. 1146).

Representing the heats of the pairs of reactions :

$$\begin{aligned}&\text{RX(liq.)} + \text{AgNO}_3\text{(aq. alc.)} + \text{H}_2\text{O(aq. alc.)}\\&\quad \longrightarrow \text{AgX(ppt.)} + \text{ROH(aq. alc.)} + \text{HNO}_3\text{(aq. alc.)} + Q_1 \quad . \quad . \quad . \quad . \quad (3a)\end{aligned}$$

$$\text{HX(aq.)} + \text{AgNO}_3\text{(aq. alc.)} \longrightarrow \text{AgX(ppt.)} + \text{HNO}_3\text{(aq. alc.)} + Q_2 \quad . \quad . \quad . \quad (3b)$$

by Q_1 and Q_2, one may then write

$$\text{RX(liq.)} + \text{H}_2\text{O(aq. alc.)} \longrightarrow \text{ROH(aq. alc.)} + \text{HX(aq.)} + (Q_1 - Q_2) \quad . \quad . \quad . \quad (4)$$

From eqn. (4) we may further obtain

$$Q_f(\mathrm{RX,liq.}) = Q_f(\mathrm{ROH,aq.\ alc.}) + Q_f(\mathrm{HX,aq.}) - Q_f(\mathrm{H_2O,\ aq.\ alc.}) + (Q_2 - Q_1) \quad . \quad . \quad (5)$$

Values for the terms in Q_f on the right-hand side of eqn. (5) are known with relatively high accuracy, so that by the measurement of $(Q_2 - Q_1)$, the heat of formation of RX can be obtained. The value of Q_f(RX) so obtained is, of course, subject to the conditions that the reaction between RX and $AgNO_3$ in aqueous ethyl alcohol proceeds substantially according to eqn. (2), or that such side reactions as may occur have a similar overall molar heat of reaction to (2).

Studies of the reactions between alkyl halides and silver nitrate in aqueous and in aqueous-alcoholic solution have been made by various investigators (Nef, *Annalen*, 1899, **309**, 126; Burke and Donnan, *J.*, 1904, **85**, 555; *Bull. Soc. chim.*, 1904, **32**, 1153; Gand, Thèse, Marseille, 1939; *Bull. Soc. chim.*, 1944, **11**, 511). The main side reaction to reaction (2) is that in which the hydrolysis is accompanied by an alcoholysis :

$$\mathrm{RI + AgNO_3 + EtOH \longrightarrow ROEt + AgI + HNO_3} \quad . \quad . \quad . \quad . \quad (6)$$

Fortunately, from the thermochemical point of view, this reaction generates a similar overall heat to the main reaction (2)—*e.g.*, in case where R = Et, the heats of reactions (2) and (6) do not differ by more than 2 kcals./mole. Moreover, we have used alcohol–water mixtures in which the molar concentration of water was roughly twice that of the alcohol. The side reaction

$$\mathrm{RI + AgNO_3 \longrightarrow RNO_3 + AgI} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

according to Gand (*loc. cit.*) does not occur in aqueous solutions to more than 5—10%, and should not, in that event, seriously interfere with the usefulness of equation (5).

An independent check on the validity of the assumed thermochemical method has been obtained by study of the reactions in which RI = CH_3I and C_2H_5I. In these cases, the values of Q_f(RI) are known, from independent studies (Carson, Hartley, and Skinner, *Proc. Roy. Soc.*, 1949, **195**, *A*, 500; Hartley and Skinner, unpublished results), within relatively small limits. The values found by use of equation (5), and the measured heats of hydrolysis, agreed within ±2 kcals. with those obtained by more reliable methods. Accordingly, we feel justified in claiming that the thermochemical method we have used gives results which are reliable within the limits ±3 kcals., although our values require independent confirmation.

EXPERIMENTAL.

The reactions were initiated by breaking a phial containing the alkyl halide into a solution of silver nitrate in aqueous alcohol, contained within a Dewar vessel calorimeter of simple design, similar to that described by Bichowsky (*J. Amer. Chem. Soc.*, 1923, **45**, 2225). The temperature rise was followed on a Beckmann thermometer, and after a suitable time of reaction (usually 10 minutes with the benzyl halides, and about 30 minutes with the allyl halide reactions), reaction was terminated by flooding the reaction mixture with an excess of standard potassium thiocyanate solution. The extent of reaction was determined by back titration of the excess of thiocyanate. In general, 2—4 g. of alkyl halide were used in each run, and 300 c.c. of aqueous-alcoholic silver nitrate were contained within the Dewar vessel.

The results obtained with allyl and benzyl iodide and bromide are set out in the Table I (Q_1 is in kcals./mole; W.E. = water equivalent of calorimeter in cals./°c.).

The ΔT values given are corrected for small solution heats, due to the heat of solution of the *unreacted* alkyl halide in the reaction mixture.

The heat quantities Q_2 (equation 3*b*) were measured by breaking phials containing concentrated hydriodic or hydrobromic acid into the aqueous-alcoholic silver nitrate solution. Since part of the observed temperature rise was due to the addition of the water admixed with the acid, corrections were made for this spurious heat effect. The results are summarised in Table II. The Q_2 values in the aqueous alcohol mixture (200 c.c. EtOH; 100 c.c. H_2O) are thus rather less (by *ca.* 2 kcals.) than in the purely aqueous solution.

The term $(Q_2 - Q_1)$ in eqn. (5), as found from these experiments, has the values : C_3H_5Br(liq.), −3·7; C_3H_5I(liq.), 2·1; CH_2PhBr(liq.), −1·9; CH_2PhI(liq.), 3·0 kcals.

The remaining terms in eqn. (5) were taken from published heats of formation, with some small adjustments to take care of small solution heats that were measured wherever necessary. These terms (in kcals.) are summarised below;

Q_f(HX, aq.)	$Q_f(\mathrm{HI,7H_2O})$ = 12·1 [1]	Q_f(ROH, aq. alc.)	$Q_f(\mathrm{C_3H_5{\cdot}OH})$ = 40·3 [2]
	$Q_f(\mathrm{HBr,11H_2O})$ = 27·8 [1]		$Q_f(\mathrm{CH_2Ph{\cdot}OH})$ = 36 [3]
$Q_f(\mathrm{H_2O}$, aq. alc.)	Q_f = 68·5 [1]		

[1] Rossini, *op. cit.*, Tables 11-2, 12-2.

[2] Dolliver, Gresham, Kistiakowsky, Smith and Vaughan,, *J. Amer. Chem. Soc.*, 1938, **60**, 440.

[3] Stohmann, *Z. physikal. Chem.*, 1890, **6**, 334.

Substituting these various values into eqn. (5), we obtain the following (in kcals./mole^{-1}) :

$Q_f(\mathrm{C_3H_5{-}Br,\ liq.}) = -\ 4{\cdot}1$ $\qquad$ $Q_f(\mathrm{CH_2Ph{-}Br,\ liq.}) = -\ 6{\cdot}6$

$Q_f(\mathrm{C_3H_5{-}I,\ liq.}) = -\ 14{\cdot}0$ $\qquad$ $Q_f(\mathrm{CH_2Ph{-}I,\ liq.}) = -\ 17{\cdot}4$

TABLE I.

(a) *Allyl bromide and silver nitrate (aqueous alcohol).*

C_3H_5Br added (g.-mole).	C_3H_5Br reacted (g.-mole).	ΔT.	W.E.	Q_1.	C_3H_5Br added (g.-mole).	C_3H_5Br reacted (g.-mole).	ΔT.	W.E.	Q_1.
0·0142	0·0102	1·14°	211	23·6	0·0166	0·0121	1·285°	211	22·4
0·0166	0·0120	1·295	213	22·8	0·0166	0·0120	1·315	211	23·1

Mean-value of Q_1 = 23·0 kcals. Max. deviation from mean = ± 0·6 kcal. Average reaction time ~40 mins.

(b) *Allyl iodide and silver nitrate (aqueous alcohol).*

C_3H_5I added (g.-mole).	C_3H_5I reacted (g.-mole).	ΔT.	W.E.	Q_1.	C_3H_5I added (g.-mole).	C_3H_5I reacted (g.-mole).	ΔT.	W.E.	Q_1.
0·0154	0·0136	1·53°	211	23·7	0·0154	0·0142	1·56°	211	23·2
0·0154	0·0141	1·57	211	23·5	0·0154	0·0135	1·505	211	23·5

Mean value of Q_1 = 23·5 kcals. Max. deviation from mean = ± 0·3 kcal. Average time of reaction = ~ 30 mins.

(c) *Benzyl bromide and silver nitrate (aqueous alcohol).*

CH_2PhBr added (g.-mole).	CH_2PhBr reacted (g.-mole).	ΔT.	W.E.	Q_1*.	CH_2PhBr added (g.-mole).	CH_2PhBr reacted (g.-mole).	ΔT.	W.E.	Q_1*.
0·0164	0·0147	1·50$_5$°	213	21·8	0·0163	0·0144	1·45$_5$°	213	21·5
0·0166	0·0146	1·48	,,	21·6	0·0152	0·0137	1·37$_5$	,,	21·4

* The benzyl bromide was dissolved in 5 c.c. of alcohol, and then introduced into the reaction mixture. The value of Q_1* includes a solution heat, and the true Q_1 for benzyl bromide (liq.) is 0·4 kcal. less than Q_1*.

Mean Q_1* = 21·6 kcals. Mean Q_1 = 21·2 kcals. Max. deviation from mean = ± 0·2 kcal. Average reaction time = ~ 10 mins.

(d) *Benzyl iodide and silver nitrate (aqueous alcohol).*

CH_2PhI added (g.-mole).	CH_2PhI reacted (g.-mole).	ΔT.	W.E.	Q_1*.	CH_2PhI added (g.-mole).	CH_2PhI reacted (g.-mole).	ΔT.	W.E.	Q_1*.
0·0149	0·0115	1·27°	213	23·5	0·0157	0·0129	1·41°	213	23·3
0·0150	0·0134	1·46	213	23·2	0·0156	0·0134	1·43	213	22·7
0·0145	0·0130	1·44$_5$	213	23·8					

* The iodide was dissolved in 5 c.c. of alcohol, and then introduced into the reaction mixture. The value of Q_1* thus includes this heat of solution. The true Q_1 for benzyl iodide (liq.) is less than Q_1* by 0·7 kcal.

Mean Q_1* = 23·3 kcals. Mean Q_1 = 22·6 kcals. Max. deviation from mean : ±0·5 kcal. Average reaction time = 10 mins.

TABLE II.

	Q_2 (obs.), kcals.		Q_2 (obs.), kcals.
(1) $HI(7H_2O) + AgNO_3\ (750H_2O)$	27·5	(2) $HBr(11H_2O) + AgNO_3\ (750\ H_2O)$	21·2
(1*a*) $HI(7H_2O) + AgNO_3$ (aq. alc.) ...	25·6	(2*a*) $HBr(11H_2O) + AgNO_3$ (aq. alc.)	19·3

Discussion.—The heats of vaporization of the allyl and benzyl halides do not appear to have been measured. It is probable, however, that those of the allyl halides are *ca.* 8 kcals., and those of the benzyl halides *ca.* 9 kcals. Assuming these values, we can obtain Q_f(RX), and the bond dissociation energies D(R–X), as follows (in kcals.) :

	Q_f(R-X).	D(R-X).		Q_f(R-X).	D(R-X).
C_3H_5–Br	−12·1	45·5	CH_2Ph–Br	−15·6	48·5
C_3H_5–I	−22·0	34·4	CH_2Ph–I	−26·4	36·5

The uncertainty in these figures—as discussed earlier—is estimated at *ca.* ±3 kcals.

We may note that our value for $Q_f(C_3H_5\text{–}Br)$ agrees reasonably closely with that derived from Thomsen's heat of combustion. With allyl iodide, however, there is a large discrepancy between our value and $Q_f(C_3H_5\text{–}I)$ as derived from Berthelot's data.

The D(R–I) values (R = allyl or benzyl) obtained by Butler and Polanyi (*Trans. Faraday Soc.*, 1943, **39**, 19) from kinetic studies of rates of pyrolysis run some 4—5 kcals. higher than the values given here. However, more extensive studies on the benzyl iodide and allyl iodide pyrolyses by Horrex and Szwarc (in the press; see also Szwarc, *loc. cit.*), and by Szwarc and Shaw (private communication) have since been made, and are indicative of lower values for the bond dissociation energies in these compounds than were first reported.

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