394. *The Heats of Hydrolysis of Chloral and Bromal, and the C—C Bond Dissociation Energies in Chloral and Bromal.*

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From measurements of the heats of reaction of liquid chloral and bromal with aqueous sodium hydroxide at room temperature, the following values (kcals. mole^{-1}) were obtained for the heats of formation: $Q_f(\mathrm{Cl_3C{\cdot}CHO,liq.}) = 52{\cdot}1$, $Q_f(\mathrm{Br_3C{\cdot}CHO,liq.}) = (x + 20{\cdot}7)$, where x is the heat of formation of liquid bromoform. An estimate of x as 0·5 kcal. is given, corresponding to $Q_f(\mathrm{Br_3C{\cdot}CHO,liq.}) = 21{\cdot}2$ kcals. mole^{-1}.

The C–C bond dissociation energy in chloral is calculated at 62 kcals. mole^{-1}, and a similar value is found for C–C in bromal on the assumption that the C–H dissociation energies are the same in bromoform as in chloroform.

Both chloral and bromal react readily at room temperature with aqueous alkalis, according to the equation :

$$\mathrm{X_3C{\cdot}CHO + NaOH(aq.) \longrightarrow X_3CH + H{\cdot}CO_2Na(aq.)} \quad . \quad . \quad . \quad . \quad (1)$$
$$(\mathrm{X = Cl\ or\ Br})$$

From the measured heat of reaction (1), it is possible to derive the heat of formation, $Q_f(\mathrm{X_3C{\cdot}CHO})$, of $\mathrm{X_3C{\cdot}CHO}$. By combining the $Q_f(\mathrm{X_3C{\cdot}CHO})$ values with other thermal data, the heats of dissociation of the C–C bonds in these compounds can be derived.

The heat of reaction of liquid chloral with aqueous potassium hydroxide was first measured some 70 years ago by Berthelot (*Ann. Chim. Phys.*, 1877, **12**, 536; 1880, **20**, 521), whose results agree substantially with those given in this paper. No previous measurements of the heat of hydrolysis of bromal have been reported.

Experimental.

Preparations.—Chloral (anhydrous) (a B.D.H. product) was purified by careful fractionation in a steel-gauze-packed column, dried by distillation over phosphoric oxide, and re-distilled through an efficient packed column; it then had b. p. 97·7—98°/766 mm. The pure product was distilled *in vacuo* and collected in weighed glass ampoules.

The bromal (anhydrous) (a B.D.H. sample) was purified by careful fractionation at 8—9 mm. The early fractions containing hydrogen bromide as impurity were discarded, and the pure, almost colourless product was collected in weighed glass ampoules.

The formic acid and sodium hydroxide were of analytical quality.

Calorimeter.—The reactions were carried out by breaking the glass ampoules into an excess (750 c.c.) of 0·2N-sodium hydroxide. The reaction vessel was a Dewar flask, and the calorimetric system was that described by Pritchard and Skinner (*J.*, 1950, 272). The temperature changes were recorded in terms of the resistance changes of a thermistor element (R_i = initial and R_f = final resistance of the thermistor element).

RESULTS.

Chloral.—The results obtained from 4 measurements of the heat of reaction ($Q_{obs.}$) of liquid chloral with aqueous sodium hydroxide are listed in Table I. In the final column of this table, calculated values of Q_f(Cl$_3$C·CHO,liq.) are given, which were obtained from the equation:

$$Q_f(\text{Cl}_3\text{C·CHO,liq.}) = Q_f(\text{H·CO}_2\text{Na,aq.}) + Q_f(\text{Cl}_3\text{CH,aq.}) - Q_f(\text{NaOH,aq.}) - Q_{obs.} \quad . \quad . \quad (2)$$

The terms in Q_f appearing on the right-hand side of equation (2) were assumed to have the following values:

$$Q_f(\text{NaOH, 275 H}_2\text{O}) = 112{\cdot}06 \text{ kcals. mole}^{-1}$$
$$Q_f(\text{H·CO}_2\text{Na,aq.}) = 155{\cdot}12 \quad ,,$$
$$Q_f(\text{Cl}_3\text{CH,aq.}) = 33{\cdot}67 \quad ,,$$

The value for Q_f(NaOH,aq.) is that given by Bichowsky and Rossini ("Thermochemistry of Chemical Substances," Reinhold, 1936), and that for Q_f(H·CO$_2$Na,aq.) we obtained by direct measurement of the heat of neutralization of formic acid in an excess of sodium hydroxide, coupled with an assumed value for the heat of formation of formic acid ("Selected Values of Chemical Thermodynamic Properties," Table 23—4, Nat. Bur. Standards, Washington). Under the conditions of our experiments, the chloroform was formed in aqueous solution, so that the appropriate Q_f value required in equation (2) is that for dissolved Cl$_3$CH. Berthelot (*loc. cit.*) measured the heat of solution of liquid chloroform in water as 2·17 kcals. mole^{-1}, which, combined with the value Q_f(Cl$_3$CH,liq.) = 31·5 kcals. mole^{-1} [Nat. Bur. Standards, Table 23—7], leads to Q_f(Cl$_3$CH,aq.) = 33·67 kcals. mole^{-1}. It should be pointed out, however, that the heat of formation of chloroform is not known with high precision, and an error of the order of ±1 kcal. is associated with the value we have used.

TABLE I.

Chloral and aqueous sodium hydroxide.

Expt.	Cl$_3$C·CHO (g.).	R_i (ohms).	R_f (ohms).	$Q_{obs.}$ (kcals.).	Q_f (Cl$_3$C·CHO, liq.) (kcals.).
1	3·0156	1728·2$_5$	1685·0	24·57	52·16
2	2·8556	1716·0	1675·2	24·63	52·10
3	3·0844	1738·8$_5$	1694·4	24·54	52·19
4	3·1626	1738·4	1692·8	24·57	52·16
			Mean	24·58	52·13

TABLE II.

Bromal and aqueous sodium hydroxide.

Expt.	Br$_3$C·CHO (g.).	R_i (ohms).	R_f (ohms).	$Q_{obs.}$ (kcals.).	Q_f (Br$_3$C·CHO, liq.) (kcals.).
1	4·8475	1736·8	1703·3	22·38	$x + 20{\cdot}68$
2	4·4810	1731·6	1700·5	22·44	$x + 20{\cdot}62$
3	5·9530	1751·2	1709·8	22·38	$x + 20{\cdot}68$
			Mean	22·40	$x + 20{\cdot}66$

Bromal.—The results obtained from 3 representative reactions of bromal with sodium hydroxide are summarised in Table II. The values of the heat of formation of liquid bromal are given in terms of a quantity x, which is the heat of formation of liquid bromoform. The value of Q_f(Br$_3$CH,liq.) is not known with any certainty at present. In view of the insolubility of bromoform in water, correction for the solution heat in this case was not considered necessary.

Bichowsky and Rossini (*op. cit.*) estimated Q_f(Br$_3$CH, g.) as −6 kcals. mole^{-1}, but gave no indication of the method by which their estimate was made. We are inclined towards a slightly different estimate, based on an argument of analogy with the case of the chloromethanes. The heats of formation of the chloromethanes are (Nat. Bur. Standards, Washington, Table 23—7, 1949) :

	Q_f (kcals. mole^{-1}).	Δ_1.	Δ_2.
CH_4 (g.)	17·9	1·7	
CH_3Cl (g.)	19·6	1·4	−0·3
CH_2Cl_2 (g.)	21	3·0	1·6
$CHCl_3$ (g.)	24	1·5	−1·5
CCl_4 (g.)	25·5		

First and second differences are listed under Δ_1 and Δ_2. If we now *assume* that the second differences column (Δ_2) is the same in the bromo- as in the chloro-methanes, we obtain the following (estimated Q_f values marked *) :

	Q_f (kcals. mole^{-1}).	Δ_1.	Δ_2.
CH_4 (g.)	17·9	−9·3	
CH_3Br (g.)	8·6	−9·6	−0·3
CH_2Br_2 (g.)	−1·0 *	−8·0	1·6
$CHBr_3$ (g.)	−9·0 *	−9·5	−1·5
CBr_4 (g.)	−18·5 *		

This estimate of $Q_f(Br_3CH, g.) = -9$ kcals. mole^{-1} corresponds to a value of *ca.* $+\frac{1}{2}$ kcal. mole^{-1} for the heat of formation of liquid bromoform, so that $x = 0·5$ kcal. and $Q_f(Br_3C{\cdot}CHO, liq.)$ is approximately 21·2 kcals. mole^{-1}.

DISCUSSION.

Knowledge of the Q_f values in chloral and bromal, combined with other thermal data, enables us to evaluate the energies of dissociation of the C–C bonds in these compounds. If the heat required to rupture the bond X_3C–CHO is represented by $D(X_3C\text{–}CHO)$, the relevant thermal equation may be written as :

$$D(X_3C\text{–}CHO) = Q_f(X_3C{\cdot}CHO, g.) - Q_f(X_3C, g.) - Q_f(CHO, g.) \quad . \quad . \quad . \quad (3)$$

The terms in Q_f on the right-hand side of equation (3) are discussed separately below.

$Q_f(X_3C{\cdot}CHO, g.)$. These differ from the heats of formation in the liquid state by the latent heats of vaporization, $\lambda_{vap.}$. Bertholet (*loc. cit.*) measured $\lambda_{vap.}$ $(Cl_3C{\cdot}CHO)$ as 8·1 kcals. mole^{-1}, and, although a direct measurement of $\lambda_{vap.}$ for bromal has not been reported, this can be estimated as 9·8 kcals. mole^{-1} with little likelihood of serious error. Using these values for $\lambda_{vap.}$, we obtain $Q_f(Cl_3C{\cdot}CHO, g.) = 44·0$, and $Q_f(Br_3C{\cdot}CHO, g.) = 11·4$ kcals. mole^{-1}.

$Q_f(X_3C{\cdot}, g.)$. The heat of formation of the $\cdot CCl_3$ radical can be derived from two independent sources. From studies of the photochemical bromination of chloroform, Braunwarth and Schumacher (*Kolloid Z.*, 1939, **89**, 184) obtained values for the energies of activation, E_a, of the forward and reverse reactions :

$$\text{(i)}\ Cl_3CH + Br \longrightarrow \cdot CCl_3 + HBr \ (E_a = 10 \text{ kcals.})$$

$$\text{(ii)}\ \cdot CCl_3 + HBr \longrightarrow Cl_3CH + Br \ (E_a = 6 \text{ kcals.})$$

from which it follows that the heat evolved in reaction (i) is −4 kcals. [i.e., E_a(ii) − E_a(i)]. Since the heat of reaction is numerically equal to the difference in the sums of the heats of formation of products and reactants, we may write :

$$-4 = Q_f(Cl_3C\cdot) + Q_f(HBr) - Q_f(Br) - Q_f(CHCl_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By use of the values (Nat. Bur. Standards, Washington, Tables 11—1, 11—2, 1948) $Q_f(Br) = -26·71$ and $Q_f(HBr) = 8·66$, with $Q_f(CHCl_3, g.) = 24$ kcals., equation (4) yields $Q_f(Cl_3C\cdot) = -15·4$ kcals. mole^{-1}.

A check on this value is provided by the experiments of Miller and Willard (Abstracts 116th Meeting, Amer. Chem. Soc., 1949) on the reaction of bromine with carbon tetrachloride. These investigators found that chlorine accelerates the bromination reaction, and suggest that this is because $\cdot CCl_3$ radicals can be formed more easily by the reaction $Cl + CCl_4 \longrightarrow \cdot CCl_3 + Cl_2$ than by the reaction $Br + CCl_4 \longrightarrow \cdot CCl_3 + BrCl$. Their results indicated an activation energy of 18 kcals. mole^{-1} for the bromine-atom reaction, and 12 kcals. mole^{-1} for the chlorine-atom reaction with carbon tetrachloride. In these reactions the activation energies set an upper limit to the endothermicity of the reactions, so that we may write :

$$\text{(iii)}\ Cl + CCl_4 \longrightarrow \cdot CCl_3 + Cl_2 - {<}12 \text{ kcals.}$$

$$\text{(iv)}\ Br + CCl_4 \longrightarrow \cdot CCl_3 + BrCl - {<}18 \text{ kcals.}$$

From the heats of these reactions, and known values for the heats of formation of Cl, Br, BrCl, and CCl_4, it follows that $Q_f(\cdot CCl_3) = -{<}15·5$ kcals. mole^{-1}.

There are no experimental data at present from which a value for $Q_f(\cdot CBr_3)$ can be deduced. However, if we make the reasonable assumption that the C–H bond dissociation energy in bromoform is the same as that in chloroform [*i.e.*, $D(H{-}CBr_3) = D(H{-}CCl_3) = 91{\cdot}4$ kcals.], we arrive at $Q_f(\cdot CBr_3) = -48{\cdot}4$ kcals.

$Q_f(\cdot CHO, g)$. Roberts and Skinner (*Trans. Faraday Soc.*, 1949, **45**, **339**) have suggested, for the heat of formation of the formyl radical, a value of 0·4 kcal., which they obtained on the assumption that the activation energy of 26 kcals. for the reaction $HCO \longrightarrow H + CO$ measured by Gorin (*J. Chem. Physics*, **1939**, **7**, **256**) is equivalent to the heat of the reaction. It has been pointed out to us by Dr. M. Szwarc that the reverse reaction, $H + CO \longrightarrow \cdot CHO$, probably requires a small activation energy, in which case the heat of the forward reaction will be slightly less than the 26 kcals. assumed by Roberts and Skinner. It seems unlikely that the reverse reaction requires an activation energy of more than a few kcals., by analogy with the similar reactions $H + O_2 \longrightarrow HO_2\cdot$ (Bodenstein and Schenk, *Z. physikal. Chem.*, 1933, **20**, *B*, 420: activation energy, *ca.* 1·5 kcals.) and $H + CH{\equiv}CH_2 \longrightarrow C_2H_5\cdot$ (Melville, *Proc. Roy. Soc.*, in the press; activation energy 2·1 kcals.). If the activation energy of the reverse reaction is assumed to be *ca.* 3 kcals., the amended value for $Q_f(\cdot CHO, g.)$ becomes $-2{\cdot}6$ kcals. mole^{-1}.

$X_3C{-}CHO$ *Bond Dissociation Energies.*—We are now able to derive the C–C bond dissociation energies in chloral and bromal by substitution of the relevant Q_f values into equation (3). The results are summarised in Table III, together with other calculated dissociation energies obtained by use of the same Q_f values for the $-CX_3$ and $-CHO$ radicals.

TABLE III.

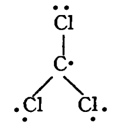
Bond dissociation energies.

	Q_f (kcals.).	Q_f (CX_3).	Q_f (R).	D (X_3C–R).
Cl_3CH	24	−15·4	−52·0	91·4
CCl_4	25·5	,,	−29·0	69·9
$Cl_3C{\cdot}CHO$	44·0	,,	−2·6	62·0
$H_3C{\cdot}CHO$	39·8	−32·1	,,	74·5
Br_3CH	−9 *	−48·4	−52·0	91·4 *
CBr_4	−18·5 *	,,	−26·7	56·6
$Br_3C{\cdot}CHO$	11·4	,,	−2·6	62·4

* Assumed or estimated values (see text).

The similarity in the calculated $X_3C{-}CHO$ dissociation energies in chloral and bromal (the small difference of 0·4 kcal. between the values given in Table III is probably not real) should be linked with our assumption of equivalence in the values $D(Cl_3C{-}H)$ and $D(Br_3C{-}H)$. If these were not identical, a corresponding displacement would be found between $D(Cl_3C{-}CHO)$ and $D(Br_3C{-}CHO)$.

It may be noted that the C–C bond in chloral is some 12·5 kcals. weaker than C–C in acetaldehyde. This weakening may be compared with that between the C–Cl bonds in methyl chloride ($D = 80{\cdot}7$ kcals.) and carbon tetrachloride ($D = 69{\cdot}9$ kcals.), and also with the results of Davidson and Sullivan (*J. Chem. Physics*, 1949, **17**, 176) who found that the C–Br bond in Cl_3CBr is at least 11 kcals. weaker than the C–Br bond in methyl bromide. The reason for the reduction in the strength of C–X bonds in $Cl_3C{-}X$ compared with $H_3C{-}X$ is probably (as suggested by Davidson and Sullivan) a resonance stabilization of the $\cdot CCl_3$ radical, the structure of which can be represented as a hybrid between



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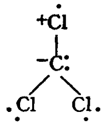

(3 structures)

An alternative reason (that of steric repulsion between the relatively bulky Cl_3C group and X) encounters a difficulty in that the weakness of $Cl_3C{-}Br$ relative to $H_3C{-}Br$ is no more marked than the weakness of $Cl_3C{-}H$ relative to $H_3C{-}H$. In view of these facts it seems to us that the weakness of the C–C bond in chloral arises mainly from the resonance stabilization in the $\cdot CCl_3$ and $\cdot CHO$ radicals, and that steric repulsion effects are here probably small (of the order 1—2 kcals.).

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