201. *Carbon–Halogen Bond Energies in the Acetyl Halides.*

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From measurements of the heats of hydrolysis of the acetyl halides, the following values (in kcals.) were obtained for the heats of formation (Q_f) : Q_f(CH$_3$·COF, liq.) = 110·6 ; Q_f(CH$_3$·COCl, liq.) = 65·8 ; Q_f(CH$_3$·COBr, liq.) = 53·9 ; Q_f(CH$_3$·COI, liq.) = 39·7. These Q_f values, taken in conjunction with a probable value, Q_f(CH$_3$·CO) = 11·3 kcals., for the heat of formation of the acetyl radical, give 110, 76·7, 62·0, and 46·0 kcals., respectively, for the C–F, C–Cl, C–Br, and C–I bond dissociation energies in the acetyl halides.

THE dissociation energy of the carbon–halogen bond in the molecule CH$_3$·COX may be expressed by the equation

$$D(CH_3 \cdot CO - X) = Q_f(CH_3 \cdot COX) - Q_f(CH_3 \cdot CO) - Q_f(X) \quad . \quad . \quad . \quad . \quad (1)$$

where the terms in Q_f are heats of formation from *elements* in their standard states. Accordingly, if Q_f(CH$_3$·CO) is known, a knowledge of the heats of formation of the acetyl halides is then sufficient to provide the bond dissociation energies of the C–halogen bonds in these compounds.

Berthelot and Longuinine (*Ann. Chim. Phys.*, 1875, **6**, 289) measured the heats of hydrolysis of acetyl chloride, bromide, and iodide, *viz.*,

$$CH_3 \cdot COX(liq.) + H_2O(aq.) \longrightarrow CH_3 \cdot CO_2H \text{ (aq.)} + HX(aq.) + Q \quad . \quad . \quad . \quad (2)$$
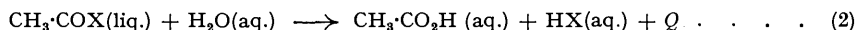
from which the value Q_f(CH$_3$·COX, liq.) may be derived as

$$Q_f(CH_3 \cdot COX, \text{liq.}) = Q_f(CH_3 \cdot CO_2H, \text{aq.}) + Q_f(HX, \text{aq.}) - Q_f(H_2O, \text{liq.}) - Q \quad . \quad . \quad (3)$$

No previous measurement of the heat of hydrolysis of acetyl fluoride appears to have been made.

We have described elsewhere (Carson, Hartley, and Skinner, *Proc. Roy. Soc.*, 1949, *A*, **195**, 500) an adiabatic calorimeter suitable for the measurement of heats of hydrolysis, which we have now used in a reinvestigation of the heats of hydrolysis of acetyl chloride, bromide, and iodide, and also of acetyl fluoride. The new measurements agree reasonably closely with those of Berthelot and Longuinine.

EXPERIMENTAL.

(a) *Preparation of Compounds.*—Acetyl chloride was a B.D.H. " AnalaR " product, carefully fractionated in a Fenske packed column; b. p. 51·2°/769 mm. The product was finally distilled over roasted lime in a vacuum, and collected in weighed glass phials. Analysis of the chlorine content of chosen samples (weighed as AgCl) showed 99·8—100% purity.

Acetyl bromide was also an " AnalaR " product, and was subjected to a careful fractionation in a Fenske column; b. p. 75·5°/758 mm. The product was finally distilled from bulb to bulb in a vacuum, and sealed in weighed glass phials. Analysis of the bromine content (weighed as AgBr) of selected samples showed 99·8—100% purity.

Acetyl iodide was prepared by reaction between the chloride and hydriodic acid (Staudinger, *Ber.*, 1913, **46**, 1417). The crude product was fractionated in the Fenske column, and the almost colourless distillate, b. p. 105·5°, shaken with a little mercury to remove traces of free iodine, and later fractionated in a vacuum. The product was finally obtained as a clear colourless liquid. Analysis of the iodine content (weighed as AgI) of selected samples showed an average purity of 99·5%.

Acetyl fluoride was prepared by reaction of potassium fluoride dissolved in glacial acetic acid with acetyl chloride (Nesmejanov and Kahn, *Ber.*, 1934, **67**, 370). The crude product was fractionated in a vacuum, the first and the last fraction being discarded. The product thus obtained was not pure, containing 10% or more of unchanged acetyl chloride. In determining the heat of hydrolysis of acetyl fluoride, we have made correction for the chlorine impurity as determined by analysis.

(b) *Heats of Hydrolysis.*—(i) *Acetyl chloride.* The heats of hydrolysis were obtained by measuring the heat generated on breaking glass phials containing a known weight of acetyl chloride into a known weight of distilled water, contained within the reaction vessel of the calorimeter. Reactions were carried out at atmospheric pressure. The results of six experiments with acetyl chloride are set out in the table. The values of Q_f(HCl, aq.) are taken from Rossini's " Tables of Selected Values of Thermodynamic Constants." Q_f(CH$_3$·CO$_2$H, aq.) values used in deriving Q_f(CH$_3$·COCl, liq.) were based on Q (CH$_3$·CO$_2$H, liq.) = 116·4 kcals. (Rossini, private communication) and the heats of dilution of liquid acetic acid (Bichowsky and Rossini, " Thermochemistry of Chemical Substances," Reinhold, 1936).

Heat of hydrolysis of acetyl chloride.

Expt.	Reaction.	AcCl (g.).	ΔT (obs.).	W.E. (cals./°c.).	$-\Delta H$ (kcals.).	Q_f(AcCl, liq.) (kcals.).
1	AcCl + 66H$_2$O	4·625	1·014°	1277	22·0	65·77
2	AcCl + 87H$_2$O	5·029	1·088	1308	22·21	65·68
3	AcCl + 74H$_2$O	4·708	1·024	1287	21·98	65·84
4	AcCl + 94H$_2$O	6·957	1·440	1359	22·09	65·83
5	AcCl + 90H$_2$O	6·051	1·280	1333	22·14	65·76
6	AcCl + 85H$_2$O	5·622	1·202	1318	22·12	65·77

Mean Q_f(CH$_3$·COCl, liq.) = 65·78 kcals. mole^{-1}. Maximum deviation from mean = ± 0·10 kcal. Standard deviation of mean = ± 0·022 kcal. $\lambda_{vap.}$ (AcCl) = 6·84 kcals. (Landolt–Börnstein). Q_f(AcCl, gas) = 58·94 kcals. mole^{-1}.

(2) *Acetyl bromide.* Results of six experiments using acetyl bromide are set out in the appropriate table. Values of Q_f(HBr, aq.) were taken from Rossini (*op. cit.*).

Heat of hydrolysis of acetyl bromide.

Expt.	Reaction.	AcBr (g.).	ΔT (obs.).	W.E. (cals./°c.).	$-\Delta H$ (kcals.).	Q_f(AcBr, liq.) (kcals.).
1	AcBr + 98H$_2$O	5·598	0·807°	1288	22·83	54·07
2	AcBr + 140H$_2$O	7·362	1·023	1359	23·21	53·77
3	AcBr + 128H$_2$O	7·916	1·080	1359	22·79	54·17
4	AcBr + 101H$_2$O	10·183	1·407	1361	23·07	53·83
5	AcBr + 125H$_2$O	8·194	1·130	1359	23·04	53·91
6	AcBr + 120H$_2$O	8·518	1·185	1359	23·25	53·70

Mean Q_f(AcBr, liq.) = 53·9 kcals. mole^{-1}. Maximum deviation from mean = ±0·27 kcal. Standard deviation of mean = ±0·067 kcal. $\lambda_{vap.}$ (AcBr) = 7·3 kcals. (Landolt–Börnstein). Q_f(AcBr, gas) = 46·6 kcals.

(3) *Acetyl iodide.* The results of five experiments using acetyl iodide are set out in the table. The values of Q_f(HI, aq.) were taken from Rossini (*op. cit.*). The final value for Q_f(CH$_3$·COI, liq.) is a slightly adjusted figure to compensate for the impurity (*ca.* $\frac{1}{2}\%$) present in the samples of acetyl iodide.

Heat of hydrolysis of acetyl iodide.

Expt.	Reaction.	AcI (g.).	ΔT (obs.).	W.E. (cals./° c.).	$-\Delta H$ (kcals.).	Q_f (AcI) (kcals.).
1	AcI + 140H$_2$O	8·458	0·804°	1334	21·56	39·98
2	AcI + 143H$_2$O	7·915	0·752	1329	21·45	40·09
3	AcI + 136H$_2$O	9·016	0·859	1339	21·68	39·87
4	AcI + 121H$_2$O	11·616	1·087	1360	21·64	39·88
5	AcI + 136H$_2$O	8·760	0·836	1335	21·63	39·92

Mean Q_f(CH$_3$·COI, liq.) = 39·95 kcals. (obs.) = 39·75 kcals. (corr.). Maximum deviation from mean = ±0·14 kcal. Standard deviation of mean = ±0·036 kcal. $\lambda_{vap.}$ (CH$_3$·COI) $\approx$ 7·9 kcals. (assumed). Q_f(CH$_3$·COI, gas) = 31·8 kcals. mole^{-1}.

(4) *Acetyl fluoride.* The heat of hydrolysis of acetyl fluoride was obtained by measuring the heat of reaction with aqueous sodium hydroxide;

$$CH_3·COF(liq.) + 2NaOH(aq.) \longrightarrow NaF(aq.) + CH_3·CO_2Na(aq.) + H_2O(liq.) \quad . \quad . \quad (4)$$
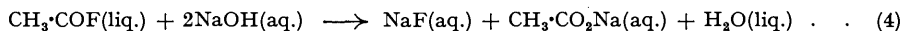
In this way, hydrogen fluoride formed by the aqueous hydrolysis is removed by the alkali, and spurious heat effects that would otherwise arise from its attack on the glass phial are avoided. The hydrolysis with alkali is a rapid reaction relative to the aqueous hydrolysis, which gives an additional reason for choosing this reaction. The products of reaction were analysed for chlorine content at the end of each measurement, to allow corrections to be made for the acetyl chloride impurity present in the fluoride samples. The results as presented in the table below are the corrected values.

Heat of hydrolysis of acetyl fluoride.

Expt.	Reaction.	AcF (g.).	ΔT (obs.).	W.E. (cals./° c.).	$-\Delta H$ (kcals.).	Q_f(AcF) (kcals.).
1	AcF + 2NaOH(67)	1·69	0·905°	1307	43·4	110·0
2	AcF + 2NaOH(50)	1·97	1·033	,,	42·5	110·8
3	AcF + 2NaOH(50)	2·35	1·221	,,	42·1	111·2
4	AcF + 2NaOH(70)	1·506	0·783	,,	43·1	110·4

Mean Q_f (AcF, liq.) = 110·6 kcals. Maximum deviation from mean = ±0·6 kcal. $\lambda_{vap.}$ (AcF) $\approx$ 6 kcals. (assumed). Q_f (AcF, gas) = 104·6 kcals.

The determination of Q_f(CH$_3$·COF, liq.) from the heat of reaction (4) requires a knowledge of the heats of formation of aqueous NaOH, CH$_3$·CO$_2$Na, and NaF; Q_f(NaOH, aq.) and Q_f(NaF, aq.) values were taken from the compilation by Bichowsky and Rossini (*op. cit.*), and the values for sodium acetate from the data of Richards and Mair (*J. Amer. Chem. Soc.*, 1929, **51**, 737) in conjunction with the value here assumed for Q_f(CH$_3$·CO$_2$H, liq.) of 116·4 kcals.

In view of the corrections made to allow for the impurity in the acetyl fluoride samples, we make no claim for high accuracy in our figures for $-\Delta H$ and Q_f(AcF, liq.) as given here. We hope to re-investigate the heat of hydrolysis of acetyl fluoride later with pure samples of substance.

<div style="text-align:center">DISCUSSION.</div>

The Value of Q_f(CH₃·CO).—Several investigators (Gorin, *J. Chem. Physics*, 1939, **7**, 256, $E \gg 17$; Benson and Forbes, *J. Amer. Chem. Soc.*, 1943, **65**, 1399, $E = 16 \pm 2$; Herr and Noyes, *ibid.*, 1940, **62**, 2052, $E \approx 18$; Blacet and Blaedel, *ibid.*, p. 3374 *) have given estimates of the activation energy (E) associated with the decomposition of the acetyl radical,

$$CH_3 \cdot CO \longrightarrow CH_3 + CO \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

There seems little doubt that the value of E is at least as high as 10 kcals., and the majority of estimates place it from 10 to 20 kcals. A fairly full discussion on the experimental data and E values has been given by Steacie (" Atomic and Free Radical Reactions," Reinhold, 1946), who recommends $E \approx 17$ kcals. as the most probable value.

It is reasonable to expect that the activation energy, E, and the dissociation energy $D(CH_3 - CO)$ are closely similar, if not identical; in this event we may write

$$D(CH_3 - CO) \approx E = Q_f(CH_3 \cdot CO) - Q_f(CH_3) - Q_f(CO) \quad . \quad . \quad . \quad . \quad (7)$$

The values $Q_f(CO) = 26 \cdot 41$ kcals. and $Q_f(CH_3) = -32 \cdot 1$ kcals. are both reasonably well established, so that (7) reduces to

$$Q_f(CH_3 \cdot CO) = E - 5 \cdot 7 \text{ kcals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If we accept Steacie's recommended value (*op. cit.*) for E (*viz.*, ≈ 17 kcals.), the value $Q_f(CH_3 \cdot CO) = 11 \cdot 3$ kcals. is obtained. Although this value for $Q_f(CH_3 \cdot CO)$ cannot claim to be well established, there is much subsidiary evidence that it is a correct assessment within limits of ± 5 kcals. (see later).

The Values Q_f(X).—The quantities Q_f(X), where $X = $ Cl, Br, and I, are now known to a high degree of precision; the figures quoted here are those recommended by Rossini (*op. cit.*), *viz.*, Q_f(Cl) $= 29 \cdot 0$, Q_f(Br) $= 26 \cdot 7$, Q_f(I) $= 25 \cdot 5$ kcals. In the case of Q_f(F), it appears to be necessary to discard the value of -32 kcals. which has hitherto been generally accepted. Some reason to doubt the old value [which corresponds to the value $D(F–F) = 64$ kcals.] first appeared from the determination of D(Cl–F) by Wahrhaftig (*J. Chem. Physics*, 1942, **10**, 248). The recent measurement of the heat of formation of ClF by Schmitz and Schumacher (*Z. Naturforsch.*, 1947, **2**, 362) [Q_f(ClF, g.) $= 15 \pm \frac{1}{2}$ kcals.], coupled with the determination of D(Cl–F) at $60 \cdot 3 \pm 0 \cdot 5$ kcals. (or possibly, $58 \cdot 9 \pm 0 \cdot 5$) by the same authors (*ibid.*, p. 359) seems definitely to prove that D(F–F) is not greater than $33 \cdot 4$ kcals. Accordingly, we have chosen Q_f(F) at $-16 \cdot 7$ kcals., as the most probable value.

Dissociation Energies of Acetyl–Halogen Bonds.—The bond dissociation energies $D(CH_3 \cdot CO–X)$ as given by eqn. (1), using the listed values of Q_f(X), Q_f(CH₃·CO), and Q_f(CH₃·COX, gas), are collected below.

<div style="text-align:center">*Values of $D(CH_3 \cdot CO–X)$, kcals.*</div>

Compound.	$D(CH_3 \cdot CO–X)$.	Compound.	$D(CH_3 \cdot CO–X)$.
CH₃·COF	110·0	CH₃·COBr	62·0
CH₃·COCl	76·7	CH₃·COI	46·0

The value $D(CH_3 \cdot CO–I) = 46$ kcals. may be compared with the figure $50 \cdot 7$ kcals. obtained by Butler and Polanyi (*Trans. Faraday Soc.*, 1943, **39**, 19) from studies of the kinetics of thermal decomposition of acetyl iodide, and with an earlier estimate of $43 \cdot 1$ kcals. by Jones (*J. Amer. Chem. Soc.*, 1939, **61**, 3284) from similar studies. Neither of these kinetic studies claims high accuracy for the estimated C–I dissociation energy. Butler and Polanyi's value for $D(CH_3 \cdot CO–I)$ corresponds to $Q_f(CH_3 \cdot CO) = 6 \cdot 6$ kcals., and lies within the limits of error (± 5 kcals.) which we have attached to the probable value of Q_f(CH₃·CO). We may note that the value $Q_f(CH_3 \cdot CO) = 11 \cdot 3$ kcals. corresponds to $D(CH_3 \cdot CO–H) = 80 \cdot 2$ kcals., and to $D(CH_3 \cdot CO–CH_3) = 72 \cdot 6$ kcals.; the former fits in well with the value $D(H–CHO) = 78$ kcals. estimated (as an upper limit) by Gorin (*loc. cit.*) from photo-dissociation studies, and the latter agrees closely with $D(CH_3–CHO) = 75(\pm 2)$ kcals., obtained by Graham and Rollefson (*J. Chem. Physics*, 1940, **8**, 98).

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* These authors consid er the disappearance of CH₃·CO radicals results from a bimolecular reaction, $CH_3 \cdot CO + M \longrightarrow CH_3 + CO + M$, to which an activation energy of $9 \cdot 6$ kcals. is ascribed.

The fact that $D(CH_3 \cdot CO-I)$ is considerably less than $D(CH_3-I)$ is at first sight puzzling—as Butler and Polanyi pointed out—since one would expect the C–I bond in $CH_3 \cdot COI$ to possess double-bond character, arising from the resonance contribution of the structure $CH_3 \cdot C {\displaystyle \mathop{\lessgtr}^{O^-}_{I^+}}$.
The difficulty disappears when one appreciates that $D(CH_3 \cdot CO-H)$ is markedly weaker than $D(CH_3-H)$, indicative of a large hyperconjugation energy in the acetyl radical. Roberts and Skinner (in course of publication) have discussed this point in more detail elsewhere.

The value for $D(CH_3 \cdot CO-F)$ enables us to make a plausible estimate of the unknown dissociation energy $D(CH_3-F)$. The bond dissociation energy differences (*idem, ibid.*), $D(CH_3-X)$ minus $D(CH_3 \cdot CO-X)$, vary with change in X as follows :

X =	H.	CH_3.	I.	Br.	Cl.	–OH.
Diff.	21·8	11·8	9·0	5·4	4·0	−6·0

i.e., decreasing in magnitude as the electronegativity of X increases. One might expect the difference in case of the highly electronegative fluorine atom to be of similar magnitude to that shown when X = OH. This would lead to a value of *ca.* 105 kcals. for $D(CH_3-F)$. A similar value is reached by a different approach; thus, if one calculates the *mean* bond-energy term values $E(C-H)$ in CH_4, and $E(C-Cl)$ in CCl_4, assuming $L = 171·7$ kcals. for the latent heat of sublimation of carbon, the E values are found to be slightly less (2—3 kcals.) than the quantities $D(CH_3-H)$ and $D(CH_3-Cl)$. For carbon tetrafluoride, the $E(C-F)$ value is 100·2 kcals. : so that one might expect $D(CH_3-F)$ to be rather larger than 100 kcals.

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