127. *The Heats of Hydrolysis of the Benzoyl Halides.*

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From measurements of the heats of hydrolysis of the benzoyl halides in aqueous acetone solutions, the following values (in kcal./mole) were obtained for the heats of formation at room temperature : $Q_f(C_6H_5{\cdot}COCl,\ liq.) = 39{\cdot}30$, $Q_f(C_6H_5{\cdot}COBr,\ liq.) = 25{\cdot}50$, $Q_f(C_6H_5{\cdot}COI,\ liq.) = 12{\cdot}55$.

These data are used to derive provisional values for the bond dissociation energies in a number of benzoyl–X molecules.

THIS paper reports values for the heats of hydrolysis of benzoyl chloride, bromide, and iodide, and is a continuation of studies on the hydrolysis heats of acid halides (Carson and Skinner, *J.*, 1949, 936; Pritchard and Skinner, *J.*, 1950, 272). The heats of hydrolysis of the benzoyl halides have not been measured previously, possibly because the reactions are slow to reach completion in a purely aqueous medium. Thermal difficulties arising from the tardiness of the aqueous hydrolyses may, however, be overcome by using aqueous acetone as the hydrolysis medium (cf. Pritchard and Skinner, *loc. cit.*). In a solvent obtained by mixing 400 c.c. of acetone and 350 c.c. of water, the hydrolysis of benzoyl chloride was virtually complete in 30 minutes, and benzoyl bromide and iodide in the same solvent were hydrolysed in less than 15 minutes.

The heats of hydrolysis can be combined with known thermochemical data to give values for the heats of formation (Q_f) of the benzoyl halides. Apart from a single measurement of the heat of combustion of benzoyl chloride by Rivals (*Ann. Chim. Phys.*, 1897, **7**, 541), corresponding to $Q_f(C_6H_5{\cdot}COCl, \text{liq.}) = 53{\cdot}2$ kcals., there are no data in the literature concerning the Q_f of the benzoyl halides.

EXPERIMENTAL.

Preparation of Compounds.—Benzoyl chloride (May and Baker) was purified by fractional distillation under reduced pressure. Benzoyl bromide was a pure Kahlbaum sample. Benzoyl iodide was made by Staudinger's method (*Ber.*, 1913, **46**, 1417), *i.e.*, interaction of hydrogen iodide and benzoyl chloride; the crude product was shaken with mercury to remove traces of free iodine, and purified by careful fractionation under low pressure.

Thermal Measurements.—The heats of hydrolysis were measured by the same technique and apparatus used by Pritchard and Skinner (*loc. cit.*). The *observed* hydrolysis heats (listed in the following tables under $Q_{\text{obs.}}$) are the heats of the reactions :

$$C_6H_5{\cdot}COX\ (\text{liq.}) + H_2O(\text{aq. acetone}) \longrightarrow (C_6H_5{\cdot}CO_2H + HX)\ (\text{aq. acetone}) + Q_{\text{obs.}} \quad . \quad . \quad (1)$$

and differ from the heats of the purely aqueous hydrolyses (listed under $Q_{\text{aq.}}$), *viz.*,

$$C_6H_5{\cdot}COX\ (\text{liq.}) + H_2O\ (\text{liq.}) \longrightarrow C_6H_5{\cdot}CO_2H\ (c) + HX\ (\text{aq.}) + Q_{\text{aq.}} \quad . \quad . \quad (2)$$

by some small terms arising from the heat of solution and mixing of the benzoic acid and halogen acid in the aqueous acetone. These solution heats were measured separately as required.

In the tables of results, R_i and R_f refer to the initial and final values of the thermistor resistance, and $Q_{\text{aq.}}$ gives the heat of reaction (2) when the product is HX ($1000H_2O$).

Heat of hydrolysis of benzoyl halides.

Wt. of acid halide (g.).	R_i (ohms).	R_f (ohms).	$Q_{\text{obs.}}$ (kcals.).	$Q_{\text{aq.}}$ (kcals.).	Q_f (liq.) (kcals.).	Wt. of acid halide (g.).	R_i (ohms).	R_f (ohms).	$Q_{\text{obs.}}$ (kcals.).	$Q_{\text{aq.}}$ (kcals.).	Q_f (liq.) kcals.).
		Benzoyl chloride.						Benzoyl bromide.			
3·5237	1710·2	1652·0	21·35	24·38	39·27	3·39	1746·8	1696·5	24·9	27·0	25·5
3·7900	1696·1	1634·4	21·23	24·26	39·39	3·0140	1748·8	1703·85	25·03	27·15	25·39
4·2940	1681·0	1611·65	21·34	24·37	39·28	3·5773	1744·0	1691·4	24·80	26·92	25·62
2·1719	1739·0	1701·6	21·36	24·39	39·26	3·0647	1746·0	1700·45	24·98	27·10	25·44
4·2040	1735·1	1663·75	21·31	24·34	39·31	3·0990	1747·0	1701·1	24·88	27·00	25·54
		Mean values	21·32	24·35	39·30			Mean values	24·92	27·04	25·50
					Benzoyl iodide.						
5·4975	1711·7	1649·2	24·29	24·60	12·42	5·3296	1694·0	1635·45	24·00	24·31	12·71
5·9529	1700·15	1633·35	24·17	24·48	12·54	6·0524	1698·3	1631·15	24·24	24·55	12·47
5·1122	1692·2	1635·0	24·14	24·45	12·57	5·7887	1704·6	1640·4	24·11	24·42	12·60
								Mean values	24·16	24·47	12·55

The main reason for the differences between the $Q_{\text{obs.}}$ and $Q_{\text{aq.}}$ values arises from the negative solution heat (*ca.* $-4{\cdot}80$ kcals./mole) of crystalline benzoic acid in the aqueous acetone; the $Q_{\text{aq.}}$ values, corresponding to reaction (2), refer to crystalline benzoic acid as one of the reaction products.

The calculated Q_f (liq.) values given in the final columns of the tables are based on assumed values for the heats of formation of the halogen hydracids ("Selected Values of Chemical Thermodynamic Constants," National Bureau of Standards, Washington, 1948) and on $Q_f(C_6H_5{\cdot}CO_2H, \text{c.}) = 92{\cdot}06$ kcals./mole (Jessup, *J. Res. Nat. Bur. Stand.*, 1942, **29**, 247). It may be remarked that the Q_f value of 53·2 kcals., derived from Rivals's heat of combustion of benzoyl chloride, corresponds to a heat of hydrolysis ($Q_{\text{obs.}}$) of only 7·4 kcals.

DISCUSSION.

The Q_f values obtained from these experiments refer to the *liquid* state at room temperature. Data are not available on the heats of vaporisation of the benzoyl halides, but a rough estimate of these can be made by use of Trouton's rule. The results are summarised below :

	$C_6H_5{\cdot}COCl$.	$C_6H_5{\cdot}COBr$.	$C_6H_5{\cdot}COI$.
Q_f (liq.) (kcals.)	39·30	25·50	12·55
Q_f (gas) (kcals.)	28·9	14·7	1·3
$\lambda_{\text{vap.}}$ (assumed) (kcals.)	10·4	10·8	11·2

The Q_f (gas) values may be correlated with the bond dissociation energies $D(C_6H_5{\cdot}CO{-}X)$ by the equation

$$D(C_6H_5{\cdot}CO{-}X) = Q_f(C_6H_5{\cdot}COX) - Q_f(X) - Q_f(C_6H_5{\cdot}CO) \quad . \quad . \quad . \quad . \quad (3)$$

where the terms in Q_f are heats of formation from elements in standard states, and $D(C_6H_5{\cdot}CO\text{–}X)$ is the heat of the reaction $C_6H_5{\cdot}CO + X \longrightarrow C_6H_5{\cdot}COX$. The term $Q_f(C_6H_5{\cdot}CO)$ in equation (3) cannot be determined directly, but can be evaluated if both $D(C_6H_5{\cdot}CO\text{–}X)$ and $Q_f(C_6H_5{\cdot}COX)$ are known for *one* specific $C_6H_5{\cdot}COX$ compound. In this event, equation (3) can be generally applied to determine D(benzoyl–X) in other benzoyl derivatives.

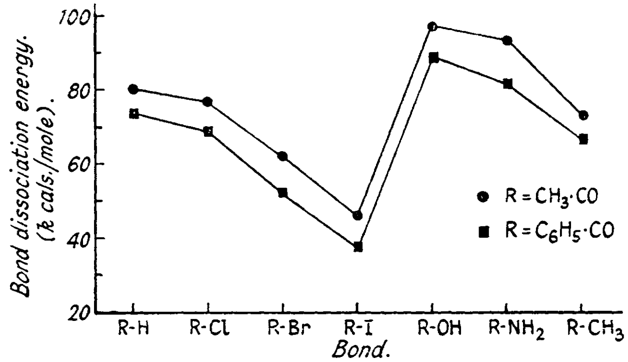
Apart from the kinetic studies of Butler and Polanyi (*Trans. Faraday Soc.*, 1943, **39**, 19) on the pyrolytic decomposition of benzoyl iodide, there are no experimental data from which D values in benzoyl–X can be assessed. Butler and Polanyi gave $D(C_6H_5{\cdot}CO\text{–}I) = 43{\cdot}9$ kcals., but this result was not claimed to be of high accuracy. In general, the D(R–I) values given by Butler and Polanyi seem to be accurate within limits of ± 5 kcals., and for the purpose of the present paper we shall adopt a value of $D(C_6H_5{\cdot}CO\text{–}I) = 42$ kcals. ($\pm x$), where x is probably less than 5 kcals. This provisional $D(C_6H_5{\cdot}CO\text{–}I)$ value corresponds to Q_f(benzoyl) $= -15{\cdot}2 \pm x$ kcals., which, substituted into equation (3), leads to the following D values in the listed benzoyl–X compounds :

Bond.	Q_f (gas).	Q_f (X).	$D(C_6H_5{\cdot}CO\text{–}X)$ ($\pm x$).	Bond.	Q_f (gas).	Q_f (X).	$D(C_6H_5{\cdot}CO\text{–}X)$ ($\pm x$).
$C_6H_5{\cdot}CO\text{–}H$ ...	11·2 [a]	−52·0	78·4 *	$C_6H_5{\cdot}CO\text{–}OH$	68 [a]	−10·0	93·2 *
$C_6H_5{\cdot}CO\text{–}Cl$ ...	28·9 [b]	−29·0	73·1	$C_6H_5{\cdot}CO\text{–}NH_2$	30 [c]	−41·0 [d]	86·2 *
$C_6H_5{\cdot}CO\text{–}Br$ ...	14·7 [b]	−26·7	56·6	$C_6H_5{\cdot}CO\text{–}CH_3$	24 [c]	−32·1	71·3 *
$C_6H_5{\cdot}CO\text{–}I$ ...	1·3 [b]	−25·5	42	$C_6H_5{\cdot}CO\text{–}C_6H_5$	−13 [e]	−69·8	72 *

Based on data listed by Wheland ("The Theory of Resonance," John Wiley, 1944). [b] This research. [c] Kharasch (*J. Res. Nat. Bur. Stand.*, 1929, **2**, 407). [d] Szwarc (*J. Chem. Physics*, 1949, **17**, 505). [e] Beckers (*Bull. Soc. chim. Belg.*, 1931, **40**, 518); Neumann and Volker (*Z. physikal. Chem.*, 1932, **161**, *A*, 33).

* Asterisked values are doubtful because of uncertainties in the heats of formation Q_f (gas).

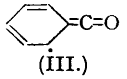
The value given for $D(C_6H_5{\cdot}CO\text{–}H)$ is a relatively " low " value for a C–H bond dissociation energy. Compared with the C–H bonds in ethylene or benzene, both of which are of the same sp^2–s hybrid type, $D(C_6H_5{\cdot}CO\text{–}H)$ is smaller by some 20 or more kcals. The weakness of the benzoyl–H bond is strongly suggestive of a powerful resonance stabilisation in the benzoyl radical.



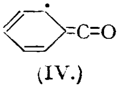
Roberts and Skinner (*Trans. Faraday Soc.*, 1949, **45**, 339) commented on the weakness of the C–H bond in acetaldehyde, $D(CH_3{\cdot}CO\text{–}H) \approx 80$ kcals., and attributed this to a stabilisation in the acetyl radical by a 3-electron bond resonance, *i.e.*, (I) $\rightleftharpoons$ (II). In so far as a resonance

$$CH_3\text{–}\dot{C}{=}\ddot{O} \qquad \text{(I.)}$$

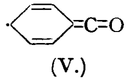
$$CH_3\text{–}\underset{-}{\ddot{C}}{=}\underset{+}{\dot{O}} \qquad \text{(II.)}$$



(III.)



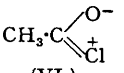
(IV.)



(V.)

stabilisation of this type occurs in $CH_3{\cdot}C\dot{O}$, it should similarly be present in the benzoyl radical, and from this point of view the low value of $D(C_6H_5{\cdot}CO\text{–}H)$ should be compared with the low value of $D(CH_3{\cdot}CO\text{–}H)$. Indeed, one might expect the $C_6H_5{\cdot}\dot{C}O$ radical to be resonance-stabilised to a greater extent than $CH_3{\cdot}\dot{C}O$, in that the excited structures of the types (III), (IV), and (V) in relation to $C_6H_5{\cdot}\dot{C}O$ are probably more significant than the structures $\dot{H}CH_2{=}C{=}O$ in relation to $CH_3{\cdot}\dot{C}O$.

In the figure, bond-dissociation energies in a series of benzoyl–X and acetyl–X compounds are plotted together,* to bring out their close similarity in respect of varying X. The present values do not correspond to a strictly constant difference, ΔD, where $\Delta D = D(CH_3{\cdot}CO{-}X) - D(C_6H_5{\cdot}CO{-}X)$, although these differences are approximately equal. Some of the D values are, however, based on not very reliable combustion-heat data, and most involve uncertainties of the order ±1 or ±2 kcals. in the heats of vaporisation, so that the trends in ΔD may be partly obscured by errors in the data we have used. Nevertheless, the data are sufficient to show that the factors influencing the strength of acetyl–X bonds are similarly operative in benzoyl–X. For example, if one accepts the importance of back-co-ordination, as represented by the resonance structure (VI) in acetyl chloride, it would seem to be no less important in benzoyl chloride.


(VI.)

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