

58. The Heats of Hydrolysis of the Chloro-substituted Acetyl Chlorides.

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From measurements of the heats of hydrolysis of $\text{CH}_3\cdot\text{COCl}$, $\text{CH}_2\text{Cl}\cdot\text{COCl}$, $\text{CHCl}_2\cdot\text{COCl}$, and $\text{CCl}_3\cdot\text{COCl}$ in aqueous-acetone solution, the following values (kcal. mole⁻¹) were obtained for the respective heats of formation (Q_i) of the liquids at room temperature: 66.2, 70.1, 68.7, and 68.8.

IN an earlier communication, Carson and Skinner (*J.*, 1949, 936) reported some new measurements on the heats of hydrolysis of the acetyl halides. The present work is an extension of these studies to mono-, di-, and tri-chloroacetyl chlorides. Only one reference exists in the literature to previous measurements on the heats of hydrolysis of this group of compounds, in which Rivals (*Ann. Chim. Phys.*, 1897, 7, 541) quoted values for the hydrolysis heats of mono- and tri-chloroacetyl chloride. The heat of hydrolysis of dichloroacetyl chloride does not seem to have been measured before.

Whereas acetyl chloride reacts very rapidly with water at room temperature, the chloro-substituted acetyl chlorides hydrolyse slowly, owing to their slow rate of dissolution in water. In aqueous acetone, on the other hand, the compounds hydrolyse quite rapidly, and we have found it convenient to use an aqueous acetone solvent in most of the present investigations.

EXPERIMENTAL.

Preparation of Compounds.—Chloroacetyl chloride was a B.D.H. product, purified by careful fractionation in a Fenske packed column; b. p. 105.4–105.5°/763 mm. The product was further purified by bulb-to-bulb distillation in a vacuum, and the pure fractions were collected and sealed in weighed glass ampoules.

Dichloroacetyl chloride was a B.D.H. product, purified in an exactly analogous manner; b. p. 107.0–107.4°/761 mm. The purified commercial sample was found on analysis to contain a small amount (0.03%) of sulphur (presumably from the thionyl chloride used in its preparation). As a check on the results obtained with the commercial sample, a further sample of dichloroacetyl chloride was prepared from dichloroacetic acid and benzoyl chloride (Brown, *J. Amer. Chem. Soc.*, 1938, 60, 1325), and carefully purified by fractionation in a Fenske column operating at a high reflux ratio: b. p. 107.7–107.8°/767 mm.

Trichloroacetyl chloride was prepared according to Leimu's method (*Ber.*, 1937, 70, 1040) by the action of thionyl chloride on trichloroacetic acid in benzene solution. The crude product was fractionated in a Fenske column, and later distilled *in vacuo* and sealed in weighed glass ampoules.

Calorimeter.—The reactions were carried out by breaking thin glass ampoules containing a known amount of the acid chloride into a large excess of water, or aqueous acetone. The reaction vessel was a silvered Dewar flask (1 l. capacity), with a single narrow neck (1½" diameter). The neck was closed with a polystyrene stopper which, in turn, was covered by a heavy close-fitting brass cap. A glass rotary propeller stirrer (100 r.p.m.) fitted centrally through the cap and stopper. Two additional holes through the stopper carried an electrical heater (for calibration purposes), and the resistance thermometer and leads. A circular brass plate, supported by two thin brass rods from the under side of the polystyrene stopper, served as a bottom bearing for the stirrer, and also for breaking the glass ampoules which could be depressed at any desired moment on to a cluster of spikes on one side of the plate. All the metal parts inside the calorimeter were rhodium-plated.

The Dewar vessel was submerged and supported in an accurately thermostated oil-bath, which, together with all the accompanying electrical apparatus, was kept in a thermostated room. The thermostat bath was a rectangular glass tank (15" × 12") fitted to a depth of 12" with white mineral oil. The bath was heated with mat heaters mounted about ¼" off the bottom, and was efficiently stirred by a 10" four-bladed propeller driven by a flexible drive from outside the bath. The temperature control was maintained at 21° by a toluene regulator (extending through the bath). A Gouy head (Sligh, *J. Amer. Chem. Soc.*, 1920, 42, 60) was used with the toluene regulator. The whole calorimeter assembly was essentially a modification of that used by Williams (*ibid.*, 1942, 64, 1395).

The calibration heater was layer wound from 35 S.W.G. silk-covered Eureka wire on a 3-mm. ebonite rod to form an element 25 mm. in length (resistance 65 Ω). The heater was impregnated with cellulose acetate and encased in a platinum cylinder sealed to the end of a glass tube.

The resistance thermometer was a "Stantel" Thermistor (F 2311/300), and was carefully and rigidly mounted inside a thin glass tube, so that the tip was protected from external shock or pressure changes (Herington and Handley, *J. Sci. Instr.*, 1948, 25, 434). Its resistance was measured to 0.05 Ω on a Cambridge glazed bridge in conjunction with a short-period reflecting galvanometer. The sensitivity of the resistance measurement is limited by the maximum continuous current rating of the thermistor: for the purpose of temperature measurement, this should not exceed 0.4 milliamp. The sensitivity under these conditions, with an optical lever of 1 metre, is ca. 1 Ω/cm.

Over small ranges of temperature, the temperature-resistance relation for a thermistor is of the form $T = k \log R$ (Becker, Green, and Pearson, *Trans. Amer. Inst. Elect. Eng.*, 1946, 65, 711). By measuring the initial and final resistance of the thermistor (*i.e.*, R_1 and R_2) over the course of an experiment, the heat change (Q) can be obtained from $Q = K \log R_1/R_2$, where K is a constant that includes the water equivalent of the system and the thermistor constant k . The constant K can be determined by passing a measured amount of electrical energy through the calibration heater (*e.g.*, see McInnes and Braham,

J. Amer. Chem. Soc., 1917, **39**, 2110) so as to obtain a change in the thermistor resistance comparable with that observed in an average experiment.

In general, a resistance change of 50—60 Ω (corresponding to a temperature change of *ca.* 0.75°) was aimed at in each experiment, so that we were able to measure the temperature changes to an accuracy of the order of 0.002°. We have found that the thermistor element gives reproducible results over long periods of time, and can successfully replace a Beckmann thermometer or other more conventional temperature-recording instrument, provided that due care is exercised in keeping the element free from strain.

Heats of Hydrolysis.—The preliminary investigation were carried out on chloroacetyl chloride, which is representative of a number of acid chlorides that react slowly with water at room temperature. Ampoules containing about 3 g. of the acid chloride were broken under 750 c.c. of water. The hydrolysis required about 2 hours to reach completion. Since an accurate estimation of the heat leakages over such a long time period is difficult, we sought to attain a faster reaction by using an equivalent amount of sodium hydroxide solution as the hydrolysing agent (see Rivals, *loc. cit.*), but found no marked increase in the rate of hydrolysis by this change in solvent. However, by using aqueous acetone as the hydrolysis medium, the rate of reaction was much increased, and the reaction times were reduced to 10 minutes with a solvent medium of 150 c.c. of acetone in 600 c.c. of water. The heats of hydrolysis observed in this solvent ($Q_{\text{obs.}}$) are convertible into hydrolysis heats in a purely aqueous medium ($Q_{\text{aq.}}$) by making small corrections for the difference in the heats of solution of the reaction products in the two solvents. These solution heat corrections (amounting to about 1 kcal. mole⁻¹) were measured as required, the most important of them being the heats of solution of the chloroacetic acids, which are roughly 1 kcal. mole⁻¹ less in the above aqueous acetone than in pure water, as shown below:

Acid.	Solvent (mole-ratio)	Q_{solution} (kcal. mole ⁻¹).
CH ₃ ·CO ₂ H (liq.)	700H ₂ O	+0.34
	(700H ₂ O + 35COMe ₂)	-0.42
CH ₂ Cl·CO ₂ H (crys.1)	1100H ₂ O	-3.30
	(1100H ₂ O + 50COMe ₂)	-4.27
CHCl ₂ ·CO ₂ H (liq.)	1350H ₂ O	+2.67
	(1350H ₂ O + 65COMe ₂)	+1.78
CCl ₃ ·CO ₂ H (liq.)	1700H ₂ O	+2.55
	(1700H ₂ O + 80COMe ₂)	+1.70

Results.

Chloroacetyl Chloride.—The results obtained from five experiments on the hydrolysis of this chloride in water are given in Table I(a), and from six experiments in the aqueous acetone solvent in Table I(b). The calculated values for Q_f (CH₂Cl·COCl, liq.) given in the final columns of these tables are derived from the equation:

$$Q_f(\text{CH}_2\text{Cl}\cdot\text{COCl}) = Q_f(\text{HCl, aq.}) + Q_f(\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H, aq.}) - Q_f(\text{H}_2\text{O, liq.}) - Q_{\text{aq.}}$$

where the symbol Q_f is used to denote the heat of formation from the elements in standard states. The values for Q_f (HCl, aq.), Q_f (CH₂Cl·CO₂H, aq.) and Q_f (H₂O, liq.) were taken from the "Selected Tables of Chemical Thermodynamic Constants" (National Bureau of Standards, Washington, U.S.A.). The values found for Q_f (CH₂Cl·COCl, liq.) in Tables I(a) and I(b) agree reasonably well with each other, due

TABLE I.
Heat of hydrolysis of CH₂Cl·COCl.

Expt.	Reaction mixture.	Wt. R·COCl (g.).	R_1 (ohms).	R_f (ohms).	$Q_{\text{obs.}}$ kcal.	$Q_{\text{aq.}}$ kcal.	Q_f (CH ₂ Cl·COCl, liq.), kcal. mole ⁻¹ .		
(a) Hydrolysis in water.									
1	R·COCl + 1300H ₂ O	3.6086	1739.5	1678.6	—	22.56	69.91		
2	R·COCl + 1520H ₂ O	3.0950	1729.4	1677.6	—	22.44	70.04		
3	R·COCl + 1590H ₂ O	2.9464	1718.7	1669.3 ₅	—	22.59	69.89		
4	R·COCl + 1470H ₂ O	3.1982	1735.1	1681.0	—	22.62	69.86		
5	R·COCl + 1510H ₂ O	3.1155	1737.9	1684.9	—	22.71	69.77		
						Mean values	22.59	69.89	
(b) Hydrolysis in aqueous acetone.									
1	R·COCl + (1280H ₂ O, 78COMe ₂)	2.9331	1707.8	1658.5	21.40	22.35	70.12		
2	R·COCl + (1190H ₂ O, 72COMe ₂)	3.1746	1745.0	1690.6	21.42	22.37	70.10		
3	R·COCl + (1320H ₂ O, 80COMe ₂)	2.8558	1743.5	1694.4	21.48	22.43	70.05		
4	R·COCl + (1220H ₂ O, 74COMe ₂)	3.0843	1725.7	1673.6	21.34	22.30	70.17		
5	R·COCl + (1270H ₂ O, 77COMe ₂)	2.9584	1742.7	1692.1	21.41	22.36	70.10		
6	R·COCl + (1630H ₂ O, 98COMe ₂)	2.3058	1744.1	1704.9	21.35	22.30	70.19		
						Mean values	21.40	22.35	70.12

allowance being made for the tardiness of the aqueous hydrolysis, and the possible small errors involved in the correction terms required by the aqueous-acetone hydrolysis.

Dichloroacetyl Chloride.—The hydrolysis of dichloroacetyl chloride was studied in the aqueous acetone mixture, in which solvent the rate of hydrolysis is rapid, requiring about 10 minutes. Results from 6 experiments are presented in Table II. The data therein were obtained with the purified commercial dichloroacetyl chloride. Some check experiments using a sample prepared by Brown's method (*loc. cit.*) gave virtually identical results; *e.g.*, two experiments gave $Q_{\text{obs.}} = 24.84$ and 24.83 kcals.

Trichloroacetyl Chloride.—The hydrolysis of this chloride was similarly studied in the aqueous acetone solvent, and, as previously, reaction times of *ca.* 10 minutes were found. The results are given in Table III.

TABLE II.

Dichloroacetyl chloride in aqueous acetone.

Expt.	Reaction mixture.	Wt. R·COCl (gs.).	R_1 (ohms).	R_t (ohms).	$Q_{\text{obs.}}$ (kcal.).	$Q_{\text{aq.}}$ (kcal.).	Q_t (kcal.).
1	R·COCl + (1150H ₂ O, 70COMe ₂)	4.2658	1749.6	1684.8	24.80	25.67	68.78
2	R·COCl + (1380H ₂ O, 84COMe ₂)	3.5676	1753.7	1699.1	24.85	25.72	68.75
3	R·COCl + (1240H ₂ O, 76COMe ₂)	3.9763	1754.2	1693.7	24.74	25.61	68.86
4	R·COCl + (1240H ₂ O, 76COMe ₂)	3.9815	1757.8	1696.5 _s	24.97	25.84	68.63
5	R·COCl + (1255H ₂ O, 76COMe ₂)	3.9272	1760.2 _s	1700.0 _s	24.84	25.71	68.76
6	R·COCl + (1265H ₂ O, 77COMe ₂)	3.8989	1754.3	1694.5	24.93	25.80	68.68
Mean values					24.86	25.73	68.74

TABLE III.

Trichloroacetyl chloride in aqueous acetone.

Expt.	Reaction mixture.	Wt. R·COCl (gs.).	R_1 (ohms).	R_t (ohms).	$Q_{\text{obs.}}$ (kcal.).	$Q_{\text{aq.}}$ (kcal.).	Q_t (kcal.).
1	R·COCl + (1400H ₂ O, 85COMe ₂)	4.3432	1754.7	1695.7	27.27	28.10	68.84
2	R·COCl + (1300H ₂ O, 79COMe ₂)	4.6746	1754.6	1691.3	27.22	28.05	68.87
3	R·COCl + (1300H ₂ O, 79COMe ₂)	4.6771	1754.9	1691.2	27.37	28.20	68.72
4	R·COCl + (1275H ₂ O, 78COMe ₂)	4.7666	1755.9	1691.3	27.23	28.06	68.86
5	R·COCl + (1225H ₂ O, 75COMe ₂)	4.9530	1754.4	1687.0	27.39	28.22	68.69
Mean values					27.30	28.12	68.80

TABLE IV.

Expt.	Reaction mixture.	Wt. R·COCl (g.).	R_1 (ohms).	R_t (ohms).	$Q_{\text{obs.}}$ (kcal.).	$Q_{\text{aq.}}$ (kcal.).	Q_t (kcal.).
(a) <i>Acetyl chloride in water.</i>							
1	R·COCl + 1410H ₂ O	2.3207	1762.0	1705.8	—	22.17	66.15
2	R·COCl + 1380H ₂ O	2.3749	1760.6	1703.7	—	21.96	66.36
3	R·COCl + 1225H ₂ O	2.6734	1762.2	1697.3	—	22.28	66.03
4	R·COCl + 1290H ₂ O	2.5501	1762.4	1701.6	—	21.86	65.45
5	R·COCl + 1310H ₂ O	2.5025	1756.5	1696.4	—	22.09	66.22
6	R·COCl + 1280H ₂ O	2.5624	1747.4	1686.6	—	21.94	66.37
Mean values					22.06	66.26	
(b) <i>Acetyl chloride in aqueous acetone.</i>							
1	R·COCl + (1060H ₂ O, 65COMe ₂)	2.4652	1759.2	1698.3	21.34	22.08	66.22
2	R·COCl + (930H ₂ O, 57COMe ₂)	2.8086	1757.5	1688.5	21.28	22.02	66.28
3	R·COCl + (1040H ₂ O, 63COMe ₂)	2.5104	1758.5	1696.6	21.30	22.04	66.26
Mean values					21.31	22.05	66.25

Acetyl Chloride.—As a check on the thermochemical method, we have remeasured the heat of hydrolysis of acetyl chloride, (a) in water and (b) in the aqueous-acetone solvent. As in the case of chloroacetyl chloride, the hydrolysis heat measured in the aqueous acetone ($Q_{\text{obs.}}$) was smaller than that measured in the purely aqueous solution ($Q_{\text{aq.}}$). After the necessary solution heat corrections had been made to $Q_{\text{obs.}}$, the derived $Q_{\text{aq.}}$ values agreed more or less exactly with one another. The results are summarised in Tables IV(a) and IV(b). Compared with the results given earlier for acetyl chloride by Carson and Skinner (*loc. cit.*), there is a close correspondence in the observed heats of hydrolysis, but an apparent discrepancy in the values given for $Q_t(\text{CH}_3\text{·COCl, liq.})$. Part of the reason for this discrepancy lies in our use in this paper of the $Q_t(\text{CH}_3\text{·CO}_2\text{H, aq.})$ values recently recommended by the Bureau of Standards, Washington, but the main point of difference rests in an incorrect assumption by Carson and Skinner of a negligible heat of mixing of the aqueous hydrochloric and acetic acids in their experiments. We have since recalculated $Q_t(\text{CH}_3\text{·COCl, liq.})$ from the earlier data, making due allowance for the small mixing terms, and obtain $Q_t(\text{CH}_3\text{·COCl, liq.}) = 66.0 \pm 0.20$ kcals. mole⁻¹. The agreement between the two sets of experimental data is thus seen to lie within the experimental error (*ca.* ± 0.2 kcal.) of the two investigations.

DISCUSSION.

The results of the present investigation are summarised in the Q_f values listed below :

	Q_f (liq.) (kcal. mole ⁻¹).	Q_f (gas) (kcal. mole ⁻¹).	ΔQ_f .
CH ₃ ·COCl	66.2	59.4	} +2.7
CH ₂ Cl·COCl	70.1	62.1	
CHCl ₂ ·COCl	68.7	60.7	} -1.4
CCl ₃ ·COCl	68.8	60.5	

The Q_f (gas) values are subject to some uncertainty, as data are not available for the heats of vaporisation (λ_{vap}) of the chloroacetyl halides. We have estimated the λ_{vap} values by Trouton's rule, assuming the same value for Trouton's constant as obtains in acetyl chloride (Mathews and Fehlandt, *J. Amer. Chem. Soc.*, 1931, **53**, 3212), viz., λ_{vap} . (CH₃·COCl) = 6.8 kcal. mole⁻¹.

The interesting feature of the above results lies in the *smallness* of the changes in Q_f arising from the successive replacement of each hydrogen atom in CH₃·COCl by chlorine atoms, and in the observed *fall* in Q_f in passing along the series CH₂Cl·COCl → CHCl₂·COCl → CCl₃·COCl (ΔQ_f values are negative). The increase in Q_f (CH₂Cl·COCl) relative to Q_f (CH₃·COCl) might be expected from analogy with other examples of chlorine substitution for which thermal data are available : e.g.,

	Q_f (kcal.).	ΔQ_f .		Q_f (kcal.).	ΔQ_f .
{ CH ₃ ·CH ₃	20.2	+4.9	{ CH ₃ ·CO ₂ H (liq.)	116.4	+3.2
{ CH ₃ ·CH ₂ Cl	25.1		{ CH ₂ Cl·CO ₂ H (liq.)	119.6	
{ CH ₃ ·CH ₂ Cl	25.1	+6.1	{ CH ₄	17.9	+1.7
{ CH ₂ Cl·CH ₂ Cl	31.2		{ CH ₃ Cl	19.6	
{ CH ₃ ·CH ₂ ·OH	56.2	+3.9			
{ CH ₂ Cl·CH ₂ ·OH	60.1				

On the other hand, the negative values of ΔQ_f in passing from CH₂Cl·COCl to CHCl₂·COCl, and from CHCl₂·COCl to CCl₃·COCl, are perhaps surprising. In the case of, e.g., the chloroacetic acids, the ΔQ_f (liq.) values, although small, remain positive :

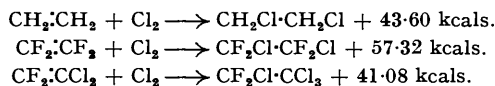
CH ₃ ·CO ₂ H (liq.)	116.4	} +3.2
CH ₂ Cl·CO ₂ H (liq.)	119.6	
CHCl ₂ ·CO ₂ H (liq.)	120.2	} +1.2
CCl ₃ ·CO ₂ H (liq.)	121.4	

but it may be that a genuine negative trend in ΔQ_f is masked by using the Q_f (liq.) values in place of Q_f (gas). At present, the negative ΔQ_f 's of the chloroacetyl chlorides are unique among the rather scanty thermochemical data on chloro-substituted compounds. It should be borne in mind, however, that the Q_f values of the chloroacetyl chlorides depend on the values we have accepted for the heats of formation of the chloroacetic acids.

There is some independent evidence that the substitution of a second and a third chlorine atom into a methyl group leads to a smaller increment in Q_f than that brought about the substitution of the first chlorine atom : e.g.,

CH ₃ ·CH ₃	20.2	} +4.9
CH ₃ ·CH ₂ Cl	25.1	
CH ₃ ·CHCl ₂	29.0	} +3.9

Recently, Lacher, McKinley, Walden, Lea, and Park (*J. Amer. Chem. Soc.*, 1949, **71**, 1334) have given values for the heats of chlorination of a number of fluoro- and fluoro-chloro-substituted ethylenes, including :



The data suggest that the C-Cl bonds in the groupings -CF₂-Cl, -CH₂-Cl, and -CCl₂-Cl are not equal in strength, but vary in the order -CF₂-Cl > -CH₂-Cl > -CCl₂-Cl. This is compatible with (but not proof of) decreasing ΔQ_f with increasing chlorine substitution on the same carbon atom.

Relatively little is known of the heats of formation of the chloro-acetaldehydes, which form an analogous group of compounds to the chloroacetyl chlorides. The increment in Q_f in passing from $\text{CH}_3\cdot\text{CHO}$ to $\text{CCl}_3\cdot\text{CHO}$, is, however, quite small ($\Delta Q_f = 3.3$ kcals.). The corresponding increment in the series of acetyl chlorides, *viz.*, 1.1 kcals., is smaller still, which might suggest that the replacement of $-\text{CHO}$ by $-\text{CClO}$ gives rise to a more powerful steric repulsion between the relatively bulky chlorine atoms of the groups CCl_3 and CClO , than exists between the groups CCl_3 and CHO . It would be useful to have further data, particularly on the bromo-acetyl halides, which should reveal steric repulsion effects in a more pronounced manner, if they indeed represent an important factor.

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