224. *The Heat of Hydrolysis of Acetyl Fluoride.*

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The heat of reaction of liquid acetyl fluoride with dilute sodium hydroxide was measured as 43·24 kcals.mole^{-1}, which leads to a value for the heat of formation at room temperature of 110·65 kcals.mole^{-1}.

IN a previous paper, Carson and Skinner (*J.*, 1949, 936) reported a preliminary value for the heat of hydrolysis of acetyl fluoride, but made no claim for high accuracy of their value, as the samples of acetyl fluoride used contained acetyl chloride, and rather large corrections were necessary in order to allow for its thermal effects. We have repeated these experiments, using pure acetyl fluoride, and now record more reliable values for the heat of hydrolysis and heat of formation of this substance.

EXPERIMENTAL.

Preparation of Acetyl Fluoride.—Acetyl fluoride was prepared by reaction of sodium hydrogen difluoride with acetyl chloride in acetic anhydride (Calloway, *J. Amer. Chem. Soc.*, 1937, **59**, 1476). A yield of *ca.* 30 g. of acetyl fluoride was obtained from 25 g. of acetyl chloride : this exceeds the theoretical yield, and, as pointed out by Calloway, indicates that the acetic anhydride itself takes part in the reaction. The crude product was distilled 3 times off freshly prepared antimony trifluoride, and was then free from acetyl chloride. It was further treated with anhydrous potassium fluoride to remove traces of hydrogen fluoride, and finally purified by fractional distillation. The pure product was stored in 1-g. batches in sealed glass ampoules.

Heat of Reaction with Sodium Hydroxide Solution.—The heat of reaction of acetyl fluoride with sodium hydroxide solution was measured in the calorimeter described by Pritchard and Skinner (*J.*, 1950, 272). The experiments were carried out at 16°, by breaking the acetyl fluoride ampoules into a large excess (750 c.c.) of 0·2N-sodium hydroxide, and following the temperature change by observing the change in resistance of a thermistor element. The results are summarised in the table. Initial and final values of the thermistor resistance are given under R_i and R_f, respectively, and the observed heats of reaction under $Q_{\text{obs.}}$ (1 kcal.mole^{-1} $\equiv$ 4183·3 int. joules per mole). Derived heats of the purely aqueous hydrolysis

Heat of hydrolysis of acetyl fluoride.

Expt.	$CH_3 \cdot COF$ (g.).	R_i (ohms).	R_f (ohms).	$Q_{\text{obs.}}$ (kcal.).	$Q_{\text{aq.}}$ (kcal.).	$Q_f(CH_3 \cdot COF$, liq.) (kcals.)
1	1·1987	2059·7	1974·8	43·21	13·39	110·68
2	1·2548	2047·7	1959·3	43·28	13·46	110·61
3	1·0725	2040·2	1964·8	43·20	13·38	110·69
4	1·0120	1906·8	1840·2	43·26	13·44	110·63
			Mean	43·24	13·42	110·65

$$CH_3 \cdot COF(\text{liq.}) + H_2O(\text{liq.}) \longrightarrow CH_3 \cdot CO_2H(1000) + HF(1000)$$

are listed under $Q_{\text{aq.}}$, and calculated values of the heat of formation are given in the final column. The latter are based on assumed values for the heats of formation of aqueous solutions of sodium hydroxide and fluoride, given by Bichowsky and Rossini ("Thermochemistry of Chemical Substances," Reinhold, 1936), and on heat of formation data for acetic acid solutions given in the Tables of Selected Values of Thermodynamic Properties (Bureau of Standards, Washington, 1948—1949). The final value for $Q_f(CH_3 \cdot COF,\text{liq.}) = 110\cdot65$ kcals.mole^{-1} agrees well with the preliminary value given by Carson and Skinner, *viz.*, 110·6 kcals.; the limits of error (excluding possible errors in the assumed thermochemical data) we would estimate at less than $\pm\frac{1}{4}$ kcal.mole^{-1}. Combining the value for $Q_f(CH_3 \cdot COF,\text{liq.})$ with the latent heat of vaporization ($\lambda_{\text{vap.}} = 6\cdot2$ kcals.; Selected Values of Chemical Thermodynamic Properties, Table 23—18 : Series II), one obtains $Q_f(CH_3 \cdot COF,\text{gas}) = 104\cdot4$ kcals.mole^{-1}. This corresponds to a heat of dissociation of the acetyl–F bond (cf. Carson and Skinner, *loc. cit.*) of $D(CH_3 \cdot CO–F) = 93\cdot1 + \frac{1}{2}D(F_2)$ kcals., where $D(F_2)$ is the dissociation energy of molecular fluorine.

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