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THE HEATS OF DISSOCIATION OF
ACETOACETIC ETHYL ESTER AND
OF NITROMETHANE

BY

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In the study of the kinetics of prototropic rearrangement it was of interest to know the heat of dissociation of the prototropic substance. In this paper the heats of dissociation of acetoacetic ester and of nitromethane in dilute aqueous solution were determined.

If the heat of dissociation of the acid HA in aqueous solution is denoted by $U_{\text{HA}, \text{H}_2\text{O}}$, and, similarly, the heats of neutralization of HA and of the oxonium ion by $U_{\text{HA}, \text{OH}^-}$ and $U_{\text{H}_3\text{O}^+, \text{OH}^-}$, the following relation holds

$$U_{\text{HA}, \text{H}_2\text{O}} = U_{\text{HA}, \text{OH}^-} - U_{\text{H}_3\text{O}^+, \text{OH}^-}. \quad (1)$$

$U_{\text{H}_3\text{O}^+, \text{OH}^-}$ has been determined with great accuracy by RICHARDS and ROWE¹. They find at 20° and infinite dilution $U_{\text{H}_3\text{O}^+, \text{OH}^-} = 13.65 \text{ kcal}_{20^\circ}$.

In this paper the ratio $U_{\text{HA}, \text{OH}^-}/U_{\text{H}_3\text{O}^+, \text{OH}^-}$ has been determined by calorimetric measurements, HA being the two weak acids acetoacetic ethyl ester and nitromethane. From this ratio it is easy to calculate the heat of dissociation of the acids by means of equation (1) and the above value for $U_{\text{H}_3\text{O}^+, \text{OH}^-}$.

The acetoacetic ester was purified through the sodium bisulphite compound as described by ELION². A deter-

¹ RICHARDS and ROWE, J. Amer. Chem. Soc. 44 (1922) 684.

² ELION, Rec. trav. chim. Pays-Bas 3 (1884) 246.

mination of the sodium hydroxide used for hydrolysis of the purified preparation gave 100.1% of the calculated. The nitromethane was purified by several distillations. Its boiling point was 100.7°—100.9°.

The measurements consisted in a determination of the temperature increase by adding 100 cc. solution containing about 0.5 moles of sodium hydroxide to 2040 cc. solution containing about 0.2 moles of hydrochloric acid, acetoacetic ester or nitromethane. In order to find the rise in temperature due to the neutralization, that caused by the dilution of the sodium hydroxide solution must be subtracted. For each series of measurements a blank experiment was carried out. In this the sodium hydroxide solution was added to 2040 cc. of water. The (negative) rise in temperature in the blank experiment was subtracted in the experiments with acid. A small content of carbonate in the sodium hydroxide solution is without importance, the solution being strongly alkaline (about 0.15 n NaOH) after the reaction. An impurity of carbon dioxide in the acid solution may effect the rise of temperature, but the error cancels out, because the blank experiment, which was always done with water from the same bottle as used for the acid solution, has the same error.

Before the reaction the acetoacetic ester and the nitromethane are practically completely undissociated. After this they are almost completely dissociated. From the dissociation constants at 25° of water¹ $10^{-13.98}$, of acetoacetic ester² $2 \cdot 10^{-11}$ and of nitromethane³ $0,7 \cdot 10^{-11}$ it is calcu-

¹ BJERRUM and UNMACK, Kgl. Danske Vid. Selsk. Math.-fys. Medd. 5 (1929) No. 1.

² GOLDSCHMIDT and OSLAN, Ber. Deutschen Chem. Ges. 33 (1900) 1146.

³ HANTZSCH and LEY, Ber. Deutschen Chem. Ges. 39 (1906) 3152.

lated that $\frac{1}{3}$ % of the acetoacetic ester and 1 % of the nitromethane is undissociated in the 0.15 n NaOH.

The experiments were carried out in a copper calorimeter. All metallic parts which touched the solution were gilt. The calorimeter was placed inside a brass vessel, and thus quite surrounded by an air jacket. The brass vessel stood in a water bath at room temperature. Before an experiment 2040 cc. acid solution were poured into the calorimeter. 100 cc. sodium hydroxide solution were pipetted out into a thin-walled glass flask of the shape shown in the Figure. The flask was immersed in the acid solution up to the lower part of the neck, which went up through a hole in the cover of the calorimeter. The flask was held at the top by means of a clamp, and closed by a rubber stopper. Before the experiment the loaded calorimeter was left sufficiently long time for the attainment of temperature equilibrium between the two solutions. During the last 10 minutes before the mixing of the solutions took place, the temperature of the acid solution was read off on a BECKMANN thermometer. The mixing was performed by putting a glass rod down into the thin-walled flask which was broken by a light blow on the top of the rod. After this the temperature was again read off every minute until the rate of change had been constant for some time. In the experiments with acetoacetic ester and, to a smaller degree, in those with nitromethane there was found a constant increase of temperature in the period after the neutralization. In the case of acetoacetic ester this was undoubtedly caused by a slow hydrolysis of the ester. The



Table 1.

100 cc. of sodium hydroxide solution (0.524 moles) + 2040 cc. of acetoacetic ester solution (0.1820 moles). The time is given in minutes calculated from the moment of mixing:

Time	Temp.	Time	Temp.	Time	Temp.	Time	Temp.
— 10	1.383	— 5	1.378	0	(1.933)	6	1.975
— 9	1.381	— 4	1.377	1	1.940	7	1.982
— 8	1.381	— 3	1.376	2	1.947	8	1.989
— 7	1.380	— 2	1.376	3	1.952	9	1.998
— 6	1.379	— 1	1.374	4	1.959	10	2.005
		0	(1.373)	5	1.968		

Temperature increase.....	0.560°
Correction for the dilution of the sodium hydroxide ...	+ 0.047°
Correction for incomplete dissociation ($1/3$ %/o).....	+ 0.002°
Temperature increase (corrected).....	0.609°
Temperature increase per mole acid	3.346°

rise in temperature due to the mixing of the solutions was found by simple linear extrapolation of the readings before the mixing and of those after the mixing where the rate of change was constant. The result of an experiment with acetoacetic ester is given in Table 1.

The object was only to determine the ratio between the heat evolved in the different experiments and it was therefore unnecessary to know the accurate absolute value of the units on the BECKMANN thermometer. The readings were only corrected for relative errors in the calibration of the thermometer capillary, which were determined by comparing the length of a short separated mercury column at different parts of the thermometer scale. It is assumed that the heat capacity of the loaded calorimeter is with sufficient approximation the same in all the experiments. This is probably permissible because the sodium hydroxide solution was always the same, and there was always used

the same volume of the diluted acid solution containing 0.2 moles of one of the three acids. All the glass flasks used had approximately the same weight. The ratio between the temperature increases found in the different experiments is a direct measure of the ratio between the heats evolved.

The temperature increase in each experiment was first corrected for the heat of dilution of the sodium hydroxide solution by subtraction of the result of the blank experiment. Finally, it was corrected for incomplete dissociation by adding $\frac{1}{3}\%$ in the acetoacetic ester experiments and 1% in the nitromethane experiments. The increase per mole acid was found by dividing with the number of moles of the acid used in the experiment. The results are compiled in Table 2. The temperature after the mixing was not the same in all the experiments. According to RICHARDS and ROWE¹ the temperature coefficient of the heat of neutralization of the oxonium ion is -0.0544 kcal per degree or -0.40% per degree. By means of this value the results of the 5 hydrochloric acid experiments were recalculated to the temperature 20.5° , which is the mean of the temperatures after the mixing in the acetoacetic ester and nitromethane experiments. The values given in the last column of Table 2 agree well among themselves.

The mean values of the molar temperature increases found are

for hydrochloric acid (20.5°)	6.261°
for acetoacetic ester (20.4°)	3.340°
and for nitromethane (20.6°)	3.383°

Consequently the ratio of the heats of neutralization of the oxonium ion, acetoacetic ester and nitromethane is

¹ RICHARDS and ROWE, loc. cit.

Table 2.

Moles of acid	Temp. after mixing. °C.	Temp. rise, uncorr.	Corr. for dilution of NaOH	Corr. for incomplete diss.	Temp. rise, corr.	Molar temp. rise	Molar temp. rise, 20.5°
Hydrochloric acid							
0.2020	21.3	1.220	0.039	..	1.259	6.232	6.252
0.2020	20.8	1.219	0.041	..	1.260	6.237	6.245
0.2018	21.2	1.210	0.046	..	1.256	6.223	6.243
0.2018	20.8	1.220	0.047	..	1.267	6.278	6.286
0.2018	20.6	1.220	0.047	..	1.267	6.278	6.281
Acetoacetic ester							
0.2000	20.8	0.618	0.046	0.002	0.666	3.333	..
0.1820	20.0	0.560	0.047	0.002	0.609	3.346	..
Nitromethane							
0.1950	20.7	0.612	0.039	0.007	0.658	3.374	..
0.1984	20.4	0.625	0.041	0.007	0.673	3.392	..

1:0.5335:0.5403. If we assume that the ratio is the same at 20° and infinite dilution we get from equation (1) and RICHARDS and ROWE's value of the heat of neutralization of the oxonium ion 13.65 kcal_{20°} the following values of the heats of dissociation at 20° and infinite dilution

for acetoacetic ester — 6.37 kcal_{20°}
 and for nitromethane — 6.28 kcal_{20°}

In conclusion I wish to thank Professor BJERRUM for his kind interest in my work.

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 and Agricultural College. Copenhagen.*

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