

The Acidities of Carboxylic and Sulfonic Acid Amides and Hydrazides

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While investigating the *N*-sulfenylation of hydrazides¹ we encountered anomalies that aroused our interest in the acidities of simple amides and hydrazides. The relevant pK_a values were partly found in the literature²⁻⁶ and partly determined by us.

Inspection of Table 1 reveals the expected trend in the acidities of the proton-

methanesulfonic hydrazide, the synthesis of which will be described in a forthcoming paper.¹

Approximately 0.001 mole of the amide or hydrazide was dissolved in 10 ml water and the pH of the solution was determined after each addition of a measured quantity of either 0.0965 N NaOH or 0.1026 N HCl. Glass electrodes were employed, a calomel electrode serving as reference. The mixed acidity constants pk_a^* were converted to the thermodynamic acidity constants pK_a by means of the Debye-Hückel equation, $pk_a^* = pK_a + (z_a - 0.5) \sqrt{\mu} / (1 + \sqrt{\mu})$, where z_a is the electric charge of the acid and μ the ionic strength of the solution.

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Table 1.

Amides			
Compound	Temp. (°C)	pK_a (Ref.)	
CH ₃ CONH ₂	25	15.1 (2)	
C ₆ H ₅ CONH ₂	25	14–15 (2)	
CH ₃ SO ₂ NH ₂	25	10.80 (3)	
CH ₂ ClSO ₂ NH ₂	22.5 ± 0.5	9.26 (this work)	
C ₆ H ₅ SO ₂ NH ₂	25	10.11 (3)	
Hydrazides			
Compound	Temp. (°C)	pK_{a1} (Ref.)	pK_{a2} (Ref.)
CH ₃ CONHNH ₃ ⁺	24 ± 1	3.24 (4)	12.6 ^a (this work)
C ₆ H ₅ CONHNH ₃ ⁺	25.0	3.27 (5)	12.53 (5)
	24 ± 1	2.97 (6)	12.28 ^a (this work)
CH ₃ SO ₂ NHNH ₃ ⁺	22.5 ± 0.5	1.67 (this work)	11.46 (this work)
CH ₂ ClSO ₂ NHNH ₃ ⁺	22.5 ± 0.5	not determined	9.70 (this work)
C ₆ H ₅ SO ₂ NHNH ₃ ⁺	22.5 ± 0.5	1.44 (this work)	11.00 (this work)

^a Measured at 22.5 ± 0.5°C.

ated hydrazides, but at the same time one is struck by the fact that whereas acetamide and benzamide are weaker acids than acethydrazide and benzhydrazide, respectively, the reverse holds for the amides and hydrazides of methane-, chloromethane-, and benzenesulfonic acids. So far, no simple explanation for this has occurred to us.

As we do not intend to pursue this matter we are presenting our data without additional comments.

The compounds employed were known from the literature except for chloro-

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