

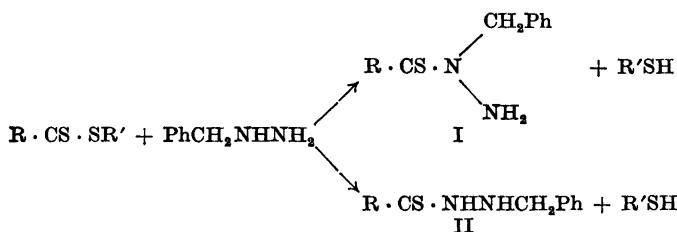
Reactions between Benzylhydrazine and Dithioesters

BJÖRN FORSGREN and JAN SANDSTRÖM

Department of Organic Chemistry, University of Lund, Lund, Sweden

The formation of pairs of isomeric thiohydrazides in reactions between benzylhydrazine and four different dithiocarboxylic esters has been investigated. The neutral isomers give thiohydrazones, and the acidic isomers thiadiazolines, in reactions with benzaldehyde. pK_a -values for the acidic thiohydrazides in aqueous ethanol are given. Separation of pairs of isomers by paper chromatography is described.

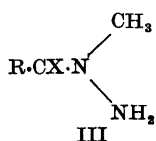
In the course of a current investigation of heterocyclic compounds derived from thiocarbohydrazide, it was considered desirable to prepare methyl 2-benzylthiocarbamate (Ia). The reaction between benzylhydrazine and dimethyl trithiocarbonate was expected to provide a suitable route. However, the reaction product was found to consist of a mixture of only 20 % of the desired compound and 80 % of the 3-isomer (IIa).



a, R=CH₂S; b, R=Ph; c, R=CH₂O; d, R=PhCH₂O.

This result at first seemed somewhat surprising, since monosubstituted aliphatic hydrazines, and also benzylhydrazine, react with cyanic acid^{1,2} and thiocyanic acid^{3,4} and with their *isoesters*^{2,5} as if the —NH—group were more nucleophilic than the NH₂-group, *i.e.* the products are 2-substituted semicarbazides and thiosemicarbazides. As has been pointed out by Greer and Smith⁶, this is explained by the electron-donating properties of the alkyl group.

On the other hand, arylhydrazines give 1-arylsemicarbazides and 1-arylthiosemicarbazides⁷ as stable products. This is explained by the interaction between the aromatic nucleus and the —NH-group, which makes the latter less nucleophilic than the NH₂-group. The same effects are taken into account to explain why methylamine is more basic and aniline less basic than ammonia⁸. The same difference in orientation is found when methylhydrazine and phenylhydrazine react with carboxylic acid chlorides⁹ and with dithioesters such as carboxymethyl dithiobenzoate^{10,11} and alkyl trithiocarbonates^{12,13}. With methylhydrazine, 1-methyl-1-acyl(thioacyl)-hydrazines (III), and with phenylhydrazine, 1-phenyl-2-acyl(thioacyl)-hydrazines (IV) are formed.



a, X=S; b, X=O



IV

a, X=S b, X=O

R₁=Ph R₁=CH₃

However, there is evidence for the operation of a steric effect in the reactions between methylhydrazine and carboxylic esters. Von Brüning¹⁴ has shown, that methylhydrazine and diethyl oxalate react readily to give 1,1'-oxalyl-bis-2,2'-methylhydrazine, (CO·NHNHCH₃)₂ (V).

In a recent investigation, Hinman and Fulton¹⁵ have shown, that methyl acetate, propionate, isobutyrate, and benzoate, react with methylhydrazine to give mixtures of 1-acylated (IIIb), and 2-acylated (IVb) methylhydrazine, where the latter isomer predominated. With the aliphatic esters both the yield of (IIIb) and the reaction rate fell off with increasing size of the acyl group. On the other hand, reactions between methylhydrazine and carboxylic acid anhydrides gave high yields of the 1-acyl-methylhydrazines (IIIb).

It seems as if dithioesters should occupy a position intermediate between, on the one hand carboxylic esters, and on the other hand cyanic acid and thiocyanic acid and their derivatives, with regard to sensitivity to steric effects in reactions with aliphatic hydrazines. Therefore, it was considered desirable to investigate the reactions of benzylhydrazine with a selection of dithioesters. Carboxymethyl dithiobenzoate, O,S-dimethyl xanthate, O-benzyl-S-carboxymethyl xanthate, and carboxymethyl dithiocarbamate were chosen, together with dimethyl trithiocarbonate. The carboxymethyl dithiocarbamate did not give definable products with benzylhydrazine, but the other esters reacted rapidly and gave mixtures of the possible isomers (I) and (II). The yields and ultra-violet absorption data are recorded in Table 1.

For separation of the isomers the reaction mixtures were dissolved in ether, and the solutions were extracted with a quantity of N NaOH equivalent to the total amount of thiohydrazide present. With the dithiocarbamate and thiobenzhydrazide mixtures one extraction was enough to transfer practically all of the acidic isomer (II) into the alkaline solution, but when the thioncarbazate mixtures were so treated, appreciable quantities of the acid forms

Table 1. Yields and ultraviolet absorption data for the compounds I and II.

Starting material	Yield %	$\lambda_{\max} \text{ m}\mu$	ϵ_{\max}
$\text{CH}_3\text{S} \cdot \text{CS} \cdot \text{SCH}_3$	Ia: 20	255	10 300
		276	11 100
	IIa: 74	277	10 800
		288	11 200
$\text{Ph} \cdot \text{CS} \cdot \text{SCH}_2\text{CO}_2\text{H}$	Ib: 23	245	12 400
		298	6 500
	IIb: 72	—	—
		250	12 000
$\text{CH}_3\text{O} \cdot \text{CS} \cdot \text{SCH}_3$	Ic: 25	—	—
		250	12 000
	IIc: 70	252	15 000
		252	11 600
$\text{PhCH}_2\text{O} \cdot \text{CS} \cdot \text{SCH}_2\text{CO}_2\text{H}$	Id: 76	252	15 000
		252	11 600
	IId: 22	—	—
		—	—

All spectra were taken in absolute ethanol, c , 5×10^{-5} , with a Beckman DU spectrophotometer.

(IIc) and (IId) remained in the ether solution after the first extraction. The progress of the extraction could be followed by paper chromatographic examination of the ether solution after each extraction. For this purpose ordinary paper chromatography with water as the stationary phase was found unsuitable. In the solvents used by Hinman¹⁶ these hydrazides travelled with the solvent front, and the same result was obtained with chloroform saturated with water, a system used with success by Kjær and Rubinstein¹⁷ for substituted thioureas and thiosemicarbazides. Instead, the system developed by Wickberg¹⁸, with dimethyl sulphoxide as the stationary phase and ethers or aliphatic hydrocarbons as the mobile phase, was found very useful. In all the four isomer mixtures obtained in this investigation the acidic isomer travelled slower than the neutral one, which is to be expected, since dimethyl sulphoxide has weakly basic properties¹⁹.

By this method it could be shown that methyl 3-benzylthioncarbazate (IIc) was extracted by two successive extractions with N NaOH beyond the limit of detection in the ether solution, but that the benzyl analogue (IId) could still be detected after six successive extractions. The partition of an acid between ether and aqueous alkali is governed by the partition coefficient, C , of the undissociated acid between ether and water, by the dissociation constant of the acid, and by the activities of the hydrogen ions and the anions of the acid in the aqueous phase. The partition observed, $P = \frac{[\text{HA}]_{\text{ether}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}}$

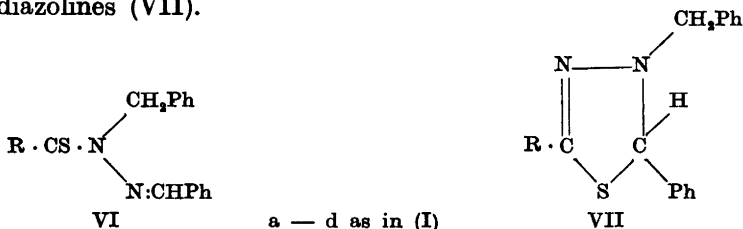
can be expressed in the above quantities by inserting $\frac{K_a \times [\text{HA}]_{\text{aq}}}{a_{\text{H}^+} \times f_{\text{A}^-}}$ for $[\text{A}^-]_{\text{aq}}$

and C for $\frac{[\text{HA}]_{\text{ether}}}{[\text{HA}]_{\text{aq}}}$. In this way we obtain $P = \frac{C \times a_{\text{H}^+} \times f_{\text{A}^-}}{a_{\text{H}^+} \times f_{\text{A}^-} + K_a}$

The values of the dissociation constants, K_a (Table 2) were determined by electrometric titration with a glass electrode in 20 % and in 3 % aqueous ethanol (w/w). For reasons of solubility no determinations were made in pure water, but approximate values can easily be obtained by extrapolation. However, these can not be the same as in water saturated with ether. The coefficients of partition, C , of the acids between ether and pure water were determined

spectrophotometrically. This method could not be used in alkaline medium because of the rapid oxidation mentioned below. Instead, known quantities of the thioncarbazates were equilibrated between ether and aqueous NaOH, and P was determined by evaporating the ether solutions and weighing the dry residues. For a_{H^+} was inserted the expression $\frac{K_w}{([\text{OH}^-] - [\text{A}^-]) \times f_{\text{OH}^-}}$ where $[\text{OH}^-]$ is the concentration of hydroxyl ions in the aqueous phase before equilibration. The activity coefficients f_{A^-} and f_{OH^-} are not known with certainty, but their ratio should not differ much from unity. In solutions with $a_{H^+} < 10^{-12}$, the first term in the denominator of P can be neglected. The value of K_w is probably not the same in water as in water saturated with ether, but the ratio K_w/K_a should not be very much different in the two solvents. The values of C obtained from determinations of P with aqueous alkali were found to rise with pH. For the methyl thioncarbazate (IIc) the increase of C was moderate, but for the benzyl analogue (IId), which is much less soluble in water, the value of C rose steeply with pH (Table 2). This change of C with pH can be correlated with the diminishing mutual solubility of ether and water with increasing alkalinity²⁰. Much more clear-cut conditions can be expected by using organic solvents, which are practically insoluble in water, but with benzene and *isopropyl* ether the partition coefficient C has so high values that the extraction from these solvents becomes much more tedious than from ether. Instead, ethanol was added to the aqueous phase in order to increase the mutual solubility of ether and water and to reduce the partition coefficient, and thereby the extraction was considerably facilitated. When the N NaOH used for extraction was diluted with ethanol to about 30 % (v/v), only three successive portions were necessary for a complete extraction of the benzyl thioncarbazate (IId). From the expression for P and the values in Table 2 it is obvious that the extraction of the thiohydrazides (IIa) and (IIb) is favoured both by dissociation constants and by partition coefficients. The extraction of (IIc) is somewhat impeded by a low dissociation constant, and the extraction of (IId) is highly impeded by low dissociation constant and high partition coefficient.

Both types of thiohydrazides react with benzaldehyde. The neutral isomers (I) with free amino group give hydrazones (VI) and the acidic isomers (II) give thiadiazolines (VII).



The recording of the ultra-violet absorption spectra of the acidic isomers (II) is complicated by a reaction in very dilute solution with formation of benzaldehyde hydrazones:

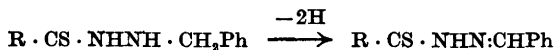


Table 2. pK_a -Values (thermodynamic) and partition coefficients (C) between ether and water for the thiohydrazides, $R-CS-NHNHCH_2Ph$.

R	pK_a			C	
	20 % ethanol	3 % ethanol (w/w)	water	0.1 N NaOH	0.5 N NaOH
CH_3S	7.66	7.56	35		
Ph	7.82	7.63	310		
CH_3O	9.38	9.24	260	330	800
$PhCH_2O$	9.26	9.16	2 400	17 000	39 000

The ether and water used for the partition experiments were saturated with respect to one another prior to measurements. Because of the uncertainties in K_a and K_w and the activity coefficients the values of C must be regarded as very approximate.

The oxidation products have been identified by paper chromatography and UV-spectrum. The change is particularly rapid in alkaline medium. The reaction can be illustrated by the spectra in Fig. 1.

The thiadiazoline (VIIb) is rather unstable and is oxidized by air to a compound $C_{21}H_{18}N_2OS$, probably the 2-hydroxy derivative of the thiadiazoline. Holmberg¹⁰ has found a similar facile oxidation of the 3-methyl analogue.

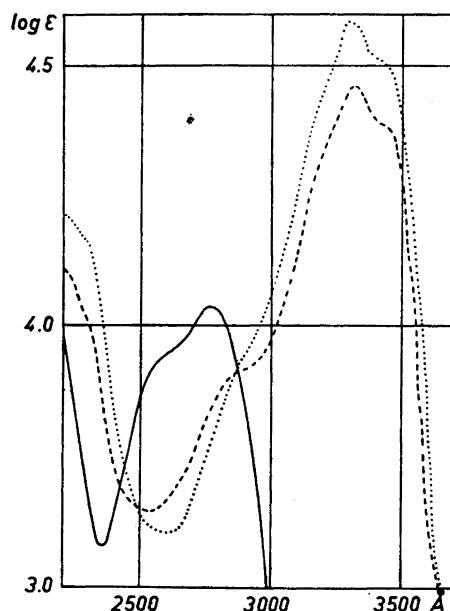


Fig. 1. Ultraviolet absorption curves of:

- $CH_3S-CS-NHNHCH_2Ph$, fresh 5×10^{-5} M solution in absolute ethanol.
- - - - - The same solution after two days.
- $CH_3S-CS-NHN:CHPh$ ²¹, 5×10^{-5} M solution in absolute ethanol.

The present investigation shows that different types of dithiocarboxylic esters react with benzylhydrazine to give mixtures of the two possible thiohydrazides. The discussion of a possible steric effect must await the results of an investigation of a wider selection of other closely related esters.

EXPERIMENTAL *

Benzylhydrazine and dimethyl trithiocarbonate. Dimethyl trithiocarbonate (2.8 g) was dissolved in a mixture of ethanol (25 ml) and ether (25 ml), and the solution was added to a solution of benzylhydrazine sulphate (4.6 g) in N NaOH (40 ml) and ethanol (50 ml). On the following day the crystals of sodium sulphate were removed by filtration, and the solvents were taken off *in vacuo*. The remaining oil was dissolved in ether (50 ml), and the solution was extracted with N NaOH (20 ml). The ethereal solution on evaporation gave a solid residue (0.7 g), which crystallized from a mixture of benzene and light petroleum (b.p. 40–60°) as colourless plates with m. p. 91–92°, consisting of *methyl 2-benzyl-dithiocarbazate* ** (Ia). (Found: C 51.0; H 5.70; N 13.0; S 30.0. Calc. for $C_9H_{11}N_2S_2$: C 50.9; H 5.70; N 13.2; S 30.2.)

Acidification of the alkaline extract from the crude reaction mixture gave a crystalline deposit (2.9 g), which crystallized from a mixture of benzene and light petroleum (40–60°) as colourless prisms, m. p. 58–59°, of *methyl 3-benzyl-dithiocarbazate* (IIa). (Found: C 50.8; H 5.64; N 13.1; S 30.1. Calc. for $C_9H_{11}N_2S_2$: C 50.9; H 5.70; N 13.2; S 30.2.)

The benzaldehyde hydrazones (VI) and the thiadiazolines (VII) were prepared by reacting the appropriate thiohydrazides with the calculated amount of benzaldehyde in ethanol with a catalytic amount of hydrochloric acid. When necessary, the products were precipitated by the addition of water and purified by recrystallization.

Methyl 2-benzyl-3-benzylidene-dithiocarbazate (VIa) crystallized from ethanol as colourless needles, m. p. 134–135°. (Found: C 63.9; H 5.47; N 9.37; S 21.4. Calc. for $C_{16}H_{16}N_2S_2$: C 64.0; H 5.37; N 9.33; S 21.3.)

2-Phenyl-3-benzyl-5-methylthio-1,3,4-thiadiazoline (VIIa) was too unstable to be recrystallized, but according to analysis the crude product, m. p. 60–62°, was fairly pure. (Found: C 64.2; H 5.47; N 9.27; S 21.2. Calc. for $C_{16}H_{16}N_2S_2$: C 64.0; H 5.37; N 9.33; S 21.3.)

Benzylhydrazine and carboxymethyl dithiobenzoate. Carboxymethyl dithiobenzoate ** (2.1 g) in N NaOH (10 ml) was added to a solution of benzylhydrazine sulphate (2.2 g) in N NaOH (20.2 ml). The red colour rapidly disappeared, and a crystalline product (2.4 g) was deposited. It was dissolved in ether (50 ml) and the solution was extracted with N NaOH (10 ml). The ethereal solution on evaporation gave a solid residue (0.56 g), which crystallized from a mixture of toluene and light petroleum (80–100°) as colourless plates of *1-benzylthiobenzhydrazide* *** (Ib), m. p. 92–93°. (Found: C 69.8; H 5.93; N 11.5; S 13.1. Calc. for $C_{14}H_{14}N_2S$: C 69.4; H 5.82; N 11.6; S 13.2.)

The acidic isomer, *2-benzylthiobenzhydrazide*, (IIb), separated as pale yellow needles (1.75 g) when the alkaline extract from the crude reaction product was acidified with acetic acid. It crystallized from toluene as pale yellow needles, m. p. 146–147°. (Found: C 69.8; H 5.78; N 11.4; S 13.1. Calc. for $C_{14}H_{14}N_2S$: C 69.4; H 5.82; N 11.6; S 13.2.)

The correctness of structure (Ib) for the neutral thiohydrazide was further demonstrated by its deamination with nitrous acid to N-benzyl-thiobenzamide. The thiohydrazide (Ib) (0.25 g) was dissolved in a mixture of ethanol (5 ml) and N HCl (2 ml), and a solution of sodium nitrite (0.2 g) in water (5 ml) was added. Gas was evolved and an oil was deposited, which solidified to a crystalline material (0.19 g). This crystallized from light petroleum (80–100°) as pale yellow needles of *N-benzylthiobenzamide*, m. p. 86–87°. (Found: N 6.11; S 14.1. Calc. for $C_{14}H_{13}NS$: N 6.16; S 14.1.)

* All melting points are uncorrected and taken in capillary tubes in an electrically heated block.

** Numbering according to Chemical Abstracts (see Subject Index, Carbazic acid).

*** Numbering according to Holmberg ¹⁰.

This compound was also prepared by reaction between benzylamine and the sodium salt of carboxymethyl dithiobenzoate and was found to be identical with the compound described above. Levi²² has described the preparation of N-benzylthiobenzamide by reaction between benzylamine and sulphur at 180°, and he reports m. p. 86°.

Benzaldehyde 1-benzylthiobenzhydrasone (VIb) crystallized from toluene-light petroleum (80–100°) as yellow, rhombic prisms, m. p. 116–117°. (Found: C 76.2; H 5.34; N 8.42; S 9.80. Calc. for C₂₁H₁₈N₂S: C 76.3; H 5.49; N 8.48; S 9.70.)

2,5-Diphenyl-3-benzyl-Δ⁴-1,3,4-thiadiazoline (VIIb) was too unstable to be recrystallized, but according to analysis the crude product, m. p. 65–67°, was fairly pure. (Found: C 76.4; H 5.38; N 8.48; S 9.82. Calc. for C₂₁H₁₈N₂S: C 76.3; H 5.49; N 8.48; S 9.70.)

The crude thiadiazoline (0.4 g) was dissolved in hot ethanol (8 ml). On cooling, pale yellow needles separated, m. p. 161–162°. (Found: C 72.7; H 5.30; N 7.97; S 9.10. Calc. for C₂₁H₁₈N₂OS: C 72.8; H 5.24; N 8.09; S 9.25.)

Benzylhydrazine and dimethyl xanthate. Dimethyl xanthate (6.2 g) in ethanol (150 ml) was added to a solution of benzylhydrazine sulphate (11 g) in 2 N NaOH (50 ml). On the following day the crystals of sodium sulphate were removed by filtration, and then the solvents were removed *in vacuo* at room temperature. The oily residue was dissolved in ether (50 ml), and the solution was extracted twice with N NaOH (each portion 50 ml). After the second extraction only one spot, corresponding to the neutral isomer, could be observed when the ethereal phase was examined with paper chromatography. The ethereal solution was evaporated and gave a non-crystallizing residue (2.5 g) of *methyl 2-benzylthioncarbazate* (Ic). It was not analyzed but only used for preparation of the benzylidene derivative (VIc).

The acidic isomer, *methyl 3-benzylthioncarbazate* (IIc), separated as a crystallizing oil, when the alkaline extract from the crude reaction mixture was acidified with acetic acid. The compound (6.9 g) crystallized from benzene-light petroleum (40–60°) as colourless rods, m. p. 45–46°. (Found: C 55.0; H 6.14; N 14.3; S 16.3. Calc. for C₉H₁₂N₂OS: C 55.1; H 6.16; N 14.3; S 16.3.)

Methyl 2-benzyl-3-benzylidene-thioncarbazate (VIc) crystallized from light petroleum (80–100°) as colourless prisms, m. p. 99–100°. (Found: C 67.5; H 5.77; N 9.74; S 11.2. Calc. for C₁₈H₁₆N₂OS: C 67.6; H 5.67; N 9.85; S 11.3.)

2-Phenyl-3-benzyl-5-methoxy-Δ⁴-1,3,4-thiadiazoline (VIIc) crystallized from ethanol as colourless rods, m. p. 63–66°. (Found: C 67.5; H 5.62; N 9.93; S 11.2. Calc. for C₁₈H₁₆N₂OS: C 67.6; H 5.67; N 9.85; S 11.3.)

Benzylhydrazine and O-benzyl-S-carboxymethyl xanthate. O-Benzyl-S-carboxymethyl xanthate²⁴ (6.0 g) was dissolved in N NaOH (25 ml) and added to a solution of benzylhydrazine sulphate (5.5 g) in N NaOH (50 ml). A non-crystallizing reaction product separated rapidly, and it was dissolved in ether (100 ml) and extracted three times with aqueous ethanolic NaOH (each portion 25 ml N NaOH and 10 ml of ethanol). Then the ether solution on paper chromatography showed only one spot, corresponding to the neutral isomer (Id). The ether solution was evaporated to dryness, and the crystalline residue (5.1 g) crystallized from ethanol as colourless rods of *benzyl 2-benzylthioncarbazate* (Id), m. p. 47–48°. (Found: C 66.0; H 5.97; N 10.4; S 11.8. Calc. for C₁₈H₁₆N₂OS: C 66.1; H 5.92; N 10.3; S 11.8.)

The acidic isomer, *benzyl 3-benzylthioncarbazate* (IIId), was obtained as a crystallizing oil, when the alkaline extract from the crude reaction mixture was acidified with acetic acid. The yield was increased when the ethanol was removed *in vacuo*. The product (1.5 g) crystallized from benzene-light petroleum (40–60°) at –30° as colourless rods, m. p. 51–52°. (Found: C 66.1; H 5.90; N 10.3; S 11.7. Calc. for C₁₈H₁₆N₂OS: C 66.1; H 5.92; N 10.3; S 11.8.)

Benzy 2-benzyl-3-benzylidene-thioncarbazate (VIId) crystallized from light petroleum (80–100°) as colourless rods, m. p. 92–93°. (Found: C 73.0; H 5.78; N 7.98; S 9.09. Calc. for C₂₂H₂₀N₂OS: C 73.3; H 5.59; N 7.77; S 8.89.)

2-Phenyl-3-benzyl-5-benzoyloxy-Δ⁴-1,3,4-thiadiazoline (VIIId) crystallized from ethanol as colourless rods, m. p. 96–98°. (Found: C 72.9; H 5.79; N 7.90; S 9.05. Calc. for C₂₂H₂₀N₂OS: C 73.3; H 5.59; N 7.77; S 8.89.)

Paper chromatography. The impregnation of the papers with dimethyl sulphoxide was performed as described by Wickberg¹⁸. Before use the papers were stored in a desiccator over dimethyl sulphoxide and silica for at least 24 h to attain equilibrium. Mixtures of di-*n*-butyl ether and *n*-heptane were used as the mobile phase, and generally the *R_F*-

values rose with increasing proportion of ether in the solvent. The ascending technique was used, and 20 cm length of paper was in most cases enough to obtain a satisfactory separation of the isomeric pairs (I) and (II). The spots could be made visible by spraying the papers with an aqueous solution 0.1 N in AgNO_3 and CuSO_4 and 2 N in ammonia. The neutral isomers gave grey spots and the acidic ones brown spots. A more general spray reagent is the iodine-azide reagent²⁵, but it gave less distinct spots. The different compounds could also conveniently be localized by photographing the papers in UV-light.

Dissociation constants. Titration graphs were recorded with a glass electrode, Radiometer 202 B, against a calomel electrode in saturated KCl, when 0.05 N NaOH in 20 % and 3 % (w/w) aqueous ethanol was added to 3×10^{-2} – 3×10^{-4} M solutions of the thiohydrazides (II) in aqueous ethanol of the same composition. Before use the glass electrode was stored over night in the appropriate aqueous ethanol, and then it was calibrated with a standard buffer in water. From 6–9 points around the value for half-neutralization the dissociation constants were calculated and corrected for the activity of the anion.

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