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Physicochemical Properties of 4-*tert*-Butylbenzoic Acid *N*',*N*'-Dialkylhydrazides

D. A. Pashkina, V. Yu. Gusev, and A. V. Radushev

Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, ul. Koroleva 3, Perm, 614013 Russia
e-mail: info@itch.perm.ru

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Abstract—Properties of hydrazides of 4-*tert*-butylbenzoic acid, important for their application in extraction technology, have been studied: solubility, acid-base properties, distribution between immiscible liquids, and hydrolytic stability. pH ranges of existence of different forms of the compounds have been determined. The *N',N'*-dialkyl derivatives with alkyl chains longer than C_6 are readily soluble in nonpolar solvents, are not transferred into aqueous phase, and are stable with respect to hydrolysis in acidic and basic media. Linear correlations of the studied physicochemical parameters with the compounds structure and the medium properties have been elucidated.

Keywords: hydrazide of 4-*tert*-butylbensoic acid, solubility, distribution coefficient, acid-base properties

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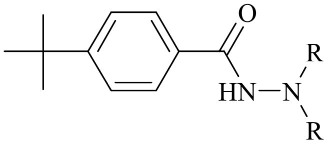
Extraction of Cu(II) compounds from their solution is an important stage of the solvent extraction–electrowinning method of copper production. In order to isolate copper from its ammoniacal media, two types of extracting agents are commonly used: oxyoximes and β-diketones [1]. Even though efficiency of the extraction with oxyoximes is sufficiently high, this class of extracting agents suffers from a serious drawback: they form a salt upon interaction with ammonia [2], which deteriorates the solution properties essential for further electrolysis stage. Hence, using of oxyoximes requires additional stage of copper production flowchart: the removal of the salt and regeneration of the extracting agent by washing the organic phase. In contrast to the oxyoximes, β-diketones do not react with ammonia, but their efficiency towards Cu(II) extraction is a lot lower. Similarly to β-diketones, the carboxylic acid *N*',*N*'-dialkylhydrazides are inert towards ammonia and are efficient extracting agents for Cu(II) [3, 4]. It has been shown that 4-*tert*-benzoic acid *N*',*N*'-dialkylhydrazides containing linear alkyl substituents are better extracting agents than β-diketones [5].

Besides a direct technological experiment, the potential of the extracting agents application may be estimated from their physicochemical properties, for instance, from solubility in various media, distribution between immiscible liquid phases, acid-basic properties, and stability with respect to hydrolysis. In this work we determined these properties of compounds **I–VII**.



R = H (**I**), CH_3 (**II**), *i*-C_4H_9 (**III**), C_4H_9 (**IV**), C_6H_{13} (**V**), C_8H_{17} (**VI**), $C_{10}H_{21}$ (**VII**).

Solubility. The studied compounds **I–VII** were white crystalline solids. Their solubility in the common laboratory solvents (water and ethanol) as well as in the widely used extraction media (isoamyl alcohol, hexane, kerosene, and *o*-xylene) was determined gravimetrically; the results are collected in Table 1.

As seen from Table 1 compound **I** was readily soluble in aliphatic alcohols, being poorly soluble in water or hydrocarbons. Its *N*',*N*'-dialkyl derivatives were practically insoluble in water. With increasing chain length of the alkyl substituents, the compounds solubility in hydrocarbons increased, being the highest in the case of compound **IV**. Further increase in the

Table 1. Solubility of compounds **I–VII** at 25±1ºC, g/L (mol/L)[a]

Comp. no.	Water	Ethanol	Isoamyl alcohol	*o*-Xylene	Hexane	Kerosene
I	1.0 (0.005)	263.6 (1.37)	52.0 (0.27)	8.6 (0.045)	0.2 (0.001)	–
II	0.85 (0.0039)	285.8 (1.29)	157.1 (0.71)	9.7 (0.044)	1.8 (0.008)	–
III	insoluble	142.2 (0.46)	182.4 (0.60)	116.2 (0.38)	6.4 (0.021)	8.5 (0.028)
IV	insoluble	475.2 (1.56)	410.4 (1.35)	230.0 (0.76)	13.7 (0.045)	16.2 (0.053)
V	insoluble	–	437.4 (1.21)	–	>930 (>2.23)	>1020 (>2.83)
VI	insoluble	–	–	–	>1000 (>2.40)	>1380 (>3.32)
VII	insoluble	–	–	–	>450 (>0.95)	>590 (>1.25)

[a] ("–") Not determined, "insoluble" the solubility is too low and cannot be determined with any available method.

alkyl chain length reduced the solubility due to enhanced intermolecular interactions. The presence of branched alkyl substituents (compound **III**) led to decrease in the solubility as compared with that of the derivative containing linear alkyl groups. Hence, the studied compounds with *n*-hexyl (or longer) alkyl substituents were readily soluble in hexane and kerosene, being promising for extraction applications.

Figure 1 displays solubility S of compound **IV** as a function of the Hildebrand parameter δ of the solvent (δ values were taken from [6]). The experimental data were well fitted with the linear equation: $\log S = 1.98\delta - 17.76$ ($r = 0.9918$). It is seen that the compound solubility increased with the growing Hildebrand parameter.

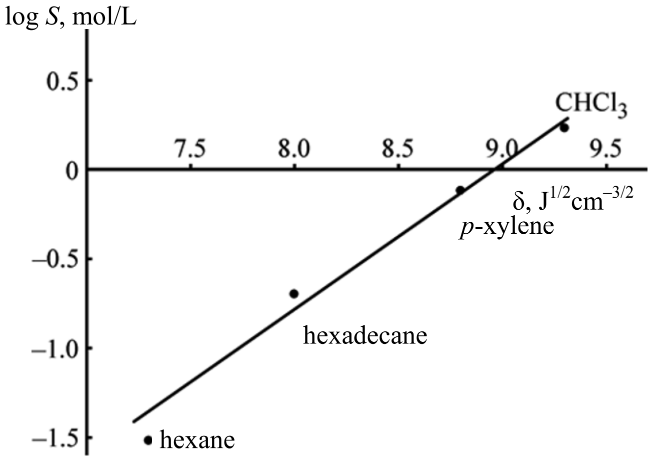


Fig. 1. Solubility of compound **IV** as a function of the Hildebrand parameter of the solvents.

Acid-base properties. The unsubstituted hydrazides and their *N*',*N*'-dialkyl derivatives are capable of proton attachment or elimination to form protonated and deprotonated forms, respectively. The acid-base equilibriums in their solutions are represented as follows: HL, the hydrazide neutral form; H_2L^+, the hydrazide protonated form; L^-, the hydrazide deprotonated form.

$$H_2L^+ \xrightleftharpoons{-H^+;\ pK_{a1}} HL \xrightleftharpoons{-H^+;\ pK_{a2}} L^-.$$

In this work we studied the hydrazides acid-base properties by means of spectrophotometry [7].

In order to determine the pH ranges of existence of different acid-base forms of the studied compounds and to calculate the corresponding acidity constants we analyzed the solutions absorbance as a function of pH and the Hammett constant. The measurements were carried out at wavelengths where the difference of different forms absorptivity was the highest. The medium acidity was altered by addition of HCl or KOH solutions. A representative example of the observed profiles is shown in Fig. 2 (compound **II**). From the plots in Fig. 2 it is seen that proton detachment from H_2L^+ occurred at pH of 2.5–4.5, whereas deprotonation of the neutral molecule HL took place at pH 13–14.5 (the latter value corresponded to 1.8 mol/L KOH). Hence, at pH < 2.5 compound **II** existed in the protonated form H_2L^+, the neutral form HL prevailed over pH range of 4.5–13, and the

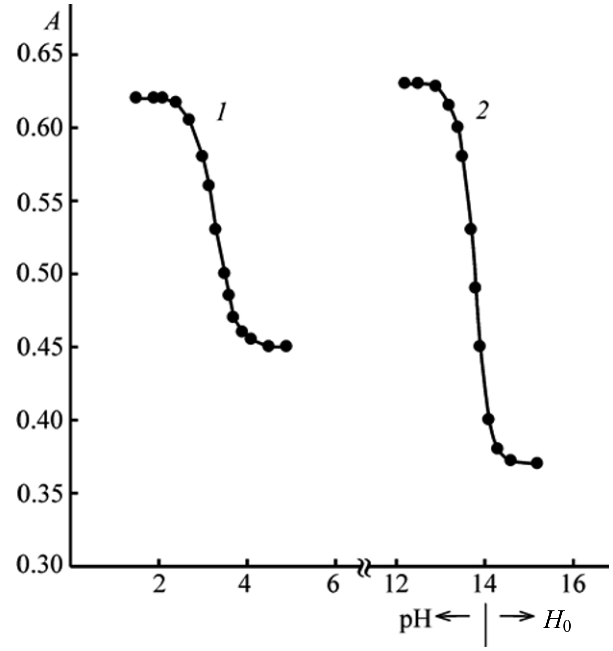


Fig. 2. Absorbance of solution of compound **II** as a function of pH and the Hammett acidity function (H_0). (*1*) $c_{\mathbf{II}} = 4 \times 10^{-5}$ mol/L, λ = 245 nm; (*2*) $c_{\mathbf{II}} = 1 \times 10^{-4}$ mol/L, λ = 237 nm. EtOH–H_2O (3 : 1), *l* = 1 cm.

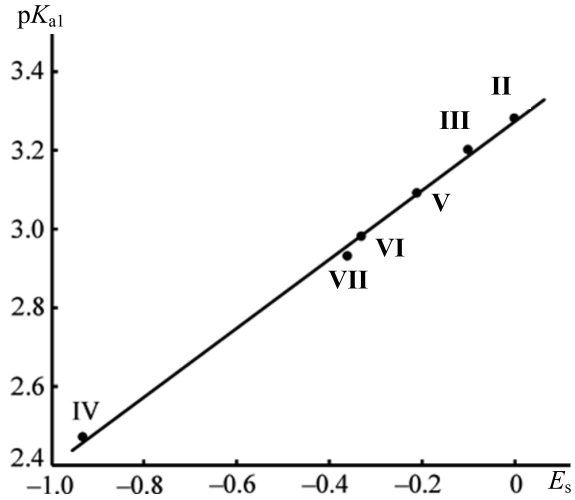


Fig. 3. pK_{a1} of compounds **II–VII** as a function of steric constant of the substituent.

deprotonated form L^- was found in the alkaline medium at $c_{KOH} > 1.8$ mol/L. The calculated acidity constants pK_{a1} and pK_{a2} are collected in Table 2.

From data in Table 2 it is seen that alkylation of the unsubstituted hydrazide **I** significantly decreased its acid (pK_{a2}) as well as basic (pK_{a1}) properties. In the **II–VII** series, the longer alkyl fragment led to weakened base properties due to steric hindrance towards proton attachment to the agent molecule. Figure 3 displays the compounds pK_{a1} value as a function of the alkyl substituent steric constant (E_s) (E_s were taken from [6]). The experimental data were well fitted with the linear equation: p$K_{a1} = 0.88E_s + 3.27$ ($r = 0.9985$).

The weakening of acid properties was due to +*I* effect of the alkyl substituents impeding the proton detachment from the substituted hydrazide molecule. Figure 4 shows the studied compounds pK_{a2} as a function of the Kabachnik constant σ_f (characterizing the +*I* effect of the substituent, the values of σ_f were taken from [6]). The experimental data were well fitted with the linear equation: p$K_{a2} = -1.30\sigma_f + 12.59$ ($r = 0.9986$).

Distribution between immiscible phases. A compound distribution between organic and aqueous phases is an important parameter for estimating the extracting agent possible application. In this work we used either *p*-xylene or hexane as the organic phase and solution of HCl (0.5 mol/L) or NH_3 (1 mol/L) in water as the aqueous phase to determine the distribution coefficients. The obtained results are collected in Table 3; it was found that the compounds distribution coefficients D_{HL} increased with the growing molecular mass *M*. The lower values of log D_{HL} in the case of aqueous HCl were due to formation of the hydrazides protonated form facilitating transfer of the hydrazide to the acidic aqueous phase. The

Table 2. pK_{a1} and pK_{a2} of compounds **I–VII** ($P = 0.95$, $n = 5$–9)

pK_a	**I**	**II**	**III**	**IV**	**V**	**VI**	**VI**
pK_{a1}	3.63±0.03	3.28±0.07	2.47±0.01	3.20±0.03	3.09±0.03	2.98±0.01	2.93±0.03
pK_{a2}	12.6±0.1	13.8±0.1	14.3±0.1	14.2±0.1	14.6±0.1	–	–

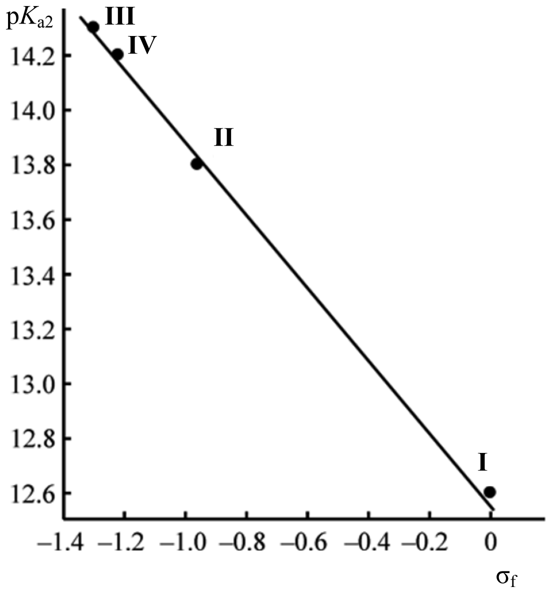


Fig. 4. pK_{a2} of compounds **I–IV** as a function of the Kabachnik constants.

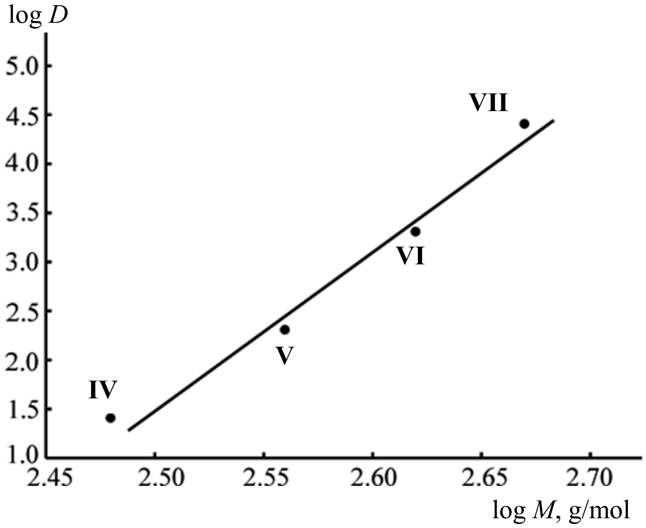


Fig. 5. Distribution coefficient of compounds **IV–VII** between *p*-xylene and aqueous hydrochloric acid solution as a function of the compound molecular mass.

amount of the com-pounds transferred to the aqueous ammonia phase was so immaterial that it could not be detected in certain cases.

Figure 5 displays log D_{HL} (*p*-xylene/aqueous HCl) of the *n*-alkyl derivatives as a function of log *M*. The experimental data were well fitted with the linear equation: log D_{HL} = 15.6log *M* – 37.48 (*r* = 0.9918). This parameter of the compounds **VI** and **VII** exceeds respective values of the industrial extractants of the oxyoxime class.

Table 3. Distribution coefficient of compounds **III–VII** between immiscible phases[a]

Comp. no.	log D_{HL}		
	HCl 0.5 mol/L	NH$_3$ 1 mol/L	
	p-xylene	*p*-xylene	hexane
III	2.7	3.1	–
IV	1.4	3.9	3.8
V	2.1	not found	4.7
VI	3.3	not found	not found
VII	4.4	not found	not found

[a] (“–”) Not determined; (“not found”) amount of the compound transferred to aqueous phase is too low and cannot be determined with any available method.

Hydrolytic stability. Stability of the extracting agents with respect to hydrolysis determines the possibility of their industrial application. Hydrazides acid or base hydrolysis can be represented as follows [8].

$$\text{R'CONHNR}_2 + \text{H}_3\text{O}^+ \rightleftarrows \text{R'COOH} + \text{NH}_3\text{NR}_2^+,$$

$$\text{R'CONHNR}_2 + \text{OH}^- \rightleftarrows \text{R'COO}^- + \text{NH}_2\text{NR}_2.$$

Hydrolytic stability of the studied compounds was expressed as the degree of hydrolysis after 4 h of refluxing in 0.5 mol/L aqueous H_2SO_4 or 1 mol/L aqueous KOH. Degree of hydrolysis of the unsubstituted hydrazide was determined via titration of the formed carboxylic acid with alkali. Hydrolysis of the dialkyl derivatives was monitored using the extraction-spectrophotometry method from the decrease of the initial compound concentration. The so obtained results are given in Table 4.

Table 4. Hydrolysis degree (α, %) of compounds **I, IV**, and **V** after 4 h refluxing

Medium	I	IV	V[a]
1 mol/L KOH	90	0.5	–
0.5 mol/L H_2SO_4	31	3	–

[a] (“–”) Hydrolysis products cannot be determined with the method used.

From Table 4 it is seen that the alkylation of the unsubstituted hydrazide **I** significantly improved the compounds hydrolytic stability. In the case of compound **V**, the degree of hydrolysis was so low that we failed to quantify it. The improvement of the hydrazides stability was due to two major reasons. Firstly, alkyl substituents sterically hampered the reactants contact by shielding of the reactive centre from water molecules. Secondly, the +*I* effect of the alkyl substituents increased the electronic density at carbon atom of the carbonyl group, preventing its interaction with nucleophilic oxygen atom of water.

EXPERIMENTAL

Electronic spectra were recorded with the SF-2000 spectrophotometer (OKB-Spectr, St-Petersburg). Absorbance was measured with the KFK-3-01 photometer. pH values were measured using the I-160M ionometer (ANTEKh, Belarus) equipped with glass and silver chloride electrodes.

The following solvents and chemicals were used: isoamyl alcohol, chloroform, and KOH (*analytical pure* grade); *p*-xylene, hexadecane, and H_2SO_4 (*pure* grade); hexane (*the highest purity*); kerosene (aviation, rectificate); ethanol (rectificate).

Unsubstituted 4-*tert*-benzoic acid hydrazide **I** was prepared via the Curtius reaction (interaction of propyl 4-*tert*-butylbenzoate with hydrazine hydrate). The *N*',*N*'-dialkyl derivatives of **I** were prepared via direct alkylation of the unsubstituted hydrazide at its β-nitrogen atom with the corresponding alkyl halides [5].

In order to determine the distribution coefficients, concentration of the compounds in the aqueous phase was measured by the extraction-photometry method [9].

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