

spectra of the ligands I-IV and V-VII medium intensity band observed in the region $3200-3170\text{ cm}^{-1}$ and $3130-3100\text{ cm}^{-1}$ respectively is assigned to NH stretching. The band observed in the region $2800-2700\text{ cm}^{-1}$ in ligands I-IV and $3480-3460\text{ cm}^{-1}$ in ligands V-VII is assigned to intramolecular hydrogen bonded OH. In the complexes the NH band is retained but OH band disappears, indicating the replacement of H of hydroxy group by metal.

The strong band around $1675-1650\text{ cm}^{-1}$ ($\nu\text{C}=\text{O}$) is present in ligands and is retained in the complexes. Three to four bands of medium to strong intensity are observed in the region $1625-1500\text{ cm}^{-1}$. These arise from various modes of vibration such as $\nu\text{C}=\text{N}$, $\nu\text{C}=\text{C}$, δOH , $\delta\text{N-H}$, etc., and their conclusive assignment is rather difficult. The band in the region $1625-1610\text{ cm}^{-1}$ is strong and shows a measurable shift to lower frequency by about $15-25\text{ cm}^{-1}$ in the complexes. Taking into consideration its intensity, the donor capacity of nitrogen and previous assignments¹⁻⁹⁻¹¹. This may reasonably be assigned to $\nu\text{C}=\text{N}$ and the shift may be due to the coordination of nitrogen to the metal. In the complexes IX, XI-XIV, the strong band observed around 960 cm^{-1} and in the complexes VIII and X the band around 890 cm^{-1} is assigned to $\nu\text{V}=\text{O}$ this probably suggests the monomeric nature of oxovanadium species^{12 13}.

On the basis of above observations it may be concluded that ligands have reacted in keto form and vanadium has coordination number five in the above complexes. Generally five coordinate oxovanadium (IV) complexes have square pyramidal structures.

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ANALYTICAL REACTIONS OF BARBITURIC ACIDS

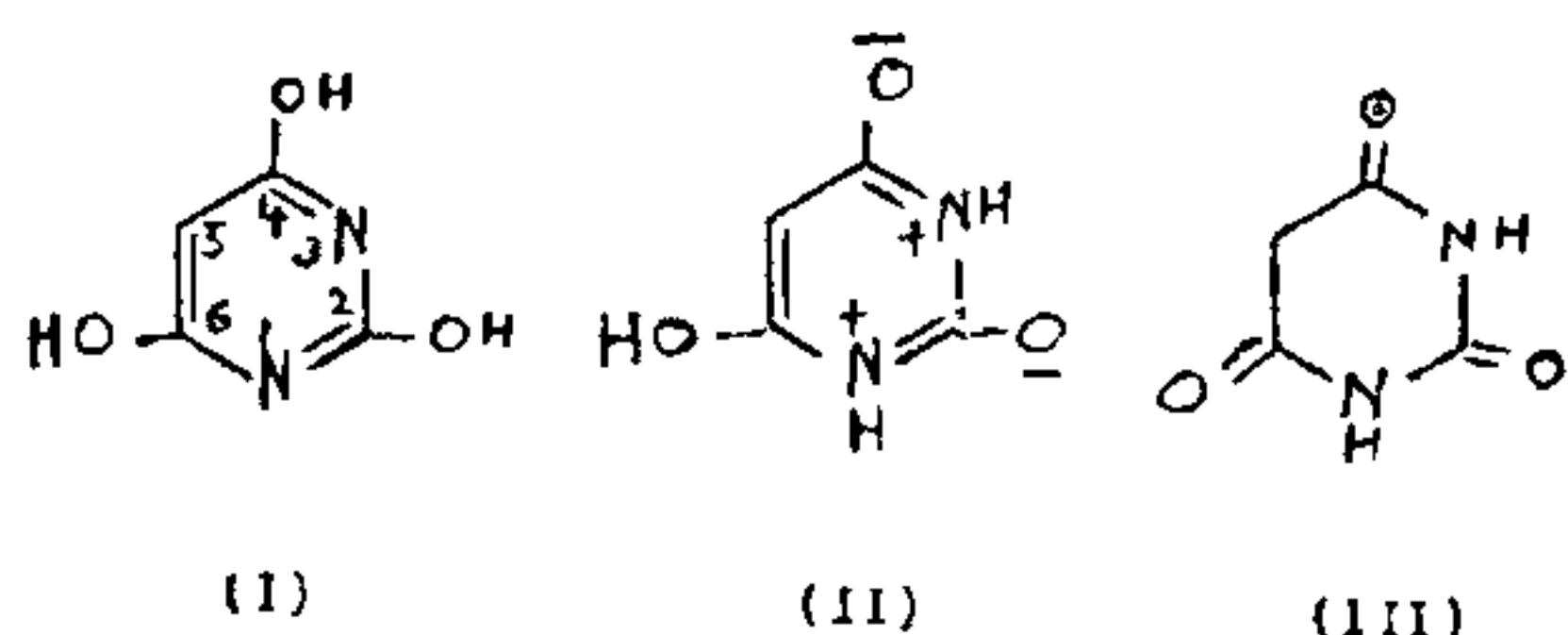
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ABSTRACT

Analytical reactions of barbituric acids used in their identification and also the role of the acids as analytical reagents have been reviewed.

THE name barbituric acid was given to the compound by Alfred von Baeyer who possibly discovered it on St. Barbara's day or wanted to honour his dear friend. It exists in the tautomeric forms, I-III, though the X-ray studies¹ of the solid favour the structure (III). Its preparation involves



the condensation of malonic acid with urea in the presence of POCl_3 . It melts at $248-252^\circ\text{C}$ (d).

Though the acid itself is not biologically active, substituents especially at 5-C atom make it so. Depressant activity of the compounds increases with heavier substituents. Also the compounds become rapidly more toxic when the molecular weights go beyond 250-300. The most commonly used barbiturates for medicinal purposes contain substituents with 6-10 C-atoms. In a recent article² (incidentally one of the authors is Barbara) the biochemical and physiological aspects of barbiturates have been summarized. It is now proposed to review the subject from analytical standpoint.

Barbituric, thiobarbituric, diphenylbarbituric and diphenylthiobarbituric acids have been used³⁻⁵ to quantitatively precipitate and estimate furfural. The method is superior to that using phloroglucinol. The

insoluble precipitate remains unaffected in dilute mineral acids. Large excess of the reagent should be avoided to eliminate its adsorption on the precipitate.

Pyridines have been indirectly determined⁶⁻⁸ with barbituric acid. The method is based on the opening of pyridine ring by CNCl to form glutaconic dialdehyde which condenses with barbituric acid to give coloured polymethine dye suitable for photometric determination. Absorption maxima for the dyes corresponding to pyridine, picolines (α -, β - and γ -), isonicotinic acid, isonicotinoyl glycine and isonicotamide lie at 578, 600-615, 600, 600-615 and 615 nm respectively. The method is extended⁹ to determine pyridine and nicotine simultaneously. Chlorine¹⁰, cyanide and thiocyanate¹¹ and CNS⁻ in cyanamide derivatives¹² have also been determined as they can liberate CNCl which subsequently reacts with pyridine and barbituric acid to form the dye. Traces of chlorine down to 2 μ g are determined¹³ in layers of selenium rectifier cells using this technique. Nikethamide has been colorimetrically determined¹⁴ by measuring the absorbance of the pink solution formed when it reacts with CNBr and barbituric acid.

Copper (II) and cobalt (II) form coloured complexes with some barbituric acids¹⁵ (Table I). Limit of identification for cobalt complexation with thio-barbituric acid is 10 μ g. The reaction is used¹⁶ for detection of barbiturates. Sodium ethyl-1-methyl-butylthiobarbiturate reacts with ammonical Cu (II) solution forming emerald green coloured complex¹⁷. The reaction though specific is not much of analytical interest because of instability of the complex. Ethyl-5-(1-methylbutyl) thiobarbituric acid is, however, identified¹⁸ using its complexation with copper (limit of identification : 40 μ g ; limit of dilution :

1 : 20,000). Silver nitrate reacts with barbituric acid and its 5, 5-diethyl derivative giving yellow precipitate soluble in alkali (λ_{max} 390-400 nm)¹⁹. The reaction is used for volumetric determination^{20,21} and chromatographic identification²² of barbituric acids. Equimolar complexes formed between UO₂ (II) ion and barbituric or thiobarbituric acid have been studied²³ in water, methanol, ethanol and acetone. They absorb maximally at 400 nm and adhere to Beer's law. The colorimetric determination of NO₂⁻ is accomplished²⁴ via conversion of 2-thiobarbituric acid to 2-thio-violic acid (λ_{max} 570 nm).

Intense coloured complexes are reported²⁵ when heavy metal ions interact with 2-thiobarbituric acid and its derivatives. The complexes of copper²⁶, bismuth²⁷ and iron²⁸ with 2-thiobarbituric acid have been characterised (Table II) and the metals are determined colorimetrically. Rh (III) and Pd (II) have been determined²⁹ gravimetrically with the acid. The reactions are sensitive and specific. The colour reactions of trithiobarbituric acid with Cu (I), Cu (II), Ag (I), Hg (I), Hg (II) and Pd (II) have been used³⁰ in detection of traces of these metal ions.

TABLE I
Colour reactions of some barbituric acids

Acid	Reaction with	
	Copper (II)	Cobalt (II)
Barbituric	.. Purple solution	Blue solution
Thiobarbituric	.. Green solution	Purple precipitate
Nitrobarbituric	.. Blue solution	Green solution

TABLE II
Characteristics of metal complexes with 2-thiobarbituric acid

Characteristic	Cu (II)-complex	Bi (III)-complex	Fe (III)-complex
Colour	.. Yellow	Yellow	Rose red
λ_{max} (nm)	.. 400	390	380
ϵ_{max}	.. 6350	26000	..
Medium for complexation	0.1 N H ₂ SO ₄	1 N HNO ₃	pH 2.7-3.0
Composition (metal : ligand)	.. 1 : 4	1 : 3	1 : 3
Range of determination	.. 0.5-12 ppm	..	4-40 ppm
Interferences	.. Ag, Hg (II), Sn (II), Bi (III), Fe (III) Pd (II)	Cu (II), Ag, Cd (II), Hg (II), Sn (II), Sb (III)	Cu (II), Ag, Hg (I), Hg (II), Sn (II), Bi (III), Cr (III), Co (II)

2-Thiobarbituric acid has been widely used for photometric determination of 2-deoxy sugars, aldehydes, ketones, uronic acids and some other organic compounds. Periodate oxidation of deoxy sugars gives malonaldehyde which reacts with 2-thiobarbituric acid to give pink dye suitable for colorimetric determination^{31,32}. In a modified procedure³⁴, the bisulphate addition compound of the aldehyde was isolated first before its reaction with the acid. A similar technique was adopted earlier in the detection of butter fat oxidation³⁴. 2-Thiobarbituric acid in concentrated HCl is used in colorimetric estimation of ketoses³⁵, viz., fructose and sucrose. The absorbance is measured at 432 nm and the optimum range of determination is 0.02–0.2 micromoles. It is also used in colorimetric determination of vitamin A aldehyde³⁶ in various tissues and sialic acid^{37,38}, an important constituent of human semen. The sialic acid is oxidised by NaIO₄ in concentrated H₃PO₄ and the oxidation product is coupled with 2-thiobarbituric acid to produce a coloured compound extractable in cyclohexanone and suitable for photometric determination. The method is specific and applied³⁹ in direct analysis of the acid in tissue hydrolyzates.

Uronic acids except galactouronic acid react with thiobarbituric acid after treatment with cold alkali giving a rose red dye (λ_{max} 548 nm) suitable for their colorimetric determination⁴⁰. Galactouronic acid⁴¹ reacts with the compound in 1 : 1 H₂SO₄ — CH₃COOH medium to produce yellow coloured species (λ_{max} 400 nm).

Sorbic acid⁴² and quinic acid⁴³ are oxidised with K₂Cr₂O₇ — H₂SO₄ and HIO₄ — H₂SO₄ respectively and the resulting malondialdehyde is coupled with 2-thiobarbituric acid to give red dye. For determination of sorbic acid, the absorbance of the dye is measured at its λ_{max} 535 nm while for quinic acid, the dye (λ_{max} 550 nm) is extracted into cyclohexanone before its absorbance is measured. The determination of 5–200 $\mu\text{g/ml}$ of formic acid⁴⁴ depends on its reaction with thiobarbituric acid in acidic medium to produce a chromophore (λ_{max} 450 nm).

Vanillin is condensed with barbituric acid and the product is used⁴⁵ as an acid-base indicator (yellow in acid and red in alkali). Azo-compound obtained by interaction of 2-amino-5-chlorophenyl-6-sulphonic acid with barbituric acid is used⁴⁶ for luminescent determination of Mg (II). Ten-fold excess of Cu (II) and Ga (III) and 100-fold excess of Hg (II), In (III), Gd (III), Ge (IV), Sn (II), Sn (IV), Sb (III) and Co (II) do not interfere. Fe (III) reacts with [5-hydroxy-2-(1, 3)-indandione-2-yl] barbituric acid dioxime⁴⁷ in 1 : 2 ratio (λ_{max}

370 nm; ϵ 890) at pH 4.2. Even 2–3 fold excess of Cu (II), Cr (III), Co (II) and Ni (II) interfere.

Malonaldehyde is condensed with barbituric acid to produce dihydrobarbituric acid trimethyne dye suitable for photometric determination of magnesium⁴⁸ (λ_{max} of the complex 540 nm). The method is applied to determine the metal in aluminium alloys by masking the interfering ions by KCN or NaF.

Uranil-N, N-diacetic acid-5-bis (carboxymethyl-aminobarbituric acid) is used for amperometric determination of Be⁴⁹ ($\geq 1.1 \times 10^{-4}$ M), In⁵⁰ ($\geq 6.4 \times 10^{-6}$ M) and Ga⁵⁰ (1.4×10^{-5} M) using a graphite electrode. The complexes contain the reactants in 1 : 1 ratio. In determination of B₂, the interference due to Cu, Mg, Ca, Zn, Al, Mn (II), Fe (II), Fe (III), Co (II) and Ni (II) is eliminated by EDTA. Ga (III) can be determined in metallic aluminum and with indium, simultaneously. Stability constants (potentiometric) of indium and gallium complexes are 12.88 and 12.05 (at 25° C) respectively.

The reactions between uranil diacetic acid and several metal ions like Cu (II), Cd (II), Ce (IV), UO₂ (II), Fe (II), Fe (III) and Ni (II), in acidic or neutral medium, have been investigated^{51–53}. The equimolar complexes of the ligand with Cu (λ_{max} 775 nm), Cd (λ_{max} 265 nm), UO₂ (λ_{max} 375 nm) and Ni (λ_{max} 390 and 635 nm) follow Beer's law and are used for absorptiometric determination of the metals in minerals and coinage metals.

It is evident from the foregoing work that the reactions of barbituric acids are very potential in several useful detections and determinations. The acids also serve as sensitive and many a time quite selective reagents for determination of metals.

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DECOMPOSITION OF NITROUS OXIDE ON LANTHANUM-NICKEL OXIDE

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INTRODUCTION

THE decomposition of nitrous oxide over simple metal oxides has been studied in detail¹⁻⁶, from the kinetic as well as mechanistic viewpoint of the reaction. In all the investigations mentioned above, only the initial stages of the reaction were considered and it appears that no satisfactory attempt has been made to study the kinetics of this reaction completely. In the present study, the decomposition of nitrous oxide has been carried out on a ternary oxide system like La_2NiO_4 , to evaluate the suitability of this compound as a catalyst in oxidation reactions, in view of the favourable structural properties reported for this compound^{7,8}.

The decomposition of nitrous oxide has been studied over lanthanum nickel oxide in a static reactor (volume 125 cc) with an electromagnetically

operated gas recirculation assembly. The course of the decomposition of N_2O was followed by following the changes in total pressure as a function of time. The N_2O decomposition was studied in the temperature range of 300°–400° C.

The catalyst was degassed for 6 hours at 420° C and at pressures $< 10^{-5}$ Torr and then treated with oxygen (10 cm pressure) for 10 hours at the reaction temperature. The pretreated catalyst was then subjected to evacuation for 2 minutes to remove excess oxygen and then decomposition of N_2O was studied by admitting 50–100 Torr of N_2O .

The catalyst La_2NiO_4 was prepared by firing a mixture of La_2O_3 (Indian Rare Earths Ltd., 99.9% pure) and nickel dimethylglyoxime complex. X-ray powder diffraction patterns of this sample agreed well with those cited in literature for this compound¹⁰. The nitrous oxide (Medical grade),