

The electrical transport behaviour of  $MgV_2O_6$  showed anomaly at the phase transition temperature as one would expect, with no change in the carrier concentration and or transport mechanism. For reasons given, in isotypic  $CdV_2O_6$ <sup>10</sup>, it is evident that the vanadium-vanadium distance increase during structural transition. This could be one of the plausible explanations for the anomaly observed at 833 K for  $MgV_2O_6$  in which case the electron hopping on equivalent vanadium sites need higher activation energy (Table I).

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#### RAPID SEPARATION OF SOME ALKALOIDS OF PHARMACOLOGICAL AND TOXICOLOGICAL INTEREST ON HYDROUS ZIRCONIUM OXIDE PAPER

VERY few reports<sup>1-3</sup> are available on the use of papers impregnated with inorganic ion exchangers for the separation of alkaloids. Several cation separations of analytical and radiochemical interest were reported from this laboratory with hydrous zirconium oxide paper<sup>4</sup>. In the present communication, the chromatographic behaviour of opium and strychnos alkaloids along with atropine and quinine has been studied on

hydrous zirconium oxide papers using aqueous solvent systems only. On the basis of the  $R_f$  values, separations of the four components have been achieved.

#### EXPERIMENTAL

##### Preparation of hydrous zirconium oxide paper :

Whatman No. 1 paper strips (14 × 3 cm) were first dipped in 0.1 M zirconium oxychloride solution, blotted to remove excess solution and then air dried at 25° ± 3° C. The strips were then dipped in 3 M ammonia solution in a glass trough for 30 seconds. The paper was dried, washed with distilled water and air dried at room temperature for twelve hours.

##### Development of chromatograms and separations :

Samples of alkaloids (10–20 µg) were spotted on the papers by micropipettes. These papers were then run in closed chambers (25 × 12 × 25 cm) conditioned for 10–15 minutes with solvent and the solvent was allowed to ascend to develop the chromatograms. The papers were dried with an air blower and alkaloids visualized by spraying with Dragendorff's reagent<sup>5</sup>.

#### RESULTS AND DISCUSSION

The  $hR_f$  values of 9 alkaloids in 10<sup>-3</sup> N hydrochloric acid and sodium hydroxide are given in Table I. As apparent from the table, morphine and narcotine are selectively retained on hydrous zirconium oxide paper in 10<sup>-3</sup> N NaOH medium, thus facilitating their separation from other alkaloids. In addition, numerous separation of mixtures containing upto four alkaloids of pharmaceutical and toxicological importance have been achieved on these papers. Some representative quaternary separations of important alkaloids are presented in Table II. All the separations were accomplished within 15–20 minutes.

TABLE I  
( $R_f \times 100$ ) values of alkaloids on hydrous zirconium oxide paper

Alkaloid	$hR_f$ value	
	HCl, 10 <sup>-3</sup> N	NaOH, 10 <sup>-3</sup> N
Codeine	72	94
Morphine	85	00
Thebaine	95	55
Narcotine	55	00
Papaverine	84	57
Strychnine	78	78
Brucine	90	78
Atropine	98	92
Quinine	62	84

TABLE II

Representative quaternary separations of alkaloids on hydrous zirconium oxide paper

Alkaloid separated ( $R_f$ values in brackets)	Eluent
Codeine (69)-Morphine (85)-Thebaine Narcotine (53)	a
Codeine (70)-Papaverine (85)-Thebaine (94)-Narcotine (53)	a
Strychnine (76)-Narcotine (54)-Quinine (62)-Brucine (88)	a
Codeine (92)-Morphine (00)-Thebaine (53)-Strychnine (75)	b
Codeine (90)-Narcotine (00)-Thebaine (53)-Strychnine (76)	b
Morphine (00)-Papaverine (54)-Strychnine (76)-Atropine (96)	b

a =  $10^{-3}$  N HCl; b =  $10^{-3}$  N NaOH.

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### REINECKE-ACID ANALOGUES WITH 2-SUBSTITUTED BENZIMIDAZOLES

In one of our previous communications<sup>1</sup> we have reported that benzimidazole (LH = BzH) forms the Reinecke-type acid,  $H[Cr(NCS)_4(LH)_2]$ , whereas 2-methyl benzimidazole (LH = MeBzH) forms the cationic-anionic complex,  $[Cr(NCS)_2(LH)_4][Cr(NCS)_4(LH)_2]$ , besides the Reinecke-acid analogue, by substitution in  $K_3[Cr(NCS)_6]$ . Here we report a more detailed study about the effect of alkyl or aryl substitution at 2-position in benzimidazole on thiocyanate replacement in  $Cr(NCS)_6^{3-}$ .

2-Ethyl- and 2-propyl-benzimidazoles have been found in the present investigation to form the acids,

$H[Cr(NCS)_4(LH)_2]$  only and not the cationic-anionic complexes, presumably on account of the increased steric hinderance. The complexes were obtained as rose-red solids by refluxing the ligand with  $K_3[Cr(NCS)_6]$  in 2 : 1 molar ratio in 95% ethanol and diluting the resulting mixture with a large volume of water. The compounds were purified by repeated reprecipitation from ethanolic solution and dried over  $CaCl_2$  (Analyses: (i) Found: Cr, 8.97; C, 46.35; H, 3.50; N, 19.76; Required for  $H[Cr(NCS)_4(EtBzH)_2]$  (I): Cr, 9.02; C, 45.75; H, 3.65; N, 19.44%. (ii) Found: Cr, 8.72; C, 47.95; H, 4.90; N, 20.12; Required for  $H[Cr(NCS)_4(PrBzH)_2]$  (II), Cr, 8.74; C, 48.48; H, 4.12; N, 19.79%.

The molar conductance values (in ethanol at 302° K) of 42.3 and 57.0  $ohm^{-1} cm^2$  for the ethyl and the propyl derivatives, respectively, fall short of the values expected for monobasic acids. This may be on account of low mobilities of the large anions and strong ion-pair formation between  $H^+$  and the complex anions in ethanol.

The room-temperature (302° K) magnetic moment of 3.83 BM for the ethyl derivative is characteristic of Cr(III) in octahedral site symmetry. The magnetic measurement of the other compound, however, could not be made on account of low yield.

In both these complexes the thiocyanate groups appear to be N-bonded as suggested<sup>3</sup> by the appearance of very strong CN stretching bands near 2120  $cm^{-1}$  (2120 in I and 2118 in II), very weak CS stretching bands near 800  $cm^{-1}$  (803 for I and 798 for II) and NCS deformation modes near 490  $cm^{-1}$  (485 for I and 490 for II). It may be mentioned here that M-NCS bonding in the case of BzH- and MeBzH-complexes were suggested by Ghosh and Mishra<sup>1</sup> mainly on the basis of  $\nu(CS)$  appearing at 775-785  $cm^{-1}$ . In the present investigation, however, we have confirmed their idea by locating strong bands at 490  $cm^{-1}$  in BzH-complex and at 495  $cm^{-1}$  in MeBzH-complex on account of NCS deformation.

The electronic spectra reveal that the ethyl and the propyl benzimidazole complexes have the same 10 Dq values, i.e., 17,700  $cm^{-1}$ , as methyl benzimidazole complex has, but lower than that of BzH-complex (18,520  $cm^{-1}$ ). These values have been calculated from the transition  ${}^4A_{2g} \rightarrow {}^4T_{2g}$ . The second ligand-field band on account of  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$  transition appears at 24,270  $cm^{-1}$  in EtBzH-derivative and at 25,000  $cm^{-1}$  in PrBzH complex. The two ligand-field bands enable us to calculate the interelectronic repulsion parameter B (588  $cm^{-1}$  for I and 631  $cm^{-1}$  for II) and nephelauxetic ratio  $\beta_{35}$  (0.63 and 0.68, respectively) which are similar to or a bit higher than those of BzH- and MeBzH-complexes.

An aryl (e.g., phenyl) substitution in benzimidazole, appears to have reduced the coordinating capacity