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MECHANISM OF SUBSTITUTION REACTIONS OF COMPLEX IONS. XV. ACID AND BASE HYDROLYSIS OF CIS- AND TRANS-DICHLORO-BIS-(ETHYLENE-DIAMINE)-CHROMIUM(III) ION.¹

Sir:

The rates of acid hydrolysis of chloro complexes of chromium(III) are always greater than those of the corresponding complexes of cobalt(III).² This is as expected on the basis of crystal field theory³ since cobalt(III), with six electrons in the stable d_{xy} , d_{xz} , and d_{yz} orbitals, will resist changes in the octahedral arrangement of ligands more strongly than chromium(III) with only three electrons in these orbitals. We recently have measured the rates of both acid and basic hydrolysis for *cis* and *trans*-Cr(en)₂Cl₂⁺. The results together with those⁴ for *cis* and *trans* Co(en)₂Cl₂⁺ are

RATE CONSTANTS AT 25° IN WATER

	k_{acid} , sec. ⁻¹	k_{base} , M. ⁻¹ sec. ⁻¹
<i>cis</i> -Cr(en) ₂ Cl ₂ ⁺	3.5×10^{-4}	2.7×10^{-2}
<i>trans</i> -Cr(en) ₂ Cl ₂ ⁺	3.9×10^{-5}	3.7×10^{-2}
<i>cis</i> -Co(en) ₂ Cl ₂ ⁺	2.5×10^{-4}	1.0×10^3
<i>trans</i> -Co(en) ₂ Cl ₂ ⁺	3.2×10^{-5}	3.0×10^3

The remarkable result is that the rates of base hydrolysis are about 1/10⁵ slower for chromium(III) than for cobalt(III). This demonstrates, at the very least, that a common mechanism is not operating throughout. The slower reaction with hydroxide ion for chromium compared to cobalt is not compatible with an S_N2 mechanism on either the basis of crystal field or valence bond theory.

The result is explicable on the basis of an S_N1CB mechanism as previously postulated.⁴ The acidities of corresponding chromium and cobalt complexes, where measurable, are found to be about equal.⁵ Hence the conjugate bases are formed with about equal ease from either Cr(en)₂Cl₂⁺ or Co(en)₂Cl₂⁺. The great reactivity of the conjugate base has been ascribed to repulsive π -type interaction between the filled p orbitals of nitrogen in the amido group

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(2) A. W. Adamson and R. G. Wilkins, *ibid.*, **76**, 3379 (1954); J. Selbin and J. C. Bailar, Jr., *ibid.*, **79**, 4285 (1957).

(3) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); C. Kihlbäll Jørgenson, *Acta Chem. Scand.*, **9**, 605 (1955).

(4) R. G. Pearson, R. E. Meeker and F. Basolo, *THIS JOURNAL*, **78**, 709 (1956).

(5) F. Woldbye, private communication; W. K. Wilmarth, H. Graff and S. T. Gustin, *THIS JOURNAL*, **78**, 2683 (1956).

and the filled d_{xy} type orbitals on the metal atom.⁶ This repulsion provides a driving force for loss of chloride ion accompanied by a rearrangement to a trigonal bipyramid intermediate which allows an attractive π -type interaction with the now empty $d_{x^2-y^2}$ orbital.

It is obvious that chromium with only half as many electrons in the d_{xy} type orbitals will not supply as much driving force for this process. Hence the over-all much lower rate of release of chloride ion in the presence of alkali can be understood. A similar explanation will hold for *cis*-Co(en)₂NO₂Cl⁺, which also reacts very slowly with hydroxide ion.⁷ In this case π -bonding from the metal atom to the nitro group reduces the electron occupancy of the d_{xy} type orbital.

The rates of chloride ion release were measured both in acid and in alkali by amperometric titration of chloride ion. The concentration of complex ion was 2.00×10^{-3} M. Ionic strength was maintained at 0.10 by NaNO₃. Rates in alkali were measured in a series of solutions containing up to 0.10 M hydroxide ion. The pseudo first order rate constant was found from the experimental half-life for one chloride ion. A plot of rate constant vs. hydroxide ion concentration was linear. From the slope, the second order rate constant given in the table was calculated. The rate constants for acid hydrolysis were found directly in 0.1 M nitric acid and also in acetate-acetic acid buffers of pH 4.2 to 4.6 containing 0.1 M acetate ion. The same rates were obtained in the two media showing that there was no direct reaction with acetate ion. The rate constant for acid hydrolysis could also be found from the intercept of the above mentioned plot. The intercept was equal to about twice the directly measured value, since in alkaline solution the intermediate Cr(en)₂OHC⁺ would rapidly lose the second chloride ion.⁸

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(7) S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

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A NEW CYCLOPROPYL CORRELATION IN THE NEAR-INFRARED REGION

Sir:

During a recent investigation of certain cyclopropyl derivatives in the near-infrared region of 1.1–2.7 microns, we have noted that in every case of nine derivatives examined, an absorption band has occurred at 1.63–1.65 microns and another at 2.22–2.27 microns.

The spectra were determined using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. All compounds were run as 10% solutions in carbon tetrachloride in a 3.0 mm. fixed thickness sodium chloride cell. Wave length was calibrated using chloroform and benzene.

The first of these bands, at about 1.64 microns, apparently is due to the first overtone of the C-H stretching fundamental at 3.23 microns, while the second band, at about 2.24 microns, is probably a combination band. At the concentration and cell thickness used, the 1.64 micron band appears as a sharp band of weak intensity. The band at about 2.24 microns also appears sharp, but is in the neighborhood of from four to six times as intense as is the 1.64 micron absorption. Table I indicates the relative constancy of position of the absorption bands, and the range of compounds examined.

TABLE I
CHARACTERISTIC ABSORPTIONS IN THE NEAR-INFRARED
FOR THE CYCLOPROPYL RING

Cyclopropane derivative	First overtone, μ	Combination, μ
α -Cyclopropylbenzhydrol	1.65	2.26
Cyclopropylethynylmethylcarbinol	1.64	2.24
Cyclopropylphenyl ketone	1.64	2.22
Ethyl 2-methylcyclopropanecarboxylate	1.64	2.27
γ -Morpholinopropyl 1-phenylcyclopropanecarboxylate	1.63	2.22
Cyclopropylethynylphenylcarbinol	1.64	2.23
Cyclopropylethylmethylcarbinol	1.64	2.23
Ethylmethyl-(1-methylcyclopropyl)-carbinol	1.64	2.23
1-cyclopropyl-1-methylpent-2-yne-4-ene-ol	1.64	2.22

While the band at 2.24 microns lies quite close to the combination bands of saturated CH_2 and CH_3 , the band at 1.64 microns is well separated from the first overtone of saturated aliphatics. The only other functional group we have found to give rise to absorptions at these wave lengths is terminal methylene ($=\text{CH}_2$). Fortunately, when doubt exists, the terminal methylene easily may be confirmed by its absorptions in the 3 to 15 micron region.

In view of the well known ambiguities encountered in detecting cyclopropyl derivatives through absorption in the 3.2-3.3 and the 9.7-10.0 micron regions,¹⁻⁴ especially in the presence of aromatic rings and most types of aliphatic unsaturation, we feel that by using the near-infrared correlations a more certain confirmation of the cyclopropyl group can be made.

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NEW FACTORS IN PYRIMIDINE BIOSYNTHESIS Sir:

It has been found that the radioactive specific pyrimidine precursors, orotic and ureidosuccinic acids, are incorporated into the acid insoluble fraction of some mammalian tissues to a greater extent than can be accounted for by the uridylic, cytidylic,

and thymidylic acids present. The data below give some of the characteristics and biosynthetic data on a substance, probably a pyrimidine nucleotide, thought to be formed from these precursors. This substance also has been shown to be present in *fresh* rat tissue as a normal constituent in the absence of added ureidosuccinic or orotic acids.

Following incubation of three to four grams of rat liver with the precursor by methods previously described,¹ protein precipitation, with cold trichloroacetic acid, and lipid extraction were carried out. The residue was dissolved in 1 *N* KOH as in the Schmidt-Thannhauser procedure.² The DNA and protein were precipitated by acidification to pH 6 with HCl and addition of concentrated trichloroacetic acid to a final concentration of five per cent. The supernatant was brought to a volume of approximately 0.5 ml., heated for one hour at 100° and submitted to paper chromatography in a tertiary butyl-HCl solvent.³ In confirmatory experiments, the silver salts of the pyrimidine nucleotides

SPECIFIC ACTIVITIES OF PYRIMIDINE NUCLEOTIDES FROM RAT LIVER SLICES AFTER INCUBATION WITH EITHER 1 MG. OF C-14-OROTIC ACID CONTAINING 2,720,000 COUNTS OR 2 MG. OF C-14-UREIDO-SUCCINIC ACID CONTAINING 2,534,000 COUNTS

	Relative amounts, μmoles	Ultraviolet max, $m\mu$, at pH 2	Ratio 278 $m\mu$ / 262 $m\mu$ at pH 2	Counts/min./ μmole^a
Expt. 1, C-14-Orotic acid				
Uridylic acid	4.2	262	0.45	5900
Substance X ^a	1.0	262	0.53	135000
Cytidylic acid	5.9	278	1.59	1070
Expt. 2, C-14-Orotic acid (lowered oxygen tension) ^d				
Uridylic acid	4.1	262	0.46	412
Substance X' ^b	0.32	266	0.80	40000
Cytidylic acid	5.7	278	1.58	44
Expt. 3, C-14-Ureidosuccinic acid				
Uridylic acid	5.0	262	0.47	16600
Substance X	0.89	262	0.54	179000
Cytidylic acid	5.9	278	1.58	566
Expt. 4, C-14-Ureidosuccinic acid (lowered oxygen tension) ^d				
Uridylic acid	4.7	262	0.46	752
Substance X'	0.32	266	0.78	29600
Cytidylic acid	6.3	278	1.60	63

^a Quantified spectrophotometrically. A molecular extinction of 8400, based on phosphorus analyses, was used for Substance X. ^b Values obtained by assuming a molecular extinction of 8400 for purposes of comparison with Substance X. (If one assumes the amount of X' to be equivalent to X and that the flattened spectrophotometric curve indicates a lower molecular extinction, then it can be calculated that the ratios of specific activity of X' to uridylic acid in Experiments 2 and 4 more nearly approximate those of X to uridylic acid in Experiments 1 and 3.) ^c In all instances uridylic and cytidylic acids were counted as the nucleotide, then hydrolyzed with formic acid and counted as the free base. The results were in good agreement except for a small drop in the specific activity of the cytosine, compared to the cytidylic acid, in the ureidosuccinate experiments. The counts of the free base are those recorded. ^d In experiments 2 and 4 alternate slices of the same batch of rat livers as used in 1 and 3 were treated in the same manner except they were incubated under a lowered oxygen tension.

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