

ening) is presumably operative in NO_2 solutions, for Atkins, *et al.*,² report that their attempts to resolve a single very broad line in such solutions have failed despite variation of temperature, concentration, and solvent over a wide range. Attempts by them to obtain rigid solutions of NO_2 by rapid cooling in liquid nitrogen have also failed, probably because dimerization was complete. On the other hand, NO_2 has been observed, while trapped in various inert matrices at low temperature (ref. 2 and other work cited therein) in which molecular rotation is largely quenched.

Adsorption on the Linde 13X sieve presumably takes place in the intracrystalline voids, comprising about half the total volume, which are connected by circular openings or pores. The resolution of the e.p.r. signal shown in Fig. 1 is ascribed to the relative isolation of the radicals (as in the dilute gas or inert solid matrix), and, in all probability, to a decreased dimerization rate. The relatively sharp lines and simple nature of the spectrum indicates that the NO_2 molecules are rotating freely while "adsorbed" in the cavities of the molecular sieves at 25° . These alkali metal aluminosilicates would appear to offer certain advantages for e.p.r. spectral studies of gaseous stable (and transitory?) free radicals. Those pressure-dependent factors which tend to broaden gaseous spectra under ordinary conditions are apparently diminished or eliminated with the technique of sieve adsorption. Also, the isotropic patterns readily obtained with the sieves can complement and confirm data derived from generally anisotropic solid matrix spectra.

NO_2 is adsorbed by both Linde Molecular Sieves 13X and 10X. The e.p.r. signal of the NO_2 on the 10X is complicated by an apparently inherent e.p.r. signal in the 10X sieve. No NO_2 signal is obtained from NO_2 on Linde Molecular Sieves 3A, 4A, or 5A. These results are consistent with the relative size of pores and cavities in these sieves.

Care must be taken to remove nearly all adsorbed water from the sieves to prevent reaction between the water- N_2O_4 - NO_2 and sieve. In general, the sieves are heated to 300° with evacuation prior to the introduction of NO_2 .

The adsorption of other free radicals by molecular sieves is under active investigation in these laboratories and preliminary results indicate that such adsorption may be a fairly general phenomenon.

The e.p.r. spectra reported herein were obtained with a Varian V-4502 e.p.r. spectrometer system employing 100 kc./sec. modulation and detection. The sample cells are 5 mm. o.d. and 7 in. long capped by side arms and a Fischer-Porter⁴ pressure valve for loading of the cells with gas and sieve.

Caution.—Some gases will react with various molecular sieves—a rapid pressure build-up occasionally results in the bursting of the sample tube. Specifically, tetrafluorohydrazine, when adsorbed on Molecular Sieves 5A and 13X, exploded at room temperature on two different occasions.

(4) Fischer & Porter Company, Hatboro, Penna

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The Reaction of Ruthenium Tetroxide with Pyridine

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The addition compound of ruthenium tetroxide and pyridine having the composition $\text{RuO}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ has been prepared and some of its properties determined. The existence of this compound is not unexpected in view of the report of $\text{OsO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ and $\text{OsO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ by Criegee, *et al.*,¹ and $\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ by Sisler, *et al.*,² and of the expected Lewis acid character of ruthenium tetroxide.

An aqueous solution of ruthenium tetroxide obtained by distillation from the acid reaction mixture in which it is formed was extracted with carbon tetrachloride.³ To the resulting carbon tetrachloride solution, cooled in an ice bath, was added a carbon tetrachloride solution of pyridine. An immediate and rapid formation of brown, needle-like crystals occurred; these gradually changed to greenish black crystals with a concurrent increase in the weight of the crystals. After 10 hr., the crystals were filtered, washed with carbon tetrachloride, and dried under vacuum.

The mole ratio of pyridine to ruthenium tetroxide in the crystals remained constant at 2:1 while the mole ratio of these two constituents in the reaction solution was varied from 1:1 to 4:1. The crystals were analyzed by thermal decomposition in a stream of hydrogen to yield a residue of ruthenium metal and by reaction with aqueous potassium hydroxide to yield the pyridine constituent.⁴

Anal. Calcd. for $\text{RuO}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$: Ru, 31.1; $\text{C}_5\text{H}_5\text{N}$, 48.9. Found: Ru, 29.6; $\text{C}_5\text{H}_5\text{N}$, 48.6.

$\text{RuO}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ is insoluble in carbon tetrachloride, chloroform, benzene, and acetone, but dissolves in water, alcohol, acetic acid, and pyridine to give greenish black solutions. Its spectrum has broad absorption bands at 257 (weak), 420, and 720 $\text{m}\mu$. The color of the aqueous solution is so intense as to be observable in concentrations as low as 2 p.p.m. The aqueous solu-

(1) R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 118 (1942).

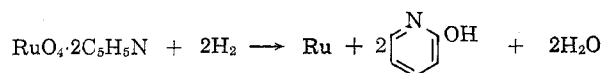
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(3) Y. Koda, *J. Inorg. Nucl. Chem.*, **25**, 314 (1963).

(4) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley & Sons, New York, N. Y., 1942, p. 495.

tion colors cotton cloth green. Its green color is fairly stable. $\text{RuO}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ is slowly absorbed from aqueous solution by the cation exchanger Dowex-50, but is unaffected by the anion exchanger Dowex-1. The aqueous solution of the compound is fairly stable when acidic. However, basic solutions are unstable. In hot potassium hydroxide solutions, rapid decomposition to pyridine and ruthenium dioxide (RuO_2) occurs.

Heating the solid compound results in its gradual decomposition without melting. Differential thermal analysis revealed that this decomposition is exothermic. Use of a thermogravimetric balance showed that in the range 50–400° the decomposition proceeds through four steps with the weight at the final step corresponding to the compound RuO_2 . Vigorous reactions accompanied by marked reductions in weight were observed at about 160 and 220°. Thermal decomposition in a stream of hydrogen takes place in accordance with the equation



A detailed report of this work will be published at a later date.

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Computer Analysis of Stability Constants in Three-Component Systems with Polynuclear Complexes¹

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Recently we published some results of studies on the chelation of a cation which was also a rather strong aquo acid.² There are several indications that this cation, the dimethyltin(IV) ion, exists in solution as $[(\text{CH}_3)_2\text{Sn}(\text{OH})_2]^{+2}$.^{2,3} By using bidentate ligands, the tendency toward the formation of mixed hydroxo complexes was minimized; nevertheless, the analysis of the experimental data was quite complicated because of the hydrolysis of the cation to $[(\text{CH}_3)_2\text{Sn}(\text{OH})(\text{OH}_2)]^+$ and the partial condensation of this species to the dimer. The determination of the complexing constants in such systems has rarely been undertaken, for it is very laborious. An iterative procedure must be employed, and this is not necessarily strongly convergent. In the case cited,² the estimated standard errors in the complexing constants were quite large, *ca.* 0.1 to 0.2 log unit.

Since the completion of this work, we have obtained

access to a CDC 1604 computer which vastly reduces the labor involved in evaluating such experimental data. This note is concerned with our observations on the use of two types of Fortran 60 programs for the refinement of the constants.

Computation⁴

The first type of program used was based on the usual Gauss method^{5–9} while the second type was based on the "pit mapping" procedure recommended by Sillén.^{10,11}

The experimental data¹² were the tetrads C_H , the analytical hydrogen ion concentration; B , the total metal concentration; C_L , the total ligand concentration; and $[\text{H}^+]$, the equilibrium hydrogen ion concentration. In addition, the errors in each of these quantities were estimated and used for the computation of the variances. The constants to be refined were the acid dissociation (hydrolysis) constants for the aquo metal ion including that for the formation of the dimer of the simple conjugate base, the acid dissociation constants for the ligand conjugate acids, and the complexing constants.

The two types of program were both designed to minimize the sums of the squares of the weighted residuals in the analytical hydrogen ion concentration where this residual is

$$R = C_H - [\text{H}^+] + K_w[\text{H}^+]^{-1} + \sum_l \sum_m \sum_n n[\text{L}]^l [\text{M}]^m [\text{H}^+]^{-n} \beta_{lmn}$$

where

$$\beta_{lmn} = [\text{M}_m \text{L}_l \text{H}_{-n}] [\text{H}^+]^n / [\text{L}]^l [\text{M}]^m$$

and $[\text{M}]$ and $[\text{L}]$ are the free metal and ligand concentrations, respectively. The only restrictions on the coefficients l , m , and n are the following: $l \geq 0$, $m \geq 0$, and n may have any positive value for hydrolysis of the metal ion and any negative value for proton dissociation of the ligand conjugate acids.

The initial values of the free metal and ligand concentrations were calculated using the experimental data together with the approximate values of the constants reported earlier.² A Newton–Raphson iteration in the mole balance equations for total metal and total ligand was employed. The two equations for the frac-

(4) Complete deck listings, flow sheets, and duplicate card decks of all programs described in this communication may be obtained by writing to R. S. T.

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(12) These data were deposited as Document No. 7350 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(1) This work was supported, in part, by the National Science Foundation under Grants NSF-G14173 and GP-653.

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