

COMMUNICATIONS TO THE EDITOR

TRANSFORMATION OF POLYMERIC RUTHENIUM(IV) TO THE MONOMERIC SPECIES ON ION EXCHANGE RESIN

Sir:

Although the existence of polymeric forms of ruthenium(IV) had been suspected, Gortsema and Cobble¹ were able to prepare both the monomeric and polymeric species and study them extensively in perchloric and nitric acid solutions. Ion exchange provided a simple method for transforming the polymeric form to the monomeric. This was done by equilibrating a quantity of low cross-linked Dowex 50W resin (2 to 4%) with Ru(IV) solution known to contain extensive amounts of polymer and then eluting the resin with 0.1 *M* cerium(III) perchlorate or 1 *M* perchloric acid. They make no statement as to whether the ion exchange is a separation of RuO⁺⁺ (the monomer) from solutions of high polymer concentration, or whether there is a transformation of the polymer to the monomer on the resin. From direct observation of the spectrum of Ru(IV) on the resin it can be concluded that an actual transformation of polymer to monomer occurs as it passes through the ion exchange resin. This is also significant in that it shows that the polymeric Ru(IV) structure is not extremely stable and that it can be broken down into monomer by use of rather mild conditions.

The spectra were scanned with a Cary Model 14 recording spectrophotometer. One cm. Beckman fused silica cells were fitted with cell spacers to reduce the optical path to 2 mm. By increasing the dynode voltage on the phototube it was possible to record data down to 250 m μ or less. The ruthenium(IV) perchlorate solutions were prepared using a procedure described by Yaffe and Voight² and by Niedrach and Tevebaugh.³ Gortsema and Cobble¹ determined the absorbancy index, *A* (1 cm., moles/liter), to be about 700 for the monomeric Ru(IV) and 800 to 1600 for the polymer at 480 m μ . The 0.0025 *M* ruthenium perchlorate solutions with *A*₄₈₀ ranging from 730 to 1000 were stirred with Dowex 50WX2, 200 to 400 mesh, ion exchange resin. After a short period of time the resin containing Ru(IV) was washed repeatedly with distilled water to remove any ruthenium ion not in the resin phase. A portion of the loaded resin then was tapped and settled in one of the 2-mm. cells and the spectrum scanned *versus* a blank of the unloaded resin in the other 2 mm. cell. After equilibration with the resin, no ruthenium could be found in the residual solution. This enabled calculation of the concentration of the ruthenium in the resin phase.

Data were obtained for several determinations on three different preparations, both of

monomeric Ru(IV), *A*₄₈₀ = 733, and polymeric Ru(IV), *A*₄₈₀ = 1003. The results, given in Table I, indicate that the absorbancy index in the resin phase is a constant, independent of the value for the original solutions and approximates the value for the monomeric Ru(IV).

TABLE I
ABSORBANCY INDEX OF Ru(IV) ON RESIN
Sample no.

Expt.	A. Monomeric Ru(IV)			Average
	1	2	3	
1	800	863	785	806
2	806	816	764	
	B. Polymeric Ru(IV)			
1	686	895	882	801
2	817	842	755	
3	..	808	782	

(4) From the Ph.D. thesis of D. K. A. entitled "A Study of Ru(III), and Ru(IV) Species in Aqueous Perchloric Acid Solutions," Purdue University, August, 1960.

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SPECIFIC CLEAVAGE OF METHIONYL PEPTIDES

Sir:

Sulfonium derivatives of methionine have been known to undergo easy elimination of the sulfur function with concomitant formation of homoserine lactone.^{1,2,3} It has now been demonstrated that in peptides of methionine this intramolecular displacement occurs with participation and cleavage of the C-peptide bond (I—IV) in high yields. The data presented in Table I show that the extent of

TABLE I
INFLUENCE OF ALKYL GROUP ON THE CLEAVAGE OF SULFONIUM SALTS DERIVED FROM ETHYL N-ACETYLMETHIONYL-GLYCINATE

Alkylating agent	Molar concn. of peptide in reaction mixture ^a	Equivalents of alkylating agents	Per cent. of peptide cleavage ^b
Iodoacetic acid ^c	0.005	3	6.0
Methyl iodide ^{c,d}	.01	4	3.6
Ethyl bromoacetate ^{c,d}	.01	4	43
Iodoacetamide ^e	.01	3	53
2,4-Dinitrofluorobenzene ^e	.01	4	~2
Diethyl bromomalonate ^e	.01	3	5

^a Reactions were allowed to proceed at room temperature for 24 hr. ^b After removal of excess of alkylating agent by ether extraction the reaction mixture was heated for one hour at 100°. The liberated amino acid was determined by ninhydrin assay.⁴ ^c Reaction medium was 0.1 *M* pH 3 citrate buffer. ^d Alkylation was conducted in a sealed tube. ^e Reaction medium was 1:1 mixture of EtOH and 0.1 *M* pH 3 citrate buffer.

(1) F. P. Gortsema, Doctoral thesis, Purdue University, January, 1960; *Dissert. Abstracts*, **21**, 48 (1960), L. C. Card No. Mic 60-2206.

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