Apparatus and Procedure.—The apparatus and procedure were similar to those described previously.[6]

Infrared spectral analyses were used for the determination of the hydrocarbons obtained from the reactions. The gaseous products were analyzed by means of a mass spectrograph.

Experiments. 5,5-Dimethyl-3-methylenecyclohexene (I).—This hydrocarbon, 16 g., was refluxed in the presence of a catalyst prepared from 1 g. of sodium and 0.5 g. of *o*-chlorotoluene.[6] The composition of the liquid condensate at various intervals of refluxing is given in Table I.

The concentration of *m*-xylene and of the starting compound I was determined by infrared spectroscopy, using 9.15 and 11.65 μ as the respective analytical bands. The mixture of II and III was calculated by difference. The tabulated results agree with the approximate evaluation of the concentration of compounds II and III using 13.8 and 13.9 μ as the respective analytical bands.[16]

1,1,3-Trimethylcyclohexadienes (II and III).—Twelve grams of a mixture of II and III was refluxed in the presence of a catalyst prepared from 1.5 g. of sodium and 0.75 g. of *o*-chlorotoluene. After 8 hours of refluxing the distillate consisted of *m*-xylene. Almost the theoretical amount of methane was produced.

α-Pyronene (IV).[17]—About 4 g. of the compound IV was refluxed using a similar catalyst as given in the preceding experiment but prepared from about 0.3 g. of sodium. After 3 hr. of refluxing the liquid hydrocarbon consisted of 1,2,3-trimethylbenzene.

5-Methyl-5-ethyl-1,3-cyclohexadiene (XI).—XI, 6.8 ml., was refluxed with a catalyst prepared from 2 g. of sodium and 0.8 g. of *o*-chlorotoluene. After 3 hr. of refluxing at 142–148°, 1050 ml. of gas was produced, which was composed of 92.4% of methane and 7.6% of ethane. The liquid distillate, 4.5 ml., was composed of 8% toluene and 92% ethylbenzene.

Acknowledgment.—The authors wish to thank Miss Hildegard Beck for the elementary analyses and Professor D. F. Mason of the Chemical Engineering Department for the mass spectral analyses.

(16) The infrared spectra of compounds I, II and III are given in reference 1.

(17) The experiment was carried out by Dr. M. Kolobielski.

EVANSTON, ILLINOIS

COMMUNICATIONS TO THE EDITOR

ADSORPTION OF THORIUM BY ANION-EXCHANGE RESINS FROM NITRIC ACID MEDIA

Sir:

It has been reported recently that thorium is not adsorbed by anion-exchange resins from hydrochloric acid solutions, probably due to the low stability of the negatively charged complex chlorides of this element.[1] However, in the course of our studies on the ion-exchange and solvent-extraction behavior of elements in nitric acid media,[2] we observed that thorium is strongly adsorbed by some anion-exchange resins at high nitric acid molarities.

The adsorption of thorium was investigated by the equilibrium method with Dowex-1, 8% DVB, 50–100 mesh, using Th_{234} (β, γ, 24.1 days period) as tracer. This isotope was extracted from uranyl nitrate according to the procedure of Dyrssen[3] and the radiochemical purity of our source was controlled by radiation absorption measurements.

The adsorption of thorium, expressed as usually by the distribution coefficient D (amount of thorium per gram of dry resin divided by the amount of thorium per ml. of solution), increases with M HNO_3 from D = 12 at 1.4 M HNO_3 to D = 110 at 5.1 M HNO_3, reaches a maximum near 7 M HNO_3 with D = 300 and decreases slowly to D = 210 at 10 M HNO_3.[4] According to the interpretations proposed for the adsorption of elements by anion-exchange resins, this suggests that the negatively charged complexes of thorium are being formed[5] or are dominant[4] at nitric acid solutions stronger than 7 M.

Trace amounts and weighable quantities of thorium are completely adsorbed in 50–100 mesh columns from 7–8 M HNO_3 solutions. The radioelement can be eluted with hydrochloric acid solutions. In a typical experiment 2 ml. of a 7 M HNO_3 solution with Th_{234} was added to a 1 cm.^{2} × 7 cm. column which has been pretreated with 7 M HNO_3. The column was washed with acid of the same concentration and any activity was detected in the effluent. Thorium was next eluted with 2.4 M HCl and a flow rate of 0.4 ml./min. The course of the elution was followed by sampling the effluent in volumes of 2 ml., which were evaporated and the activity in each measured with a G.M. counter. It was found that essentially all activity was removed by one column volume of the hydrochloric acid solution. In another experiment with weighable quantities of thorium, we ran through the column at a flow rate of 0.2 ml./min., 10 ml. of a 0.01 M solution of Th_{232} in 7.3 M HNO_3 with Th_{234} added as tracer. Essentially all thorium was retained in the column and subsequently removed with 2.4 M HCl. Good results were obtained with 20–40 mesh Amberlite IRA-410 columns. In these experiments the adsorption and elution of thorium were determined by spot testing with alizarine[6] and it was observed that elution can be achieved both with dilute and concentrated hydrochloric acid solutions. Since

(1) K. A. Kraus, G. E. Moore and F. Nelson, THIS JOURNAL, **78**, 2692 (1956).

(2) J. Danon and A. A. L. Zamith, *Nature*, **177**, 746 (1956).

(3) D. Dyrssen, *Svensk Kem. Tid.*, **7**, 153 (1950).

(4) The data obtained at high M HNO_3 may be considered as approximate since, as has been reported by F. Nelson and K. A. Kraus [THIS JOURNAL, **76**, 5916 (1954)], the resin is possibly attacked in these conditions. However these authors carried out their research with 200–230 mesh Dowex-1 and we observed that better results at high concentrations of nitric acid are obtained using less finely ground resins.

(5) C. D. Coryell and Y. Marcus, *Bull. Res. Council Israel*, **3**, 500 (1954).

(6) F. Pavelka, *Mikrochem.*, **4**, 199 (1926).

most elements exhibit a higher tendency to form negatively charged complexes in hydrochloric acid media than in nitric acid media, these results may be useful for separations and purification of thorium with anion-exchange resins.

On the basis of ionic radius considerations alone, one would conclude that the tendency of the chloride ion to form complexes should be higher than that of the nitrate ion. It has been shown that reversal in this order can be expected as a consequence of the structure of the nitrate ion and resulting high polarizability.[7] However, it is interesting to observe that among the elements previously studied only Nd(III), Pr(III), Sm(III), Eu(III)[7] and the transuranic elements in the +3 and +4 state such as Pu(III), Pu(IV),[7] Am(III)[8] and possibly Np(IV)[7] have less tendency to complex formation with the chloride ion than with the nitrate ion.

(7) J. C. Hindman, "Ionic and Molecular Species of Plutonium in Solution," National Nuclear Energy Series, Vol. 14-A, pp. 333, 346, 463.

(8) G. N. Yakolev and V. N. Kosyakov, "Spectrophotometric Studies of the Behaviour of Americium Ions in Solution," Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Vol. 7, p. 363, United Nations, 1956.

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RECEIVED SEPTEMBER 27, 1956

UNEXPECTED FORMATION OF ANHYDRO COMPOUNDS IN THE SYNTHESIS OF ASPARAGINYL AND GLUTAMINYL PEPTIDES[1]

Sir:

It was of considerable interest to find that some peptide-forming reagents lead to what appear to be intramolecular dehydrations during the formation of asparaginyl peptide bonds and, to a minor degree, during the formation of glutaminyl peptide bonds. Carbobenzoxy-L-asparagine previously has been coupled with the benzyl and methyl esters of S-benzyl-L-cysteine by the *o*-phenylene chlorophosphite,[2] diethyl chlorophosphite,[3] tetraethyl pyrophosphite,[3] phosphorazo[4] and *sec*-butyl chlorocarbonate[4] methods of peptide synthesis. We wish to report that the use of the tetraethyl pyrophosphite or N,N′-dicyclohexylcarbodiimide reagents for the preparation of asparaginyl-S-benzyl-cysteine peptides leads to the formation of compounds having the composition of anhydrides of the expected products, in addition to the expected protected peptides. The coupling of carbobenzoxy-L-asparagine with S-benzyl-L-cysteine methyl ester by the pyrophosphite procedure in diethyl phosphite solution gave the expected product ($C_{23}H_{27}O_6N_3S$, m.p. 199–200°) in 35% yield, and 27% of a compound of m.p. 128–129°, $[\alpha]^{24}D$ −42.1° (*c* 1, acetic acid) (*Anal.* Calcd. for $C_{23}H_{25}O_5N_3S$: C, 60.6; H, 5.53; N, 9.22; S, 7.04. Found: C, 60.6; H, 5.73; N, 9.11; S, 7.08). The use of dicyclohexylcarbodiimide in tetrahydrofuran solution for this coupling gave 39% of the protected dipeptide ester and 26% of the anhydro compound. Treatment of tosyl-L-glutaminyl-L-asparagine and S-benzyl-L-cysteine benzyl ester with dicyclohexylcarbodiimide in dimethylformamide solution yielded 40% of the tosyl tripeptide ester, m.p. 228–229°, $[\alpha]^{23}D$ −30.7° (*c* 1, dimethylformamide) (*Anal.* Calcd. for $C_{33}H_{39}O_8N_5S_2$: C, 56.8; H, 5.63; N, 10.0; S, 9.17. Found: C, 56.6; H, 5.75; N, 10.0; S, 9.04), and 15% of its anhydro derivative, m.p. 210–211°, $[\alpha]^{23}D$ −33.5° (*c* 1, dimethylformamide) (*Anal.* Calcd. for $C_{33}H_{37}O_7N_5S_2$: C, 58.0; H, 5.40; N, 10.3; S, 9.43. Found: C, 58.0; H, 5.56; N, 10.3; S, 9.14). No by-product of the type described could be detected when carbobenzoxy-L-asparaginyl-S-benzyl-L-cysteine methyl ester was prepared in tetrahydrofuran solution through the mixed anhydrides of carbobenzoxy-L-asparagine with carboxylic or alkyl carbonic acids. The best preparative procedure employed isovaleryl chloride to form the mixed anhydride, and gave a 58% yield of the protected dipeptide ester.

Dehydration took place to a lesser extent during the preparation of carbobenzoxy-L-glutaminyl-S-benzyl-L-cysteine methyl ester. Tetraethyl pyrophosphite in diethyl phosphite gave a 70% yield of the expected product, m.p. 201°, $[\alpha]^{23}D$ −28.0° (*c* 1, dimethylformamide) (*Anal.* Calcd. for $C_{24}H_{29}O_6N_3S$: C, 59.1; H, 5.99; N, 8.62. Found: C, 59.2; H, 6.07; N, 8.53), and only 5% of the anhydro compound, m.p. 103–104°, $[\alpha]^{23}D$ −35.0° (*c* 1, dimethylformamide) (*Anal.* Calcd. for $C_{24}H_{27}O_5N_3S$: C, 61.4; H, 5.75; N, 8.94. Found: C, 61.7; H, 5.90; N, 8.75). The dicyclohexylcarbodiimide coupling, in tetrahydrofuran solution, gave 76% of the protected dipeptide ester, and no detectable anhydro compound.

(1) Alteration of asparagine during the course of peptide synthesis using tetraethyl pyrophosphite has been independently demonstrated in this laboratory by C. Ressler (THIS JOURNAL, **78**, 5956 (1956)). In the synthesis of the cyclic disulfide of L-cysteinyl-L-tyrosyl-L-isoleucyl-L-glutaminyl-L-asparaginyl-L-cysteinamide, a side product was isolated in which it was found that the asparagine had undergone change.

(2) S. J. Leach and H. Lindley, *Aust. J. Chem.*, **7**, 173 (1954).

(3) R. A. Boissonnas, St. Guttmann, P.-A. Jaquenoud and J.-P. Waller, *Helv. Chim. Acta*, **38**, 1491 (1955).

(4) J. Rudinger, J. Honzl and M. Zaoral, *Collection Czechoslov. Chem. Communs.*, **21**, 202 (1956).

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RECEIVED AUGUST 15, 1956

ON THE MOLECULAR WEIGHT, SIZE AND SHAPE OF THE MYOSIN MOLECULE

Sir:

Despite progress in several laboratories on the macromolecular characterization of myosin, no conclusive results have hitherto appeared. Part of the difficulty has recently been ascribed to spontaneous, strongly temperature dependent, side-to-side molecular aggregation.[1] Consequently, the molecular unit can be studied only by extremely rapid preparation and experimental analysis of the protein, working entirely in the cold up to the moment of actual measurement. We present here a summary of results obtained observing these precautions.

(1) A. Holtzer, *Arch. Biochem. & Biophysics*, in press.