In the reaction of cyclohexene with ethylene both the carbanion and the free radical mechanisms were postulated to yield 3-ethylcyclohexene. However, ethylcyclohexene originating from the carbanion reaction showed a strong infrared band which is characteristic of a trisubstituted olefin, whereas the ethylcyclohexene resulting from the thermal reaction was predominantly a *cis*-olefin. A similar trend was found also in the carbanion and free radical reactions of the other alkylcyclohexenes. These results are not entirely unexpected since it was observed previously that the catalyst used in the carbanion reactions catalyses migration of double bonds.[8,10a,b,16,17]

Experimental Part

Materials.—Ethylene, propylene, 1-butene and isobutylene were of 99.0% purity (The Matheson Co., Inc.).

Cyclohexene (Eastman Organic Chemicals) was purified by treating with acidic ferrous ammonium sulfate, drying and distilling.

Cyclopentene was prepared by dehydrating cyclopentanol over activated alumina (The Harshaw Chemical Co.) at 420–430°, yield 77%, b.p. 43°, $n^{20}_{\rm D}$ 1.4230.

Apparatus and Procedure.—Carbanion reactions were carried out in a 250-ml. capacity Magne-Dash autoclave[18] using the procedure described previously.[1a] Thermal reactions also were carried out in the same autoclave, except for experiments 7–10 in which a rocking autoclave[19] of one liter capacity was used.

Analytical Procedure.—Infrared spectroscopy was used for qualitative and quantitative analysis. Individual hydrocarbons were identified by matching their spectra with those of synthetic specimens. Quantitative determinations were made by matching band intensities. A double beam spectrophotometer[20] was used in this work.

Displacement chromatography on silica gel[21] (Davison Chemical Co.) was used to separate hydrocarbon mixtures into saturated, olefinic and aromatic fractions, respectively.

Refractive indices were determined at 20°. In some cases quantitative determinations of mixtures of hydrocarbons were made using the linear relationships in the refractive indices.[22]

Distillations were made, in most of the experiments, in a 40 × 1 cm. column which was packed with stainless steel gauze.

Gaseous compounds were analyzed by means of a mass spectrometer.

3-Isobutylcyclohexene was prepared from 3-bromocyclohexene and isobutylmagnesium bromide.

3-Bromocyclohexene was prepared by the method of Ziegler[23] from 2.5 moles of freshly distilled cyclohexene, 0.5 mole of N-bromosuccinimide and 370 ml. of carbon tetrachloride as solvent. The product distilled at 62° at 28 mm., $n^{20}_{\rm D}$ 1.5300, yield 71%.

The reaction of isobutylmagnesium bromide (prepared from 0.4 mole of isobutyl bromide, 0.4 g. atom of magnesium in 180 ml. of dry ether with 3-bromocyclohexene (0.35 mole in 50 ml. of ether)) yielded 0.15 mole, 43%, of 3-isobutylcyclohexene, b.p. 53° at 10 mm., $n^{20}_{\rm D}$ 1.4550, and 8.7 g. of a product, b.p. 85° at 4 mm., $n^{20}_{\rm D}$ 1.5090. The higher boiling compound is believed to be 3-(2-cyclohexenyl)-cyclohexene.

The crude 3-isobutylcyclohexene after passing over silica gel yielded a bromine free hydrocarbon of $n^{20}_{\rm D}$ 1.4530.

Alkylcyclohexanes.—The reference alkylcyclohexanes, which were required for infrared spectral analyses, were made by hydrogenation of the corresponding aromatic hydrocarbons.

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

EVANSTON, ILLINOIS

---

[16] H. Pines and H. E. Eschinazi, THIS JOURNAL, **78**, 1178 (1956).

[17] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955).

[18] Autoclave Engineers, Inc., Erie, Pa.

[19] American Instrument Co., Silver Spring, Md.

[20] Baird Associates, Inc., Cambridge, Mass.

[21] B. J. Mair, *J. Research Natl. Bur. Standards*, **34**, 435 (1945).

[22] S. S. Kurtz in "The Chemistry of Petroleum Hydrocarbons," edited by B. T. Brooks, C. E. Boord, S. S. Kurtz and L. Schmerling, Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 315.

[23] K. Ziegler, *Ann.*, **551**, 110 (1942).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. XXIX.[1] Sodium-catalyzed Aromatization of Geminal Alkylcyclohexadienes. Synthesis of 5-Methyl-5-ethyl-1,3-cyclohexadiene[2,3]

BY HERMAN PINES AND H. E. ESCHINAZI[4]

RECEIVED MAY 28, 1956

Geminal alkylcyclohexadienes or their double bond isomers underwent aromatization with the loss of an alkane when refluxed in the presence of a sodium–organosodium catalyst. 5,5-Dimethyl-3-methylenecyclohexene and the conjugated 1,1,3-trimethylcyclohexadienes underwent a reversible isomerization and aromatization to *m*-xylene with a loss of methane. α-Pyronene was converted to 1,2,3-trimethylbenzene and methane when refluxed in the presence of sodium–benzylsodium catalyst. 5-Methyl-5-ethyl-1,3-cyclohexadiene underwent a competitive reaction; toluene and ethylbenzene were formed, the latter predominating. The gases were composed of methane and of a smaller amount of ethane. The mechanism of aromatization is discussed. The synthesis of 5-methyl-5-ethyl-1,3-cyclohexadiene is described.

It was previously shown that monocyclic terpenes such as limonene,[5,6] *l*-α-phellandrene,[6] 2,4(8)- and 3,8(9)-*p*-menthadiene[6] undergo isomerization and dehydrogenation to *p*-cymene when refluxed in the presence of sodium and an organosodium compound. Monocyclic dihydroterpenes, namely, *p*-menthenes, undergo racemization and reversible isomerization but not dehydrogenation.[7] Inasmuch as some of the monocyclic terpenes which are being studied in our laboratory contain a geminal carbon atom in the cyclohexadiene ring,[1,8] it was of interest

---

[1] For paper XXVIII of this series see H. Pines and R. H. Kozlowski, THIS JOURNAL, **78**, 3776 (1956).

[2] Paper VII of the Series of Base Catalyzed Reactions. For VI see V. Mark and H. Pines, *ibid.*, **78**, 5946 (1956).

[3] Reported in part before the Division of Organic Chemistry, American Chemical Society Meeting, Dallas, Texas, April 8 to 13, 1956.

[4] Vladimir Ipatieff Post-doctoral Fellow, 1953–1955.

[5] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

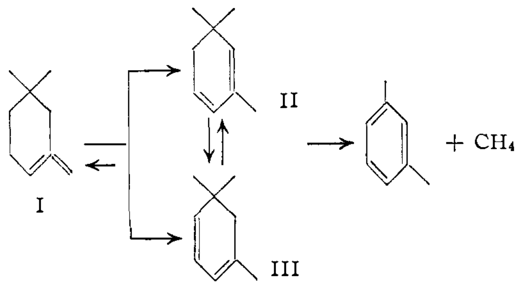
[6] H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

[7] H. Pines and H. E. Eschinazi, *ibid.*, **78**, 1178 (1956).

[8] H. Pines and J. Ryer, *ibid.*, **77**, 4370 (1955).

to determine whether such hydrocarbons would undergo aromatization by the elimination of one of the alkyl groups attached to the geminal carbon atom.

5,5-Dimethyl-3-methylenecyclohexene (I).—This hydrocarbon undergoes conversion to the two isomeric 1,1,3-trimethylcyclohexadienes (II and III) and demethanation to *m*-xylene when refluxed in the presence of sodium–benzylsodium catalyst.



The course of the reaction was followed by withdrawing at various intervals samples of the continuously renewed condensate, according to the procedures described previously.[6] The composition of the various samples, which was determined by means of infrared spectral analysis, is summarized in Table I.

TABLE I

COMPOSITION OF THE PRODUCTS OBTAINED FROM THE SODIUM-CATALYZED REACTION OF 5,5-DIMETHYL-3-METHYLENECYCLOHEXENE

Duration of expt., hr.	Composition of condensate			Gas produced mole %
	m-Xylene	I	II + III	
4.5	2	91	7	6
8	24	57	19	17
11.5	61	25	14	63
15	82	10	8	85
24	100	0	0	105[a]

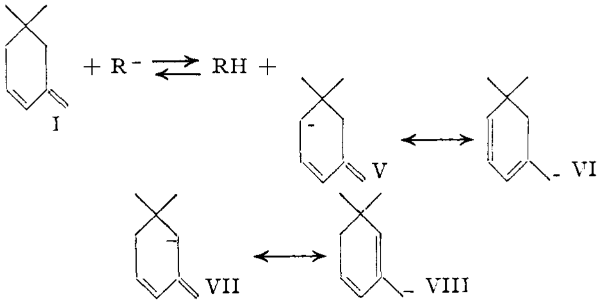
[a] Composed of 95% methane and 5% hydrogen.

The extent of *m*-xylene formation parallels the amount of gas formed. It is interesting to note that the concentration of compounds II and III, which have the two double bonds in the ring, increases in relation to compound I with the duration of the experiment. In a similar study with exo- or semicyclic *p*-menthadienes an isomerization to endocyclic *p*-menthadienes, namely, α- and β-phellandrene, was not observed.[6] It was suggested that the phellandrene, once formed, underwent a rapid dehydrogenation to *p*-cymene. The relatively more rapid aromatization of phellandrenes than that of 1,1,3-trimethylcyclohexadienes is not too surprising since the formation of *p*-cymene from phellandrenes involves, according to the suggested mechanism,[6] a loss of a hydride ion, while in the formation of *m*-xylene from either compound I or II, a methide is eliminated. It was shown previously that a hydride ion is more stable than a methide and therefore the former would be produced with greater ease than the latter.[9]

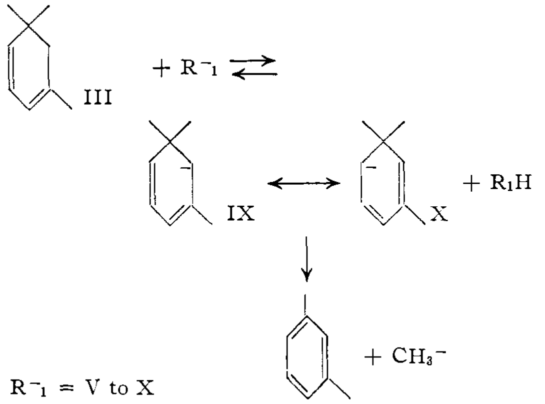
1,1,3-Trimethylcyclohexadienes (II and III).—These hydrocarbons on refluxing in the presence of sodium–organosodium catalyst underwent demethanation to *m*-xylene. A small amount of compound I, less than 1% based on the starting material, was also present in the condensate. When the reaction was permitted to proceed to completion, almost a quantitative yield of *m*-xylene was produced. These results show that geminal endocyclic cyclohexadienes, unlike α-phellandrene,[6] may undergo a double bond rearrangement to form the semicyclic isomer I.

α-Pyronene (1,5,5,6-Tetramethyl-1,3-cyclohexadiene) (IV).—This terpene underwent demethanation to 1,2,3-trimethylbenzene when refluxed in the presence of sodium–benzylsodium catalyst.

Mechanism.—The isomerization and aromatization of the hydrocarbons described above (compounds I–IV) seems to proceed by an ionic mechanism similar to the one suggested previously[6] and which can be illustrated by the following scheme, using compound I as an example.



$$\mathrm{VI} + \mathrm{I} \rightleftarrows \mathrm{III} + \mathrm{V} \text{ or } \mathrm{VII}$$



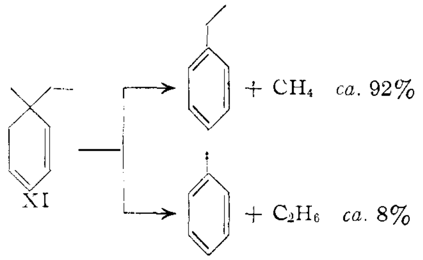
$$\mathrm{I, II \text{ or } III} + \mathrm{CH_3^-} \longrightarrow \mathrm{R^-_1} + \mathrm{CH_4}$$

5-Methyl-5-ethyl-1,3-cyclohexadiene (XI).—The proposed mechanism for the aromatization of a geminal polymethylcyclohexadiene involves the intermediate formation of an alkylcarbanion. For that reason, barring steric factors, it should be possible to determine the relative stabilities of alkylcarbanions from the composition of alkanes produced from the aromatization of geminal alkylcyclohexadienes, in which the alkyl groups are different. In order to determine the relative stability of a methide and an ethide ion, 5-methyl-5-ethyl-1,3-cyclohexadiene (XI) was synthesized and subjected, at its reflux temperature, to the action of a sodium–benzyl sodium catalyst. The liquid product consisted of toluene and ethylbenzene and the gases of methane and ethane.

Thus it can be concluded that the relative stabilities of $CH_3^-/C_2H_5^-$ were about 12/1. The lower

---

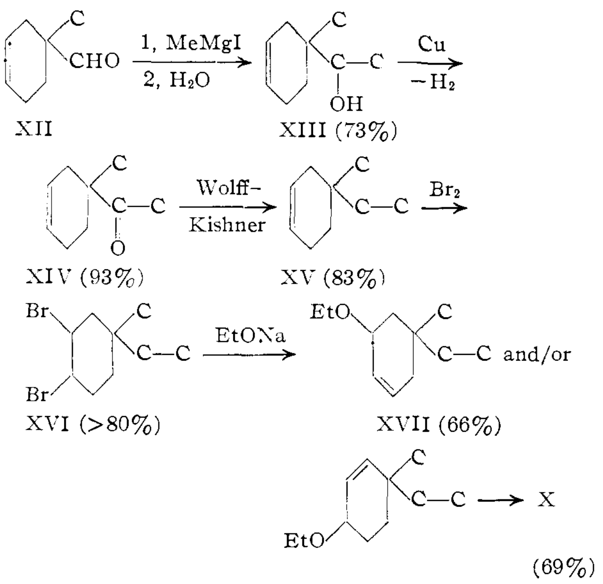
[9] H. Pines and V. Mark, THIS JOURNAL, **78**, 4316 (1956).



stability of an ethyl as compared with methylcarbanion may be due to the inductive effect of a methyl group. Such an effect also was observed in the study of the addition of arylcarbanions[9] and alkylcarbanions[2] to olefinic hydrocarbons.

Unlike sodium-catalyzed reaction, the pyrolysis of 1,5-dimethyl-5-ethyl-1,3-cyclohexadiene, which is similar in structure to compound XI, yielded 4 mole equivalents of *m*-xylene per mole equivalent of *m*-ethyltoluene.[8] The pyrolytic reaction showed that the ethyl group is removed in preference to the methyl group from the geminal carbon atom in cyclohexadiene ring. Since the pyrolytic reactions proceed *via* a free radical mechanism, the results can be interpreted by the greater stability of the ethyl over the methyl free radical.[10]

The synthesis of 1,5,5-trimethylcyclohexadiene-(III) and its double bond isomers I and II was described previously.[1] 5-Methyl-5-ethyl-1,3-cyclohexadiene (XI), which is a new compound, was prepared according to the sequence of reactions shown below. It was assumed that the position of the double bonds in XIV is the same as in XXIII, since copper even at much higher temperatures does not cause a shift of a double bond.[11]



Experimental

Materials.—1,5,5-(III),3,5,5-Trimethyl-1,3-cyclohexadiene (II) and 5,5-5,5-Dimethyl-3-methylenecyclohexene (I).—These dienes were prepared by R. H. Kozlowski.[1]

α-Pyronene was obtained through the courtesy of Dr. J. P. Bain.[12]

Synthesis of 5-Methyl-5-ethyl-1,3-cyclohexadiene (XI). a. **4-Methyl-4-formylcyclohexene (Methyl-3-cyclohexenylcarboxaldehyde) (XII).**—This aldehyde was prepared by a previously described method.[13]

b. **1-(Methyl-3-cyclohexenyl)-ethanol (XIII).**—This alcohol was prepared by allowing XII to react with methylmagnesium bromide, according to the procedure described previously[14], b.p. 90–91° at 14 mm., n^{20}_D 1.4852.

c. **Methyl 1-Methyl-3-cyclohexenyl Ketone (XIV).**—Compound XIII, 0.54 mole, was passed in a period of 9 hr. over reduced copper oxide wire (from the reduction of CuO at 350°, yielding 37 ml. of water) at 350° in a tube 60 cm. long and 12 mm. in diameter. About 14 liters of hydrogen was formed; the liquid product obtained from the reaction had a refractive index of n^{20}_D 1.4700. After a second passage over the same catalyst an additional 1.8 liters of gas was formed. The ketone distilled at 82–84° at 25 mm., n^{20}_D 1.4685.

Anal. Calcd. for $C_9H_{14}O$: C, 78.28; H, 10.15. Found: C, 78.62; H, 10.08.

d. **4-Methyl-4-ethylcyclohexene (XV).**—This hydrocarbon was prepared by means of a Wolff–Kishner reduction of 0.52 mole of XIV. The reduction was made according to the general procedure of Huang-Minlon,[15] slightly modified.[13]

The hydrocarbon XV, 52 g., distilled at 151–151.5° at 755 mm., n^{20}_D 1.4530, d^{20}_4 0.8165; MR_D calcd. 41.09, found 41.05.

Anal. Calcd. for C_9H_{16}: C, 87.03; H, 12.97. Found: C, 87.16; H, 12.78.

e. **1-Methyl-1-ethyl-3,4-dibromocyclohexane (XVI).**—The olefin XV, 0.26 mole, was dissolved in 30 ml. of acetic acid and brominated under cooling at 20° with a 50% solution of 0.25 mole of bromine in acetic acid. The reaction mixture was treated with water. The organic layer was dissolved in a small amount of benzene, then washed with a sodium bisulfite solution, then by dilute alkali and finally dried over potassium sulfate. The dibromide XV distilled at 118–120° at 7 mm., n^{20}_D 1.5274.

Anal. Calcd. for $C_9H_{16}Br_2$: C, 38.05; H, 5.62. Found: C, 38.60; H, 5.60.

f. **3-Ethoxy-5-methyl-5-ethyl- and/or 3-Ethoxy-6-methyl-6-ethylcyclohexene (XVII).**—XVI, 0.21 mole, was added to a sodium ethylate solution in ethanol, obtained from 20 g. of sodium and 500 ml. of absolute ethanol. The reactants were refluxed for a period of 5 hr. under stirring while 28 g. of sodium bromide precipitated from the hot solution. After decantation and washing of the sodium bromide with ethanol the reaction was continued for 3 more hours; an additional 5 g. of sodium bromide was precipitated out. The reaction mixture was poured over ice, extracted with ether, dried and distilled: 1, b.p. 55–65° at 25 mm., 4.2 g., n^{20}_D 1.4608; 2, b.p. 97–98° at 25 mm., 21 g., n^{20}_D 1.4563. Cut 1 on redistillation yielded a plateau at 143–144°, n^{20}_D 1.4644, which showed evidence of conjugation in the ultraviolet spectrum at 258 mμ. Cut 2 consisted of XVII, it was contaminated with a bromide as evidenced by the positive Beilstein test.

g. **5-Methyl-5-ethylcyclohexadiene (XI).**—The allyl ether XVII, 0.13 mole, was mixed with 25 g. of finely powdered potassium bisulfate in a flask which was provided with a thermometer, dipping in the reaction mixture, and a condenser. At 176–180° a sudden reaction took place and the temperature dropped to 160°. The hydrocarbon distilled off with the ethanol; near the end of the reaction a slight vacuum was applied. Ten grams of a crude diene, XI, was obtained which distilled at 144.5°, n^{20}_D 1.4658, d^{20}_4 0.8239; MR_D calcd. 40.38, found 41.00; ϵ_{mol} 4395 at 257 mμ.

Anal. Calcd. for C_9H_{14}: C, 88.52; H, 11.48. Found: C, 88.90; H, 11.18.

Compound XI, 1 g., on hydrogenation in the presence of platinum oxide formed 1-methyl-1-ethylcyclohexane which was identical, according to infrared spectra, with the previously reported hydrocarbon.[13]

---

(10) Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954.

(11) (a) V. N. Ipatieff, W. D. Huntsman and H. Pines, THIS JOURNAL, **75**, 6222 (1953); (b) H. Pines, N. E. Hoffman and V. N. Ipatieff, *ibid.*, **76**, 4412 (1954); (c) H. Pines and J. Ryer, *ibid.*, **77**, 4371 (1955).

(12) The Glidden Co., Jacksonville, Florida.

(13) H. Pines, F. J. Pavlik and V. N. Ipatieff, THIS JOURNAL, **73**, 5738 (1951).

(14) H. Pines and J. Marechal, *ibid.*, **77**, 2819 (1955).

(15) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

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).