

CarrierFree Radioisotopes from Cyclotron Targets. IX. Preparation and Isolation of Re 183, 184 from Tantalum

Jeanne D. Gile, Warren M. Garrison, and Joseph G. Hamilton

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TABLE I. Observed absorption frequencies and molecular constants for tertiary butyl halides.

	Transition $J \rightarrow J+1$	Frequency (Mc/sec.) ^a	B (Mc/sec.)	I_B (g cm ²)
(CH ₃) ₃ CCl ¹⁸	4→5	30150	3016	278.2 × 10 ⁻⁴⁰
	5→6	36210		
	6→7	42200		
(CH ₃) ₃ CCl ¹⁷	4→5	29530	2954	284.1 × 10 ⁻⁴⁰
	5→6	35460		
	6→7	41330		
(CH ₃) ₃ CBr ⁷⁹	6→7	28610	2044	410.5 × 10 ⁻⁴⁰
	7→8	32690		
	8→9	36790		
	9→10	40885		
(CH ₃) ₃ CBr ⁸¹	6→7	28610	2028	413.7 × 10 ⁻⁴⁰
	7→8	32690		
	8→9	36790		
	9→10	40885		
(CH ₃) ₃ CI ¹²⁷	8→9	28085	1562	537.7 × 10 ⁻⁴⁰
	9→10	31185		
	10→11	34310		
	11→12	37490		
	12→13	40570		

^a ±30 Mc/sec.

TABLE II. Carbon halogen distances.

Link	Tertiary butyl halides ^a		Methyl halides ^b	Added covalent radii ^c
	with ∠CCC = 111° 30'	with ∠CCC = 109° 28'		
CCl	1.82A	1.78A	1.779	1.78
CBr	1.98	1.94	1.936	1.93
CI	2.19	2.14	2.139	2.12

^a Here $d_{CC} = 1.54A$, $d_{CH} = 1.093$ and $\angle HCH = 109^\circ 28'$ are assumed.^b From Gordy, Simmons, and Smith, *Phys. Rev.* **74**, 243 (1948).^c The revised value 0.99A for the C radius proposed by Gordy (J. Chem. Phys. **15**, 81 (1947)) is used with the halogen radii from Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.

plex. These are principally the nuclear coupling of the halogen, the separation of the lines of different K by centrifugal stretching, and the torsional oscillation or restricted internal rotation of the CH₃ groups. There is also the question whether the molecules behave exactly like symmetric-top rotators. Without a complete analysis of the structure of the spectra, it was found possible to prove the symmetric-top configuration and to obtain the moments of inertia, I_B , to better than one percent accuracy.

Because of their large moments of inertia it was convenient to observe the lines of rather high J . A similar series of lines was observed for each transition. One line was prominent in each series. From qualitative considerations it is possible to conclude that this strong line is not likely more than two to four megacycles from the position of the unperturbed rotational transition of the ground vibrational state. Also, it appears that the displacement of this line for neighboring transitions is very nearly the same, probably within a megacycle of the same amount. This may be seen by substituting reasonable values for the centrifugal stretching and nuclear coupling constants in the appropriate equations. It is evident that for high J the lines of low K have the smallest perturbations from both nuclear coupling and centrifugal effects. For high J the nuclear coupling alone would produce an approximately symmetric group of lines with the stronger ones near the center of symmetry. We assume that the strongest line is for the ground vibrational state.

Table I lists the frequencies of the observed transitions, the B values and the moments of inertia, I_B . Table II gives the carbon-halogen distances obtained from these, with assumed values for other parameters. The chloride and bromide have been measured with electron diffraction.¹ For each the value $d_{CC} = 1.54 \pm 0.02A$ and $\angle CCC = 111.5^\circ \pm 2^\circ$ were obtained with $d_{CCl} = 1.78 \pm 0.03$ and $d_{CBr} = 1.92 \pm 0.03$. This value for angle CCC appears incompatible

with reasonable values for the bond lengths (see Table II). The present work indicates that this angle is tetrahedral or very nearly tetrahedral, and that the carbon halogen distances are essentially the same as those of the methyl halides.

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† Texas Company Fellow.

‡ J. W. Beach and D. P. Stevenson, *J. Am. Chem. Soc.* **60**, 475 (1938).

Carrier-Free Radioisotopes from Cyclotron Targets. IX. Preparation and Isolation of Re 183, 184 from Tantalum*

JEANNE D. GILE, WARREN M. GARRISON, AND JOSEPH G. HAMILTON
*Crocker Laboratory, Radiation Laboratory, and Divisions of Medical Physics,
Experimental Medicine, and Radiology, University of California,
Berkeley and San Francisco, California*

May 8, 1950

THE long-lived radioisotopes¹ of rhenium, Re^{183, 184}, were produced by bombardment of tantalum with 40-Mev alpha-particles in the 60-inch cyclotron at Crocker Laboratory. At this energy, radioactive rhenium is produced² by the nuclear reactions; Ta¹⁸¹(α, n)Re¹⁸⁴, Ta¹⁸¹($\alpha, 2n$)Re¹⁸³, Ta¹⁸¹($\alpha, 3n$)Re¹⁸². 46-day Hf¹⁸¹ is produced concurrently by (n, p) reaction. The short-lived² activities (Re¹⁸² and isomer of Re¹⁸⁴) were allowed to decay out prior to the chemical separation reported here.

A C.P. tantalum metal target ($\frac{1}{4}$ in. Ta strip, silver-soldered to a water-cooled copper plate) was bombarded for a total of 80 μ a-hr. at a maximum beam intensity of 10 μ a. The bombarded surface (approximately 0.5 g) was removed by milling and dissolved in a minimum volume of 16 N HNO₃ containing 10 percent HF by volume. The HF was removed by evaporation and the bulk of the tantalum acid was separated by centrifugation with repeated reduction in volume of the HNO₃ solution. The carrier-free Re^{183, 184} as perhenate, was quantitatively retained in supernatant. The HNO₃ solution was evaporated almost to dryness and transferred to an all-glass³ distilling flask with 15 ml of 36 N H₂SO₄. 9 N HBr was added dropwise while a stream of CO₂ was bubbled through the H₂SO₄ solution at 240°C. The distillate, containing the carrier-free radio-rhenium, HBr, Br₂, and a small amount of H₂SO₄, was collected in a trap of 16 N HNO₃ cooled with ice. This solution was evaporated on a steam bath to the 1 ml volume of H₂SO₄ carried over in the distillation. The H₂SO₄ was diluted to 3 N and the Re^{183, 184} was co-precipitated with 2 mg of Cu⁺⁺ by the addition of H₂S. The CuS was dissolved in a minimum volume of dilute HNO₃. This solution was evaporated to dryness, diluted with water to 25 ml, heated to 60°C and neutralized with a stoichiometric amount of NaOH. Under these conditions CuO is precipitated without scavenging the carrier-free radio-rhenium. The supernatant was evaporated to dryness on 20 mg of added NaCl and re-dissolved quantitatively with the addition of 2 ml of water to give an isotonic saline solution of carrier-free Re¹⁸³ for subsequent biological investigation.

The activity was identified by chemical separation with carrier, by absorption measurements and by half-life determinations. A tracer amount of activity added to a solution containing carrier amounts of Ta, Hf, and Re was quantitatively recovered in the Re fraction following chemical separation.⁴ The radiation characteristics were obtained by aluminum and lead absorption measurements and showed the 0.2- and 0.8-Mev beta-particles and 1.0-Mev gamma-ray previously reported² for Re¹⁸⁴. 14 days after bombardment the activity showed an approximately 60-day half-life which began to lengthen perceptibly after 6 weeks. The difference between this value and the 52-day period previously found² for Re¹⁸⁴ is presumably due to the 240-day Re¹⁸³ which is produced concurrently.

We wish to thank Professor G. T. Seaborg for helpful sugges-

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² G. Wilkinson and H. G. Hicks, *Phys. Rev.* **77**, 314 (1950).

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Polymorphism of Cesium and Thallium Halides*

L. G. SCHULZ

Institute for the Study of Metals, University of Chicago, Chicago, Illinois
May 12, 1950

SALTS having the CsCl type crystal structure were deposited by evaporation in a vacuum onto cleavage surfaces of mica, LiF, NaCl, KBr, KI, and CaCO₃. The deposits were examined with electron diffraction using the methods previously employed.¹ It was found that those crystals in a deposit which touched the substrate very often had the NaCl type structure. There was considerable variation among the individual salts. CsCl and CsBr, for example, had a NaCl structure on all the substrate materials named above, whereas TlI had this structure only on LiF. In general the nature of the atomic matching at the interface was not the dominant factor in determining the structure of the deposit.

The lattice parameters, a_0 , of the new structure could be measured to about 0.3 percent and are listed in the second column of Table I. Also included in this table are (1) the interatomic

TABLE I.

Salt	a_0 , in Å NaCl-type	Interatomic distances in Å		Differences in interatomic distances in Å
		NaCl-type	CsCl-type	
CsCl	6.94	3.47	3.56	0.09
CsBr	7.23	3.62	3.72	0.10
CsI	7.66	3.83	3.95	0.12
TlCl	6.30	3.15	3.32	0.17
TlBr	6.58	3.29	3.44	0.15
TlI	6.94	3.47	3.64	0.17

distances in the NaCl type structure; (2) the interatomic distances in the CsCl type structure;² and (3) the differences of these two interatomic distances.

A more complete discussion of the experimental details and the significance of the results will be given later.

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The Exchange Reaction of Hydroxylamine and Gaseous Nitrogen

B. A. PETHICA, E. R. ROBERTS, AND E. R. S. WINTER
Department of Chemistry, Imperial College, London, England
May 10, 1950

DURING an isotope study of the role of hydroxylamine in biological nitrogen fixation, it became of interest to investigate the possibility of isotope exchange between hydroxylamine and gaseous nitrogen. Previous communications in this journal concerning such exchange have been conflicting. Nishina,¹ using radioactive N¹⁵, claimed to have demonstrated exchange with a variety of compounds, including sodium nitrite and hydroxylamine hydrochloride in aqueous solutions. Norris,² also using radioactive nitrogen, found very slight exchange with sodium

nitrite. Joris³ used a non-equilibrium mixture of the nitrogen isotopes N¹⁴ and N¹⁵ as the gas phase, and observed no change in the ratio N₂²⁹:N₂³⁰ when the mixture was enclosed over nitrite and hydroxylamine hydrochloride solution, and therefore concluded that exchange was absent. In view of the above disagreement it was considered advisable to reinvestigate this problem and also to examine exchange of nitrogen in a solution containing free hydroxylamine. The method used by Joris is open to the objection that hydroxylamine solutions are unstable, producing some gaseous products^{4,5} including N₂ and N₂O. N₂O could give rise to NO of mass 30 in the mass spectrometer. The experiments reported were carried out by exposing two solutions of hydroxylamine hydrochloride to a nitrogen atmosphere containing 10 percent N¹⁵. One solution comprised 0.1M NH₂·OH·HCl in distilled water, the other 0.1M NH₂·OH·HCl in a nitrogen free bacteriological culture medium buffered to pH 7.3. This latter solution contained largely free hydroxylamine. The exposure was for 24 hours at room temperature. The hydroxylamine was then reduced to ammonia, the solutions used being saturated with hydrogen to prevent any re-exchange with the atmosphere. The ammonia was quantitatively converted to gaseous nitrogen by means of sodium hypobromite and analyzed for N¹⁵. No exchange could be demonstrated in either solution, the mass spectrometer analyses showing no enrichment of N¹⁵. The absence of exchange between N₂ and NH₂·OH at a physiological pH is an additional argument against the suggestion by Virtanen⁶ that nitrogen fixation in legumes can occur by reversal of the reaction between NH₂·OH and hemoglobin.

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The Number of Unilateral Solute Impacts on Unit Surface in a Dilute Solution

HOWARD REISS

Department of Chemistry, Boston University, Boston, Massachusetts
May 4, 1950

IN a recent paper¹ the author discussed the rate of nucleation for a liquid phase transition. To compute this rate on an *a priori* basis it was necessary to know how many times each second any square centimeter of planar surface in a dilute solution was struck, on one side, by a solute molecule. The present letter provides this result, β_a , to a degree of accuracy sufficient for the above purpose.

If the solution is dilute, and Fick's law holds,² it can be shown by means of a stochastic procedure³ that the coefficient of diffusion, D , is given by

$$D = \frac{1}{6} n \langle l^2 \rangle, \quad (1)$$

where n is the jumping frequency and $\langle l^2 \rangle$ is the mean square jump length. If the average modulus of the jump length, $|l|$, is approximated by

$$|l| \simeq \langle (l^2) \rangle^{1/2}, \quad (2)$$

the average speed of progression of a solute molecule between impacts can be written in the form

$$\bar{v} = n |l| \simeq \frac{6D}{\langle (l^2) \rangle^{1/2}}. \quad (3)$$

We thus obtain \bar{v} in terms of the macroscopic parameter, D , and the modulus of the mean jump length, which can be nicely approximated by the distance between equilibrium positions in the liquid lattice. The latter cannot vary greatly from solution to solution and can be estimated when the molar volume of the solvent is known. The necessity for computing the difficult quantity, n , has been obviated. The issue of liquid partition functions and diffusional activation energies is therefore avoided.