Defining

$$D_1 = (1)_r/(1);\ D_2 = (2)_r/(2);\ D_3 = (3)_r/(3) \text{ and } D_0 = T_r/T \quad (15)$$

where D_0 is the observed distribution coefficient, D_1, D_2 and D_3 those of the "pure" species and T_r and T the concentrations of niobium in the resin and solution, respectively, setting (HF) = f and combining equations (13), (14) and (15) one obtains

$$D_0 = (D_1 + D_2K_{12}f^n + D_3K_{12}K_{23}f^{n+n'})/(1 + K_{12}f^n + K_{12}K_{23}f^{n+n'}) \quad (16)$$

In the limits, *i. e.*, when the two reactions do not overlap, equation (16) reduces to

$$D_0 = (D_1 + D_2K_{12}f^n)/(1 + K_{12}f^n)$$

and

$$D_0 = (D_2 + D_3K_{23}f^{n'})/(1 + K_{23}f^{n'}) \quad (17)$$

The 9 M HCl data could not be fitted to equation (16) taking $n = 1$ and $n' = 1$. Satisfactory agreement was obtained using $n = n' = 2$ as shown by the solid line Fig. 4 which represents the calculated values. The constants $D_1 = 415$, $D_2 = 1.0$, $D_3 = 60$, $K_{12} = 1.5 \times 10^4$ and $K_{23} = 1.25$ were evaluated by trial and error. They can only be considered rough approximations in view of the limited number of data available. An analogous calculation for the 3 M HCl data was not attempted since the slight increase in E at very high HF concentration suggests the formation of a fourth species. However, it is apparent that K_{23} must be at least a factor of 10 smaller in 3 M HCl than in 9 M HCl. Since niobium is known to form oxygenated ions (of the type $NbOX_n{}^{+3-n}$)[17] it appears reasonable to assume that species I and II contain one coördinated oxide ion. This would explain the great difference in anion exchange behavior of niobium and tantalum.[2,13,18] In species III the oxide ion has probably been replaced by fluoride ions. This would make plausible the great decrease in K_{23} with decreasing HCl concentration and the decrease in E as species III is formed since it would give a mechanism for a decrease in negative charge on addition of fluoride ions.

Acknowledgment.—It is a pleasure to acknowledge the valuable technical assistance of Mrs. Hazel Templeton and to thank Messrs. J. East, F. W. Manning, P. P. Williams and the Instrument maintenance group under R. E. Toucey for the assembly and the maintenance of the electronic equipment, Mr. F. King for the construction of the automatic scanner, and Dr. G. E. Boyd for many valuable discussions.

Summary

1. The behavior of zirconium(IV) and niobium(V) on the anion exchange resin Dowex-1 was studied in a number of HF–HCl mixtures.

2. Separation of the two elements is excellent under a number of conditions. Although zirconium is usually eluted first, the elements can be eluted in reverse order under some conditions.

3. Attempts have been made to interpret the data in terms of ionic species and their equilibria. In the case of niobium at least three species were observed in 9 M HCl differing by two fluoride ions each. The first two species, existing at low fluoride concentration, are probably oxygenated.

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[17] A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, Oxford, 1945, p. 424.

[18] In ref. (2) this difference was attributed to a difference in charge between the niobium and tantalum complexes and it was assumed that the more strongly adsorbed tantalum carries a greater negative charge. This was equivalent to the assumption that the cross-over point P would occur at chloride concentrations so high as to be practically unattainable in aqueous solutions. As pointed out above, this assumption now appears very unlikely.

OAK RIDGE, TENN. RECEIVED MAY 15, 1950

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

Anion Exchange Studies. II. Tantalum in Some HF–HCl Mixtures[1]

BY KURT A. KRAUS AND GEORGE E. MOORE

In the previous paper[2] results on the anion exchange behavior of niobium and zirconium in HCl–HF mixtures were given. This paper will deal with a similar study of tantalum and the subsequent one will deal with protactinium and a general discussion of the separation of the triad niobium, tantalum and protactinium.[3]

Experimental

Details of the general experimental procedure were given earlier.[2] Suffice it to repeat that the studies were carried out with Dowex-1 columns of *ca.* 0.023 sq. cm. cross-section at 25 ± 1°. Ta^{182} tracer (β-emitter, $T_{1/2} = 117$ d.)[4] was used, obtained by slow neutron bombardment of spectroscopically pure tantalum metal. Identity of the tracer was checked by standard radiochemical techniques. Elution rates were determined by monitoring the effluent and by direct scanning of the columns.

Results and Discussion

The results of the experiments are summarized in Table I where the molarities of HCl and HF of the eluents are given and the observed values of the elution constant E_{Ta} defined[2] as

$$E_{Ta} = dA/V \quad (1)$$

where d is the distance (cm.) the band maximum moves after passage of V ml. of eluent through a

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[1] This document is based on work performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] K. A. Kraus and G. E. Moore, THIS JOURNAL, **73**, 9 (1951).

[3] For a preliminary communication on the separation of niobium and tantalum see K. A. Kraus and G. E. Moore, *ibid.*, **71**, 3855 (1949).

[4] Information from "Table of Isotopes," by G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.*, **20**, 585 (1948).

column of cross-sectional area A sq. cm. In the last column of Table I are given calculated values of the formal first order elution constant E'_{Ta} defined as

$$E'_{Ta} = E_{Ta}/(Cl^-) \qquad (2)$$

(parentheses indicate molar concentrations).

TABLE I

ELUTION CONSTANTS OF TANTALUM IN HCl–HF MIXTURES

M HCl	M HF	$E_{Ta} \times 10^3$	$E'_{Ta} \times 10^4$
9.0	0.004	*ca.* 0.15	0.17
9.0	.01	8.0 ± 0.3[a]	8.9
9.0	.02	4.9	5.4
9.0	.05	4.4 ± 0.6[b]	4.9
9.0	.1	4.8 ± 0.3[a]	5.3
9.0	.18	4.7	5.2
9.0	1.0	5.8	6.4
9.0	6.9	25	27.8
3.0	0.1	1.2 ± 0.1[a]	4.0
3.0	0.5	1.1	3.7
3.0	2.0	2.2	7.3
3.0	5.0	5.6 ± 0.2[a]	18.7
3.0	10.0	15	50
3.0	17.3	36	120
0.5	0.1	0.28	5.6
0.5	0.5	0.32	6.4

[a] Average of two experiments with maximum deviation given. [b] Average of three experiments with maximum deviation given.

In 9 M HCl E_{Ta} is practically independent of HF concentration from *ca.* 0.02 to 1 M. It is similarly independent of HF concentration in 3 M HCl (0.1 to *ca.* 1 M) and 0.5 M HCl (0.1–0.5 M HF). It is of interest that in these "plateaus" E'_{Ta} is approximately constant (4–5 × 10^{-4}) suggesting[2] a charge of minus one and the formula TaX_6^- where X represents a chloride, fluoride, hydroxide or one-half oxide ion. The constancy of E'_{Ta} actually is surprisingly good since one might expect deviations due to changes in activity coefficients of the ions, particularly at the very high ionic strengths used. This, however, appears barely possible since both exchanging ions had unit charge, since essentially only one electrolyte determined the ionic strength and since only a ratio of activity coefficients is involved.

In 9 M HCl the plateau is bounded by two regions of increasing E_{Ta}. At high HF concentrations this increase is quite dramatic and apparently repeated in the 3 M HCl solutions. It will be discussed below. At low HF concentrations the increase is slight (factor of two) and is followed by an abrupt decrease. The extremely low value reached (E_{Ta} = *ca.* 1.5 × 10^{-4}) in 0.004 M HF is probably due to a polymerization or precipitation reaction of a practically neutral tantalum species. This is supported by the fact that adsorption behavior becomes irreversible. Thus a band first exposed to an 0.004 M HF–9 M HCl eluent will not move with E_{Ta} values given in Table I for higher HF concentrations until it exceeds *ca.* 0.02 M. Further support of the assumption of a polymerization or precipitation reaction comes from the slight increase in E_{Ta} in 9 M HCl–0.01 M HF. It is probably due to the loss of at least one fluoride ion, *e. g.*, according to the reaction

$$TaX_5F^- + H_3O^+ \rightleftarrows TaX_5 + HF + H_2O \qquad (3)$$

A molecularly dispersed neutral species TaX_5 should have E_{Ta} = *ca.* 3 (the theoretical maximum). Thus after a very small amount of TaX_5 is formed causing an increase in E_{Ta}, polymerization becomes the dominant reaction, fixing Ta on the resin and causing an abrupt decrease in E_{Ta}.

The increase in E_{Ta} at high fluoride concentrations is probably due to the formation of a new complex ion according to an equation of the type

$$TaX_5F^- + nHF + jH_2O \rightleftarrows H_{n-j}TaX_{5-m}F_{1+n}^{-1-j+m} + mX^- + jH_3O^+ \qquad (4)$$

with the equilibrium constant (molarity constant)

$$K_{12}^* = \frac{(2)}{(1)}\frac{h^jx^m}{f^n} \qquad (5)$$

where (2), (1), h, x and f are the concentrations of $H_{n-j}TaX_{5-m}F_{1+n}^{-1-j+m}$, TaX_5F^-, H_3O^+, X^- and HF, respectively. Letting D_1 and D_2 be the distribution coefficients (amount of Ta per cc. of resin/amount of Ta per cc. of solution) of the two species, E_{Ta} at constant HCl concentration should follow[2] the equation

$$E_{Ta} \approx \frac{f^nK_{12} + 1}{f^nK_{12}D_2 + D_1} \qquad (6)$$

where $K_{12} = K_{12}^*/h^jx^m$. It was found that the observed values of E_{Ta} follow equation (6) for $n = 2$ as shown in Table II. They could not be fitted for $n = 1$. For the calculations D_1 = 213 and 910 were used for 9 M and 3 M HCl, respectively. They are obtained from the values of E_{Ta} in the "plateaus," since approximately[2] $D = 1/E_{Ta}$. The computed distribution coefficients of the "pure" species (D_1 and D_2), their elution constants ($E(1)_{Ta}$ and $E(2)_{Ta}$) and the equilibrium constant K_{12} can be found in Table III.

TABLE II

OBSERVED AND CALCULATED VALUES OF E_{Ta}

(HF)	$E_{Ta} \times 10^3$ Calcd.	$E_{Ta} \times 10^3$ Obsd.
	A: 3 M HCl, D_1 = 910	
0.1	1.1	1.2
0.5	1.1	1.1
2.0	1.9	2.2
5.0	5.6[a]	5.6
10.0	16.8	15.0
17.3	36[a]	36
	B: 9 M HCl, D_1 = 213	
0.02	4.7	4.9
.05	4.7	4.4
.1	4.7	4.8
.18	4.7	4.7
1.0	5.8[a]	5.8
6.9	25[a]	25

[a] Constants calculated using these points.

TABLE III

ELUTION CONSTANTS, DISTRIBUTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS

HCl, M	$E(1)_{Ta}$	$E(2)_{Ta}$	D_1	D_2	K_{12}
9	0.0047	0.039	213	26.8	0.28
3	.0011	.092	910	10.9	0.18

The striking differences in the values of $E(1)_{Ta}$ and $E(2)_{Ta}$ as well as their different chloride dependence suggest that the charge of the product ion of equation 4 is more negative than −1. Since TaX_6^- is stable over a considerably larger HF concentration range than NbX_6^- and since the high reactivity of the latter ion was attributed to one oxide ion in the complex,[2] it appears that TaX_6^- is not oxygenated. Thus in reaction (4) probably only chloride ions could be liberated. The HCl dependence of K_{12} is remarkably small and the sum of chloride and oxonium ions liberated is therefore probably not larger than one. Hence, since $n = 2$, the most probable formula of the product tantalum complex becomes $HTaX_5F_3^{-2}$ and equation (4) reduces to

$$TaX_5F^- + 2HF + H_2O \rightleftarrows HTaX_5F_3^{-2} + H_3O^+ \quad (7)$$

The corresponding molarity constants K_{12}^* become 2.5 and 0.53 for 9 *M* HCl and 3 *M* HCl, respectively.

Summary

1. The anion exchange behavior of tantalum was studied for a number of HCl–HF mixtures. It was found to adsorb very strongly under most conditions, even in 9 *M* HCl.

2. The species TaX_5F^- and $HTaX_5F_3^{-2}$ have been tentatively identified and the molarity constants for the probable reaction

$$TaX_5F^- + 2HF + H_2O \rightleftarrows HTaX_5F_3^{-2} + H_3O^+$$

were estimated to be 2.5 and 0.53 for 9 *M* HCl and 3 *M* HCl solutions, respectively.

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The Oxidation of Free Methyl Radicals

BY J. H. RALEY, L. M. PORTER, F. F. RUST AND W. E. VAUGHAN

Introduction

The development of the free radical theory of hydrocarbon oxidation by molecular oxygen has resulted in general acceptance of the reaction

$$R + O_2 \longrightarrow ROO \quad (1)$$

(where R is a free radical derived from the hydrocarbon RH) as representative of the initial union of oxygen and a carbon atom in the original molecule. It is also recognized that, in many instances, the peroxy radical is converted to a hydroperoxide, ROOH, by interaction with RH or some other material serving as a hydrogen atom donor, and that subsequent processes are dependent on the behavior of this hydroperoxide. However, in the absence of an efficient hydrogen atom donor or in the presence of a sufficiently high free radical concentration, processes other than hydroperoxide formation must predominate. It was toward the elucidation of these steps that the present investigation was directed. Methyl was selected for study since it is the simplest alkyl radical and is conveniently obtained in high concentrations by the vapor phase decomposition of di-*t*-butyl peroxide.[1,2] In addition, the decomposition of methyl *t*-butyl peroxide was utilized as a source of certain free radicals believed to be intermediates in the methyl radical oxidation.

Experimental

Materials.—The preparation and purification of di-*t*-butyl peroxide and methyl *t*-butyl peroxide have been described previously.[3] Commercial oxygen and helium were used without further purification.

Method.—The apparatus was similar to that employed in kinetic studies of the vapor phase decomposition of di-*t*-alkyl peroxides.[1] Liquid di-*t*-butyl peroxide was forced into the 1-l. spherical reaction vessel by a small pressure of helium, and the decomposition of the vapor was followed for a short time. Oxygen was then admitted and its partial pressure estimated by interpolation of total pressure measurements before and after its introduction. Methyl *t*-butyl peroxide was admitted as a vapor by expansion from a 5-l. storage bulb since injection of the liquid resulted in instantaneous, complete decomposition.

The reaction was halted by opening the vessel to a trap held in a block of mercury and cooled by liquid nitrogen. The residual gas was then slowly pumped through a Dry Ice-cooled scrubbing trap to a calibrated reservoir, and duplicate samples were taken for mass spectrometric analysis. The temperature of the mercury block was then raised to −120° and a second portion of gas measured and sampled. At −120° ethane is readily separated from formaldehyde and other less volatile products. In most instances the condensate in the traps was dissolved in pyridine and aliquots taken for analysis.

Analysis.—**Methanol** was determined by a procedure similar to that of Elving and Warshowsky.[4] It was identified in the condensed product by conversion to the 3,5-dinitrobenzoate (m. p. 107–107.5°, lit. for CH_3OH 107.0°, mixed m. p. 107–107.3°).

***t*-Butyl alcohol** was taken as the difference between the methanol and total alcohol contents, the latter being determined by a modified procedure based on that described by Skrabal[5] and Fischer and Schmidt.[6]

Formaldehyde was estimated colorimetrically with chromotropic acid.[7,8]

Acetone was taken as the difference between the formaldehyde and total carbonyl contents, the latter being determined by the procedure of Mitchell, *et al.*[9]

Water was determined with the Karl Fischer reagent according to the procedure of Bryant, *et al.*[10] Because of the large number of components in the reaction product, the analysis for water was carried out preferably on the condensate from a duplicate run. The product was condensed directly into the reagent solution held in a collection trap at liquid nitrogen temperature, and a second portion of the reagent, handled in a similar manner except for exposure to reaction product, was used as a blank.

Free acid was titrated directly and assumed to be **formic.**

Di-*t*-butyl Peroxide and Oxygen.—The reaction of oxygen and free methyl radicals, the latter

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[1] Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).

[2] Rust, Seubold and Vaughan, *ibid.*, **70**, 95 (1948).

[3] Rust, Seubold and Vaughan, *ibid.*, **72**, 338 (1950).

[4] Elving and Warshowsky, *Ind. Eng. Chem., Anal. Ed.*, **19**, 1006 (1947).

[5] Skrabal, *Z. Anal. Chem.*, **119**, 222 (1940).

[6] Fischer and Schmidt, *Ber.*, **59**, 679 (1926).

[7] MacFadyen, *J. Biol. Chem.*, **158**, 107 (1945).

[8] Bricker and Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

[9] Mitchell, Smith and Bryant, THIS JOURNAL, **63**, 573 (1941).

[10] Bryant, Mitchell and Smith, *ibid.*, **62**, 3504 (1940).