The Distribution of Ruthenium Tetroxide between Carbon Tetrachloride and Aqueous Alkali, Acid, and Neutral Salt Solutions.

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Vapour-pressure and distribution measurements show that solutions of ruthenium tetroxide in water and carbon tetrachloride are ideal below 0·2M. The presence of neutral salts "salts-out" ruthenium tetroxide in a manner exactly analogous to that of other non-polar non-electrolytes, *e.g.*, benzene. Distribution experiments using dilute alkalis show that the tetroxide behaves as a weak acid with dissociation constant for the first hydrogen ion of $6 \cdot 8 \pm 0 \cdot 3 \times 10^{-12}$ in aqueous solution. Similar experiments with dilute acids indicate that it is probably also a very weak base of dissociation constant about $5 \cdot 7 \times 10^{-15}$. The acid dissociation constant is discussed in connection with the probable structure of RuO_4, using Kossiakoff and Harker's theory of inorganic oxy-acids as modified by Ricci (*J. Amer. Chem. Soc.*, 1948, **70**, 109).

Reduction of ruthenium tetroxide in carbon tetrachloride solutions produces bi- or tri-nuclear products (*J.*, 1952, 2682; and unpublished work). Since one would expect a symmetrical covalent molecule such as ruthenium tetroxide to be non-associated in carbon tetrachloride solution, it is of interest to verify that such polynuclear products are not the result of " pre-association " in solution. This may be done by both vapour-pressure and distribution studies. The analogous osmium tetroxide was examined in this manner by Anderson and Yost (*J. Amer. Chem. Soc.*, 1938, **60**, 1822) who concluded that their results indicated the existence of $(OsO_4)_4$ aggregates in carbon tetrachloride solution. Hildebrand and Scott (" Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, 1950, p. 220) however pointed out that the assumption of polynuclear species is unnecessary and that the observed deviations from ideality are satisfactorily explained on the basis of the difference in internal pressure of solute and solvent. By its distribution between carbon tetrachloride and aqueous alkalis osmium tetroxide was shown by Yost and White (*ibid.*, 1928, **50**, 81) to behave as a weak acid with dissociation constant 8×10^{-13} for the first hydrogen ion in aqueous solution. There is no reported study of ruthenium tetroxide solutions except a very brief mention that its acid dissociation constant is $1{\cdot}3 \times 10^{-12}$ (Silverman and Levi, Amer. Chem. Soc. 118th Meeting, 1950).

Since polynuclear products may be obtained by reducing dilute solutions (~0·1M) of ruthenium tetroxide in carbon tetrachloride, the present investigation has been confined to this low concentration range. More concentrated solutions have an unfortunate tendency to decompose to give ruthenium dioxide. The effect of neutral salts on the activity coefficient of ruthenium tetroxide in aqueous solution (" salting-out ") and the slight basic properties have been examined by distribution between carbon tetrachloride and aqueous acids.

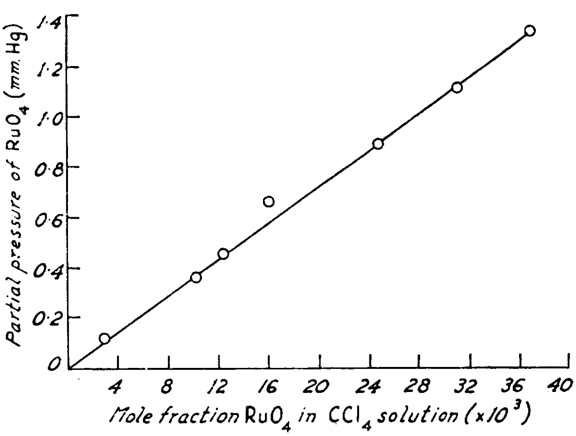


FIG. 1. *The partial pressure of* RuO_4 *in* CCl_4 *solutions at* 30°.

(*a*) *Vapour-pressure Measurements.*—The vapour pressure of ruthenium tetroxide in equilibrium with carbon tetrachloride solutions at 30° ± 0·1° was measured by a transpiration method over the concentration range 0—0·2M. Fig. 1 shows that the vapour pressure of the tetroxide is strictly proportional to its mole fraction in the liquid phase in this range and therefore Henry's law is obeyed. There is thus no detectable degree of association in these solutions below 0·2M.

(*b*) *Distribution between Water and Carbon Tetrachloride.*—This was measured over an approximately twenty-fold concentration range at 20°. The results in Table 1 show that there is no appreciable variation in the distribution coefficient *D*, whose mean value is

TABLE 1. *The distribution of ruthenium tetroxide between carbon tetrachloride and water at* 20°.

A, Molarity of RuO_4 in CCl_4 phase	*B*, Molarity of RuO_4 in H_2O phase	*D* = *A*/*B*	*A*, Molarity of RuO_4 in CCl_4 phase	*B*, Molarity of RuO_4 in H_2O phase	*D* = *A*/*B*
$11{\cdot}9 \times 10^{-2}$	$2{\cdot}05 \times 10^{-3}$	58·1	$5{\cdot}25 \times 10^{-2}$	$9{\cdot}00 \times 10^{-4}$	58·4
$6{\cdot}63 \times 10^{-2}$	$1{\cdot}15 \times 10^{-3}$	57·6	$3{\cdot}80 \times 10^{-2}$	$6{\cdot}30 \times 10^{-4}$	60·5
$5{\cdot}60 \times 10^{-2}$	$9{\cdot}60 \times 10^{-4}$	58·2	$5{\cdot}69 \times 10^{-3}$	$9{\cdot}64 \times 10^{-5}$	59·0
$5{\cdot}56 \times 10^{-2}$	$9{\cdot}70 \times 10^{-4}$	57·4			

58·4. Since the organic phase is ideal, the aqueous phase must also be virtually so, and there can be only negligible association or dissociation of the solute.

(*c*) *Distribution between Dilute Aqueous Alkali and Carbon Tetrachloride.*—By an argument analogous to that used for osmium tetroxide (Yost and White, *loc. cit.*), it is shown that the acid dissociation constant of ruthenium tetroxide is given by $K_a = K_w(D - D')/[OH^-]D'$, where D is the distribution coefficient from pure water into carbon tetrachloride and D' that from the hydroxide solution whose concentration is given by $[OH^-]$. Table 2 presents values of K_a calculated by the above equation with $D = 58{\cdot}4$, which are satisfactorily constant, the mean being $6{\cdot}8 \pm 0{\cdot}3 \times 10^{-12}$. For hydroxide concentrations below 0·01N results were reproducible, but in more alkaline solutions reduction to ruthenate slowly occurred. As the hydroxide concentration approached normality reduction became very rapid. For the low hydroxide-ion concentrations in Table 2, activity coefficient corrections have been neglected.

TABLE 2. *Distribution of ruthenium tetroxide between carbon tetrachloride and sodium hydroxide solutions.*

Aqueous phase, [NaOH] (10^{-3} M)	$[RuO_4]_{CCl_4}$ (M)	$[RuO_4]_{aq.}$ (10^{-3} M)	D	$10^{12}K_a$
0·943	0·128	3·59	35·6	6·7
0·943	0·120	3·42	35·1	6·9
0·943	0·0427	1·19	36·0	6·5
1·886	0·0435	1·72	25·3	6·8
1·886	0·0377	1·51	25·0	7·0
9·43	0·0287	3·64	7·9	6·7

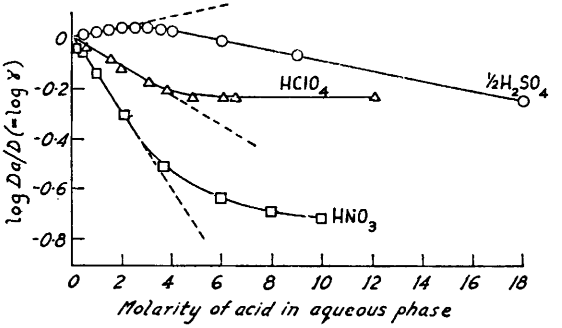


FIG. 2. *The distribution of* RuO_4 *between* CCl_4 *and aqueous acids.*

(*d*) *Distribution between Aqueous Neutral Salt Solutions and Aqueous Acids, and Carbon Tetrachloride.*—If the formation of acid in aqueous ruthenium tetroxide is due to the combination of solute and solvent, *e.g.*, $RuO_4 + H_2O \rightleftharpoons H_2RuO_5 \rightleftharpoons H^+ + HRuO_5^-$, there also exists the possibility of basic character, *e.g.*, $H_2RuO_5 \rightleftharpoons HRuO_4^+ + OH^-$. Distribution experiments similar to those reported in the previous paragraph, but using acids in the region of 0·01M, revealed no prominent decrease in D. However, as the acid concentrations were increased D decreased significantly. The experimental results for sulphuric, nitric, and perchloric acids are presented in Fig. 2, in the form of log D_a/D where D_a is the distribution coefficient for the aqueous solution. These results do not categorically indicate the presence of basic properties in ruthenium tetroxide since for these high electrolyte concentrations salting-out effects become prominent. Should aqueous acids have negative salting-out effects (salting-in) towards ruthenium tetroxide, the decrease (if any) in D_a due to acid–base interaction would be enhanced. Many theories have been advanced to account for salting-out effects on non-electrolytes (see McDevit and Long, *J. Amer. Chem. Soc.*, 1952, **74**, 1773; *Chem. Reviews*, 1952, **51**, 119) but none of these can predict with sufficient accuracy the quantitative salting-out effect to allow for this in the present case. However, comparison of the salting-out of ruthenium tetroxide by neutral salts with that of other non-polar non-electrolytes, *e.g.*, benzene (data from McDevit and Long, *loc. cit.*), shows that it follows the same general rules, *i.e.*, for electrolytes with a common anion the salting-out effect decreases in the order $Na^+ > K^+ > Li^+ > H^+$, and the effects of the different ions seem to be additive. Hence by comparing the decrease in salting-out efficiency in this series for ruthenium tetroxide with that for benzene, it is possible to observe any abnormal decrease on passing from Li^+ to H^+ for ruthenium tetroxide.

The simple Setchenow equation for the salting-out effect of electrolytes on non-electrolytes, when modified for distribution experiments, becomes $\log D_a - \log D = kc$, where D_a is the distribution coefficient of the non-electrolyte from aqueous solution of electrolyte concentration c, and k is the salting-out coefficient. D_a is proportional to the activity coefficient of the non-electrolyte in the aqueous phase; for dilute solutions in pure water this may be taken as unity. Hence we also have $\log \gamma = kc$ where γ $(= D_a/D)$ is the activity coefficient of non-electrolyte in aqueous solution containing electrolyte concentration c.

FIG. 3. *Salting-out of* RuO_4 *by alkali-metal nitrates.*

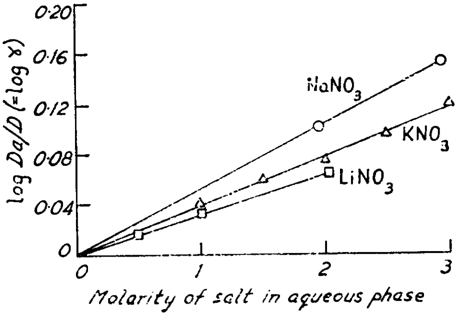


FIG. 4. *Salting-out of* RuO_4 *by alkali-metal chlorides.*

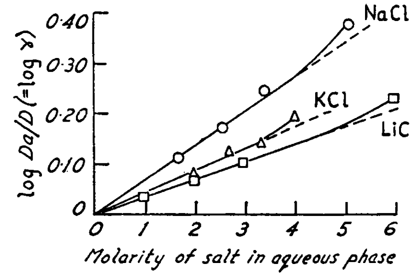
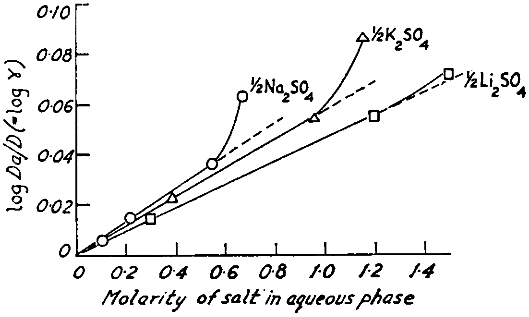


FIG. 5. *Salting out of* RuO_4 *by alkali-metal sulphates.*



The results of distribution experiments for ruthenium tetroxide between carbon tetrachloride and aqueous phases containing alkali-metal nitrates, chlorides, and sulphates are presented in Figs. 3, 4, and 5. As usual the most linear plot for $\log \gamma$ against kc is obtained when c is expressed in terms of normalities. Taking the values of k for the acids as the limiting slopes as $c \longrightarrow 0$ in Fig. 1, the graphical presentation of salting-out coefficients in Figs. 6 and 7 shows that k for nitric acid is abnormally low, and probably also for perchloric acid (the alkali perchlorates were not studied because of the insolubility of the potassium salt). There is thus some indication of chemical interaction in these two cases. Whereas salting-out is not primarily affected by the activity coefficient of the salt (or acid), chemical interaction is, and this explains the apparent lack of interaction in the case of sulphuric acid whose activity coefficients are decidedly lower than those for nitric and perchloric acids at comparable concentrations. Fig. 2 shows, however, that interaction becomes prominent for sulphuric acid at concentrations above normal. Fig. 7 shows that the true salting-out coefficient for nitric acid would have a value of approximately 0·01 and an estimate of the chemical interaction may be made.

The basic dissociation constant of ruthenium tetroxide in water is given by $K_b = K_w(D_a - D')/[\mathrm{H}^+]D'$, but D_a must be corrected for salting-out by the relation $\log D_a - \log D = kc$. For nitric acid, putting $k = 0{\cdot}01$, and applying the appropriate hydrogen-ion activity coefficient corrections (data from Conway, "Electrochemical Data," Elsevier Publ. Co., London and Amsterdam, 1952), the following values of K_b are obtained:

FIG. 6. *Comparison of salting-out coefficients of* RuO_4 *for anions having common cations.*

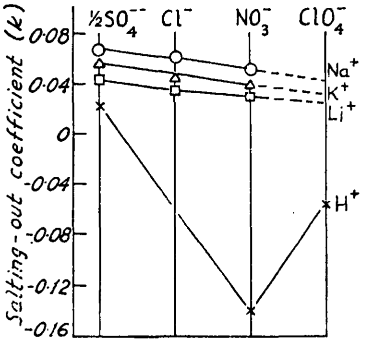
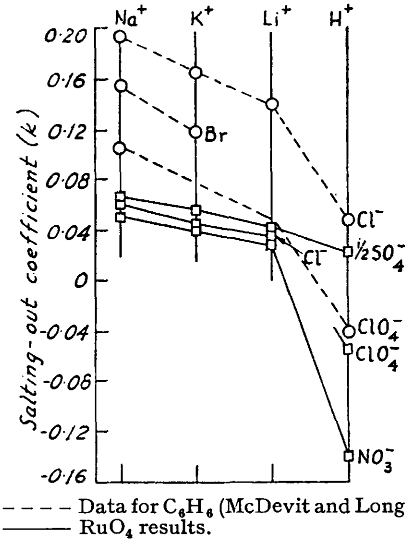


FIG. 7. *Comparison of salting-out coefficients for cations having common anions.*



Molarity of HNO_3 in aqueous phase	0·25	0·5	0·75	1·0	1·5	2·0
$10^{15}K_b$	5·4	6·0	5·2	6·1	5·9	6·5

In view of the approximate corrections involved, the values of K_b are reasonably constant, the mean being $5{\cdot}7 \pm 0{\cdot}8 \times 10^{-15}$. For sulphuric acid the values are less consistent but of the same order of magnitude:

Molarity of H_2SO_4 in aqueous phase	1·75	2·0	2·5	3·0
$10^{15}K_b$ for RuO_4	3·8	4·6	6·6	7·6

It is impossible to make a salting-out correction for perchloric acid since the requisite data are not available. Fig. 7 shows that it would probably be small and the following values of K_b are obtained without making any salting-out corrections:

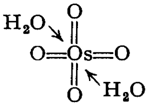
Molarity of $HClO_4$ in aqueous phase	0·5	0·75	1·0	1·5	2·0
$10^{15}K_b$ for RuO_4	2·8	3·1	3·0	2·9	2·7

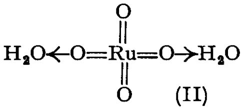
The values of K_b are again of the same order but the steady drift in values probably reflects the absence of the salting-out correction.

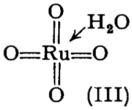
DISCUSSION

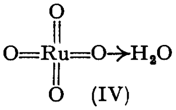
Ruthenium tetroxide resembles its analogue, osmium tetroxide, in displaying slight acidic properties in aqueous solution. However, although salts of diperosmic acid of the type $2MOH,OsO_4$ (Tschugaev, *Compt. rend.*, 1918, **167**, 162; Krauss and Wilken, *Z. anorg. Chem.*, 1925, **145**, 151) have been prepared, the preparation of corresponding ruthenium salts is precluded by the very ready reduction to ruthenate in the presence of alkalis. For osmium, Sidgwick ("Chemical Elements and Their Compounds," Oxford Univ. Press, 1950, p. 1507) considers that a covalency of ten is possible, and that acid formation by osmium tetroxide occurs by co-ordination of two water molecules to the central atom as in (I). The circumstances may of course be similar for RuO_4, but there is no experimental evidence that this is so for either case.

Contrary to the results of measurements on osmium tetroxide by Brockway (*Rev. Mod. Physics*, 1936, **8**, 260) the bond lengths in both it and ruthenium tetroxide have been found by Braune and Stute (*Angew. Chem.*, 1938, **51**, 528) not to be equal. Braune and Stute have found that the bond lengths in each case go in two equal pairs, the lengths for ruthenium tetroxide being 1·66 and 1·01 Å. The fact that two of the oxygen atoms are thus bonded differently from the other two suggests that the formation of diperruthenic acid may occur by co-ordination of two water molecules through two oxygen atoms rather than to the central atom, *e.g.*, (II). According to this formulation, the central atom maintains its maximum covalency of eight, and two of the oxygen atoms increase their co-ordination numbers to two.


(I)


$$H_2O \leftarrow O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Ru}}{=}O \rightarrow H_2O$$
(II)


(III)


$$O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Ru}}{=}O \rightarrow H_2O$$
(IV)

This structure is supported by the connection between the structure of inorganic oxy-acids and their dissociation constants. This was discussed by Kossiakoff and Harker (*J. Amer. Chem. Soc.*, 1938, **60**, 2047) who were able to predict with marked success the p*K*'s of a number of non-resonating inorganic oxy-acids. Their method of calculation was cumbersome, however, and Ricci (*ibid.*, 1948, **70**, 109) showed that a modified simple equation, $pK = 8 - 9m + 4n$, gave good results for acids of the type H_aMO_b, where m = formal charge on the nucleus and n = number of non-hydroxyl oxygen atoms in the acid molecule. The theory is really limited to non-resonating non-metallic inorganic acids, but since it seems to apply to such acids as H_4GeO_4, where the metal germanium displays covalent characteristics, it may also be applicable to H_2RuO_5 where the ruthenium behaviour is predominantly covalent.

Assuming that the Ricci equation is applicable, we have for H_2RuO_5, $-\log(7 \times 10^{-12}) = 8 - 9m + 4n$. The number of non-hydroxyl oxygen atoms (n) is taken as four. Substitution in the equation then shows that the nearest whole number value for m is $+1$. This is the formal charge on the nucleus. For the structure (III), the formal charge on the nucleus is -1 and therefore this structure would seem to be ruled out. For the other structure (IV), however, the formal charge on the central ruthenium atom is zero, but that on the appropriate oxygen atom is $+1$. In fact the whole nucleus has a small positive charge in this case, and the structure is more consistent with the Kossiakoff–Harker–Ricci theory.

EXPERIMENTAL

Pure, dry, solutions of ruthenium tetroxide in carbon tetrachloride were prepared as described previously (Martin, *loc. cit.*).

Vapour-pressure Measurements.—A standard transpiration method, in which the same stream of carrier gas is passed successively through pure solvent and solution, was used as described by Glasstone " Textbook of Physical Chemistry," MacMillan and Co., London, 1946, p. 706). A special equilibration cell was designed (Fig. 8) to facilitate equilibrations with small amounts of solution. The cell consisted of four units, each holding 2—3 ml. of solution. The carrier gas (dry air) passed through each unit in turn, the first three units acting effectively as presaturators so that the composition of the solution in the fourth unit was not detectably changed during a run. The temperature was controlled at 30° ± 0·1°. The vapours were removed from the gas by passing it through weighed traps cooled in a solid carbon dioxide–trichloroethylene slurry. By passing the carrier gas at about 10 ml. per min., about 0·5 g. both of pure carbon tetrachloride and of carbon tetrachloride–ruthenium tetroxide condensed in the traps in 15 min. This was ample for determination of the ruthenium tetroxide concentration.

Equilibration.—Equal volumes (usually 2 ml.) of the requisite carbon tetrachloride and aqueous phases were thoroughly stirred for 10 min. The phases were separated cleanly by brief centrifuging, and aliquot portions were withdrawn for analysis.

Analysis.—Distribution ratios were determined (*a*) by conversion of ruthenium tetroxide into potassium ruthenate, and colorimetric determination, or (*b*) by β-particle counting of preparation labelled with ^{106}Ru. In the first case, aqueous solutions (containing either acid or dilute alkali) of ruthenium tetroxide were made strongly alkaline (>2M) by the addition of solid potassium hydroxide. This converts the oxide into ruthenate : $2KOH + RuO_4 = K_2[RuO_4] + H_2O + \frac{1}{2}O_2$. After the solution had been made up to volume and freed from precipitate (centrifuge) (*e.g.*, K_2SO_4 from concentrated sulphuric acid solutions), the ruthenate colour was measured on a " Spekker " photometer with a combination of Wratten 50 and OB2 filters. Carbon tetrachloride solutions were shaken with 2M-potassium hydroxide, the ruthenium being rapidly and completely extracted into the aqueous phase as ruthenate. The solution was then made up to volume, and its colour was measured.

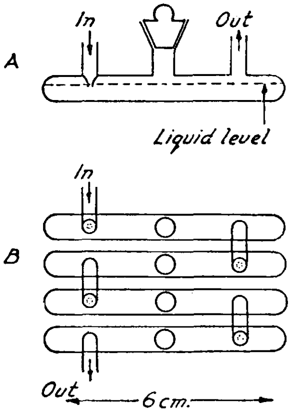


FIG. 8. RuO_4/CCl_4 *liquid–vapour equilibration apparatus for transpiration experimenls.*

A, Unit equilibrator (side view).
B, Equilibrator consisting of four units in series (top view).

In the second case, the radioactive solutions (either aqueous or in carbon tetrachloride) were pipetted on to small aluminium trays containing 1—2 drops of methanol. Immediate reduction to ruthenium dioxide occurred. A small amount of dilute collodion solution was added, and excess of solvent removed under an infra-red lamp. The samples were counted by using an end-window Geiger–Müller counter.

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