and were removed by filtration, yield 24 mg. The product was obtained in almost quantitative yield in a second experiment in which the reaction mixture was cooled after the oxidation had gone to completion. After drying in vacuum, the crystals melted, not sharply, at about 135–145° and gave analyses in agreement with the dihydrate of the expected oxidation product.

Anal. Calcd. for $C_{14}H_{16}O_6 \cdot 2H_2O$ (316.3): C, 53.16; H, 6.37. Found: C, 52.55, 52.69; H, 6.36, 6.26.

The crystals were insoluble in cold alcohol, cold acetone and hot or cold chloroform. Recrystallization did not occur from warm alcohol, but occurred slowly when water was added to the solution obtained by boiling with acetone.

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[14] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Oxygen Atom Transfer in Oxidation–Reduction Reactions. II. The Mechanism of the Sulfite–Nitrite Reaction

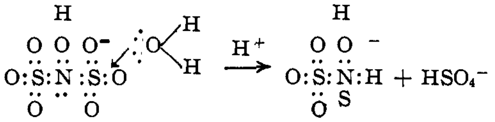
BY AARON C. RUTENBERG, JOSEPH HALPERIN[1] AND HENRY TAUBE

In an earlier communication,[2] the possibility was suggested that some oxyoxidizing agents in water may act by removing electrons from the reducing agent, the oxygen added to the reducing agent being supplied by the solvent. Consideration of the facts known about the reactions of nitrite and sulfite leads to the conclusion that the mechanism of oxidation of sulfite by nitrite is almost certainly of this type. Among others, the net changes 1 and 2 take place in the system

$$2H^+ + NO_2^- + 2SO_3^= + H_2O = NH_3OH^+ + 2SO_4^= \quad (1)$$

$$2H^+ + NO_2^- + 3SO_3^= + H_2O = NH_4^+ + 3SO_4^= \quad (2)$$

Under appropriate conditions compounds containing the complexes hydroxylamine disulfonate ($HON(SO_3)_2^=$) and amine trisulfonate ($N(SO_3)_3^{\equiv}$) can be isolated from the reaction mixture in good yield. On hydrolysis in acid solution, the former ion yields NH_3OH^+ and $SO_4^=$, and the latter yields NH_4^+ and $SO_4^=$. These complexes can therefore be regarded as intermediates for the net changes 1 and 2 above. It seems reasonable, although this has not been proven, that the "nitrite" and "sulfite" radicals in the complexes are joined by N–S bonds. The formation of $SO_4^=$ from hydroxylamine disulfonate, for example, may therefore be considered to take place in the following way.



It is clear from this formulation that each product sulfate will contain one oxygen atom derived from the solvent.

To point up this electron transfer mechanism for the action of nitrite on sulfite, the compounds $(KSO_3)_2NOH$ and $(KSO_3)_3N \cdot 2H_2O$ were prepared, and hydrolyzed by acid in water differing in oxygen isotope composition from that of the compounds. Isotopic analysis of the product sulfate showed that it contained one (and only one) oxygen atom per $SO_4^=$ derived from the solvent. The experiments remove any doubt as to the role the solvent plays as a source of oxygen in the present system. They prove furthermore that the "sulfite" bound in the complexes does not exchange oxygen with the solvent. This strengthens the formulations of the complexes as being internally joined by N–S bonds, and shows also that the complexes are not in rapid equilibrium with sulfite as a dissociation product. Sulfite in acid is known to exchange very rapidly with the solvent under the conditions of the hydrolysis.[3]

Experimental

Anhydrous $(K_2SO_3)_2NOH$ was prepared by the method of Naiditch and Yost.[4] Owing to its instability, the compound was used immediately after being prepared. $(KSO_3)_3N \cdot 2H_2O$ was prepared as described by Sisler and Audrieth.[5]

Table I gives an account of the experimental conditions, and presents the results obtained. The method used for the isotopic analysis of the product sulfate will be described in a future communication.[3]

TABLE I

OXYGEN TRANSFER IN THE HYDROLYSIS OF HYDROXYLAMINE DISULFONATE AND AMINE TRISULFONATE

N represents the mole fraction of O^{18}; the subscripts o, h and p designate, respectively, the water used in the hydrolysis, the complex salt and the product sulfate. Temp. *ca.* 25°.

Salt	Salt concn., M	(HCl) M	$N_o \times 10^3$	$N_h \times 10^3$	$N_p \times 10^3$	No. of O from solvent in each SO_4
$(KSO_3)_2NOH$	0.46[a]	0.235	15.625	2.130	5.254	0.93 ± 0.05
$(KSO_3)_2NOH$	.78[a]	.235	15.625	2.130	5.127	.89 ± .05
$(KSO_3)_2NOH$	.37[a]	*ca.* .5	15.500	2.130	5.311	.96 ± .05
$(KSO_3)_3N \cdot 2H_2O$	.24[b]	.11	15.006	2.130	5.161	.95 ± .05
$(KSO_3)_3N \cdot 2H_2O$	.18[c]	.69	15.737	2.130	5.368	.94 ± .05

[a] 1.0 mole $SO_4^=$ formed per mole of salt. [b] 2.0 moles $SO_4^=$ formed per mole of salt. [c] 1.7 moles $SO_4^=$ formed per mole of salt.

The systematic deviation from unity of the values for transfer from the solvent may be attributed in part to isotope fractionation. It is in the direction expected for H_2O^{16} reacting in the hydrolysis more rapidly than does H_2O^{18}.

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mass spectrometer used in this research were supplied by the Atomic Energy Commission under contract AT(11-1)-92.

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The Use of Ion Exchangers for the Determination of Physical-chemical Properties of Substances, Particularly Radiotracers, in Solution. IV. Activity Coefficients of Barium Nitrate in Uranyl Nitrate[1]

BY JACK SCHUBERT[2]

About 1931 it occurred to Vanselow that cation exchange reactions could be utilized for investigation of activity coefficients in mixed electrolytes.[3] The method was applied experimentally to the barium–cadmium exchange reaction with bentonite. Fair agreement between experimental and calculated activity coefficients was found. In paper I of this series,[4] it was suggested that Vanselow's approach could be applied even more successfully in conjunction with the synthetic organic cation exchangers and carrier-free radiotracers. The potentialities of this technique for elucidating the role of trace metals in biological systems are of particular interest. This communication presents the results of measurements on the activity coefficients of carrier-free $^{140}Ba^{++}$ in uranyl nitrate solutions by the use of uranyl form of the cation exchange resin, Amberlite IR-1.

The equilibrium reaction between tracer Ba and the cation exchanger is

$$Ba^{++} + UO_2R_2 \rightleftarrows BaR_2 + UO_2^{++} \qquad (1)$$

in which R is the insoluble anionic part of the exchanger. The thermodynamic exchange constant, K_a, for the reaction is[4,5,6]

$$K_a = (N_{BaR_2})\,(a_{UO_2^{++}})/(N_{UO_2R_2})(a_{Ba^{++}}) \qquad (2)$$

where N_{BaR_2} and $N_{UO_2R_2}$ are the mole fractions of Ba^{++} and UO_2^{++}, respectively, in the resin phase, and $a_{UO_2^{++}}$ and $a_{Ba^{++}}$ are the respective activities in solution. Since $UO_2R_2 >> BaR_2$ it follows that the mole fraction $m_{BaR_2}/(m_{UO_2R_2} + m_{BaR_2}) = m_{BaR_2}/m_{UO_2R_2}$, where m represents the moles of each cation in the resin phase. The concentration exchange constant, $K_{ex.}$, is defined as

$$K_{ex.} = (m_{BaR_2})(m_{UO_2^{++}})/(m_{UO_2R_2}(m_{Ba^{++}}) \qquad (3)$$

whence

$$K_a = K_{ex.}\ (\gamma_{\pm UO_2(N_2O_3)_2}/\gamma_{\pm Ba(NO_3)_2}{}^3 \qquad (4)$$

where $\gamma_{\pm}$ represents the mean activity coefficients of the ions of the specified electrolytes. It follows from equation (4) that

$$\gamma_{\pm Ba(NO_3)_2} = (K_{ex.}/K_a)^{1/3} \times \gamma_{\pm UO_2(NO_3)_2} \qquad (5)$$

The thermodynamic constant, K_a, is obtained by a plot of the experimentally determined values of $K_{ex.}$ against some function of electrolyte concentration and extrapolating to infinite dilution. The activity coefficients of uranyl nitrate are exactly those of its aqueous solution. Therefore, the only unknown in equation (5) is the activity coefficient of the barium salt.

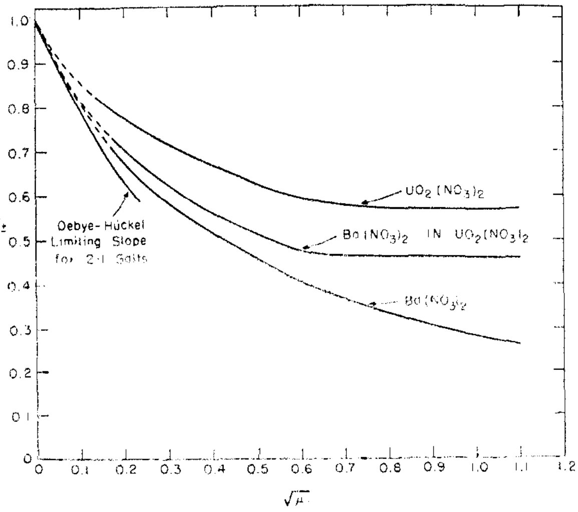

Fig. 1.

Experimental

Ten-ml. volumes of uranyl nitrate solutions (*p*H varied from 1.9–2.4 containing carrier-free ^{140}Ba were added to weighed samples (0.05–0.5 g.) of the uranyl saturated form of Amberlite IR-1 (Rohm and Haas Co., Philadelphia, Pa.). The mixtures were shaken until the absorption of ^{140}Ba reached a constant value. Assay for ^{140}Ba was made by precipitating the tracer with added barium chloride carrier and counting the radioactivity of the mounted precipitate with an end-mica window G. M. counter tube. All of the radioactive measurements were made on a strictly relative basis, thus minimizing errors due to decay, self-absorption, scattering, etc.

The UO_2R_2 contained 1.19 millimoles of UO_2^{++} per gram of oven-dried resin. The air-dried resin, 60–80 mesh, contained 15.5% moisture.

The concentrations of uranyl nitrate in solution at equilibrium were determined gravimetrically by ignition of measured aliquots to U_3O_8.

Results and Discussion

The experimental and derived data are summarized in Table I. The value of $K_a = 14$ was obtained from a plot of log $K_{ex.}$ *versus* $\sqrt{m}$ and an extrapolation to infinite dilution. We can arrive independently at an approximate value of K_a by inserting in equation (4) the known activity coefficient of barium nitrate in a dilute binary solution of the same ionic strength. This procedure for $\mu = 0.03$ gives $K_a = 15$.

The γ^+ of $Ba(NO_3)_2$ in the ternary solution is greater than its value in the binary solution. This effect is similar to that found by Harned[7] for strong acids.

The accuracy of the ion exchange method for measuring activity coefficients in mixed electrolytes can be improved by the use of monofunctional ex-

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(1) This investigation was performed under the auspices of the Manhattan District at the Clinton Laboratories during the period December, 1944, to January, 1945, Oak Ridge, Tenn., and reported in CN-1873 and CN-2563 in January, 1945, and February, 1945, respectively.

(2) Argonne National Laboratory, P. O. Box 5207, Chicago 80, Illinois.

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