The second type of bases which have been studied are neutral molecule electron pair donors, isoquinoline, quinoline, and pyridine. These are all *very much stronger* bases in selenium oxychloride than the alkali and alkaline earth chlorides. On the basis of previous studies[2b] it is believed that these substances react with selenium oxychloride to give the corresponding selenium oxychloro onium chlorides, which are strong electrolytes. In the case of pyridine the reaction may be formulated as follows

$$C_5H_5N + SeOCl_2 \longrightarrow C_5H_5NSeOCl_2^+ + Cl^-$$

It has been found that pyridine reacts with sulfur trioxide in selenium oxychloride in stoichiometric ratio of 1:1. This neutralization reaction may be formulated in two ways

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow SeOCl_2 + C_5H_5NSeOCl^+ + SO_3Cl^-$$

and

$$C_5H_5NSeOCl^+ + Cl^- + SeOCl^+ + SO_3Cl^- \longrightarrow 2SeOCl_2 + C_5H_5NSO_3$$

Luder[6] believes that the second formulation is correct but the authors of this paper believe that both reactions take place and that the predominance of one reaction over the other depends on the concentrations of the reactants. A more complete study of the system $SeOCl_2$–SO_3–C_5H_5N is projected and it is hoped that the solid phases may be isolated and their composition investigated. In titrations of the base, water, with the acid, sulfur trioxide, it appears likely that sulfuric acid, is formed. A further observation is that in some neutralization reactions salts are formed (electrolytes) while in other instances molecular "salts" (non-electrolytes) are formed at the equivalence point.

In the present investigations it has been demonstrated that the relative strengths of non-protonic acids and bases in selenium oxychloride may be estimated approximately.

Summary

1. The Müller "retarded" electrode has been adapted to potentiometric titration of non-protonic acid-base systems in selenium oxychloride.
2. An 0.1 *M* potassium chloride reference electrode for potentiometric titrations in selenium oxychloride has been developed.
3. Neutralization reactions studied are of the weak acid–weak base type.
4. The relative strength of non-protonic acids and non-protonic bases in the non-protonic solvent selenium oxychloride have been determined. The relative strengths of the acids in decreasing order are sulfur trioxide, ferric chloride, stannic chloride, and of the bases are isoquinoline, quinoline, pyridine and potassium chloride.

BROOKLYN, N. Y. RECEIVED OCTOBER 13, 1943

[6] Luder, *Chem. Rev.*, **27**, 547 (1940).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Consecutive Competitive Reactions

BY RAYMOND M. FUOSS

We consider the following sequence of irreversible reactions

$$\begin{aligned} AX_4 + RY &\longrightarrow RAX_3 + XY \\ RAX_3 + RY &\longrightarrow R_2AX_2 + XY \\ R_2AX_2 + RY &\longrightarrow R_3AX + XY \\ R_3AX + RY &\longrightarrow R_4A + XY \end{aligned}$$

in which the reagent RY can replace the X's of AX_4 one at a time by R's. Obviously, after the reaction has started, four species are competing for reagent. It is of interest to calculate the relative amounts of the five species AX_4, . . ., R_4A as a function of the amount of reagent added.

Let n molecules of RY be added to N molecules of AX_4, and let N_i be the number of molecules of R_iAX_{4-i} present. The net change dN_i in any species N_i when dn molecules of reagent are added is given by

$$dN_i = dN_i' - dN_i'' \qquad (1)$$

where dN_i' is the number of molecules of species i produced from dN_{i-1}'' molecules of species $(i - 1)$ and dN_i'' is the number of molecules of species i which react to form dN_{i+1}' molecules of species $(i + 1)$ ($dN_0' \equiv 0$ because no AX_4 is produced and $dN_4'' \equiv 0$ because no R_4A reacts). Then

$$dn = dN_0'' + dN_1'' + dN_2'' + dN_3'' \qquad (2)$$

To conserve A-atoms, we have

$$N = N_0 + N_1 + N_2 + N_3 + N_4 \qquad (3)$$

Let the reaction probabilities be in the ratio $1:\alpha:\beta:\gamma$, so that

$$\begin{aligned} dN_0'' &= \zeta N_0 dn \\ dN_1'' &= \alpha\zeta N_1 dn \\ dN_2'' &= \beta\zeta N_2 dn \\ dN_3'' &= \gamma\zeta N_3 dn \end{aligned} \qquad (4)$$

Introducing variables $x = n/N$ and $y_i = N_i/N$, we thus have the following differential equations which describe the system

$$\begin{aligned} dy_0 &= -\zeta N y_0 dx \\ dy_1 &= \zeta N(y_0 - \alpha y_1)dx \\ dy_2 &= \zeta N(\alpha y_1 - \beta y_2)dx \\ dy_3 &= \zeta N(\beta y_2 - \gamma y_3)dx \\ dy_4 &= \zeta N \gamma y_3 dx \end{aligned} \qquad (5)$$

where by (2)

$$\zeta^{-1} = y_0 + \alpha y_1 + \beta y_2 + \gamma y_3 \qquad (6)$$

When $1 \neq \alpha \neq \beta \neq \gamma$, the solutions of (5) are, in terms of y_0 as parameter

$$y_1 = y_0(y_0^{\alpha-1} - 1)/(1 - \alpha) \qquad (7)$$

$$y_2 = \alpha y_0[y_0^{\beta-1}/(\alpha - \beta)(1 - \beta) - y_0^{\alpha-1}/(\alpha - \beta)(1 - \alpha) + 1/(1 - \alpha)(1 - \beta)] \qquad (8)$$

$$y_3 = \alpha\beta y_0[y_0^{\gamma-1}/(\alpha - \gamma)(\beta - \gamma)(1 - \gamma) - y_0^{\beta-1}/(\alpha - \beta)(\beta - \gamma)(1 - \beta) + y_0^{\alpha-1}/(\alpha - \beta)(\alpha - \gamma)(1 - \alpha) - 1/(1 - \alpha)(1 - \beta)(1 - \gamma)] \qquad (9)$$

$$y_4 = 1 - y_0 - y_1 - y_2 - y_3 \qquad (10)$$

and

$$4 - x = Ay_0 + By_0 + Cy_0 + Dy_0 \qquad (11)$$

where

$$A = [1 - \beta/(\alpha - \beta) + \beta\gamma/(\alpha - \beta)(\alpha - \gamma)]/(1 - \alpha) \qquad (12)$$

$$B = \alpha[1 - \gamma/(\beta - \gamma)]/(\alpha - \beta)(1 - \beta) \qquad (13)$$

$$C = \alpha\beta/(\alpha - \gamma)(\beta - \gamma)(1 - \gamma) \qquad (14)$$

$$D = 1 - \alpha/(1 - \alpha) + \alpha\beta/(1 - \alpha)(1 - \beta) - \alpha\beta\gamma/(1 - \alpha)(1 - \beta)(1 - \gamma) \qquad (15)$$

Several examples are given below. For $1:\alpha:\beta:\gamma = 1:{}^3/_4:{}^1/_2:{}^1/_4$

$$y_1 = 4y_0(y_0^{-1/4} - 1)$$
$$y_2 = 6y_0(y_0^{-1/4} - 1)^2$$
$$y_3 = 4y_0(y_0^{-1/4} - 1)^3$$
$$x = 4(1 - y_0^{1/4})$$

This corresponds to the reaction probabilities being in the geometrical ratio; for example, on the average, R_3AX reacts on one out of four collisions with RY, assuming pure chance. If dipole-dipole interaction could produce orientations unfavorable for reaction, the probabilities α and γ for the unsymmetrical molecules should be reduced. For $1:\alpha:\beta:\gamma = 1:{}^1/_4:{}^1/_2:{}^1/_8$.

$$y_1 = 4(y_0^{1/4} - y_0)/3$$
$$y_2 = 2(y_0 + 2y_0^{1/4} - 3y_0^{1/2})/3$$
$$y_3 = 8(8y_0^{1/8} - y_0)/21 + 8(y_0^{1/2} - 2y_0^{1/4})/3$$
$$4 - x = 4(y_0^{1/4} - y_0^{1/2})/3 + (64y_0^{1/8} + 20y_0)/21$$

If, on the other hand, the symmetrical molecules react less probably than the unsymmetrical, $\alpha > 1$ and a typical case would be $1:\alpha:\beta:\gamma = 1:2:{}^1/_2:{}^2/_3$, for which

$$y_1 = y_0(1 - y_0)$$
$$y_2 = 4(2y_0^{1/2} + y_0^2 - 3y_0)/3$$
$$y_3 = 8y_0^{1/2} + 6y_0 - y_0^2/2 - 27y_0^{2/3}/2$$
$$4 - x = 40y_0^{1/2}/3 + 5y_0 - 5y_0^2/6 - 27y_0^{2/3}/2$$

In case $\alpha = \beta = \gamma = 1$, *i. e.*, if all reactions are equally probable, the solution is

$$y_1 = -y_0 \ln y_0$$
$$y_2 = (1/2)y_0 \ln^2 y_0$$
$$y_3 = (-1/6)\, y_0 \ln {}^3y_0$$
$$4 - x = y_0(3 - 3 \ln y_0 + \ln^2 y_0 - [1/6]\ln^3 y_0).$$

Examples[1] of different distributions which result from different reaction probabilities are given in Figs. 1 and 2. By adding 2 mols of RY to one mol of AX_4 and analyzing the reaction products, one can get some idea of the relative reaction probabilities. For example, Kipping[2] added 2.25 moles of phenylmagnesium bromide to one mole of silicon tetrachloride, and obtained 14 mole %

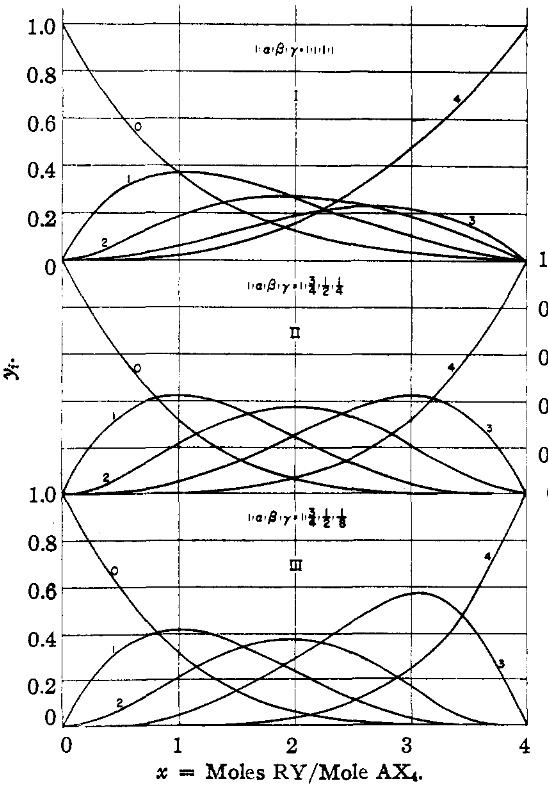

Fig. 1.—Curves showing distribution of products. I, $\alpha:\beta:\gamma$ = 1:1:1; II, ${}^3/_4:{}^1/_2:{}^1/_4$; III, ${}^3/_4:{}^1/_2:{}^1/_8$.

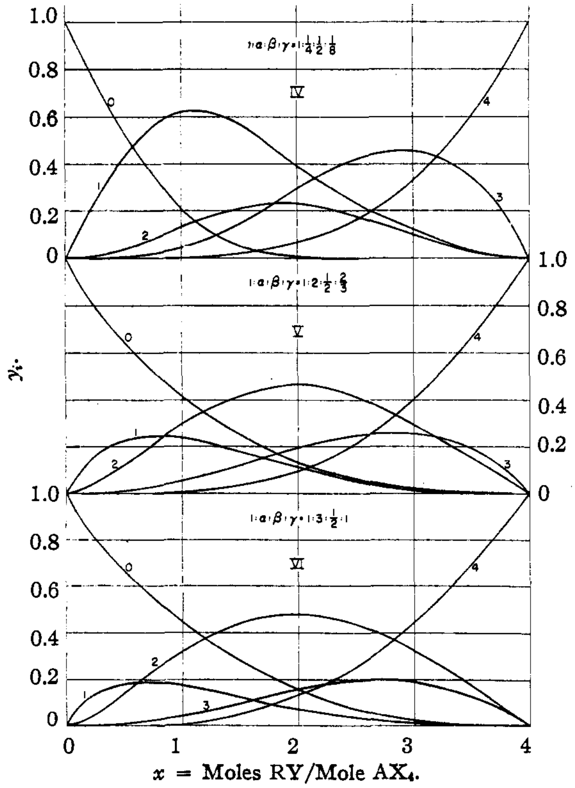

Fig. 2.—Curves showing distribution of products. IV, $\alpha:\beta:\gamma$ = ${}^1/_4:{}^1/_2:{}^1/_8$; V, $2:{}^1/_2:{}^2/_3$; VI, $3:{}^1/_2:1$.

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[1] The assistance of Miss Catherine M. Mullins in making the calculations is gratefully acknowledged.

[2] Kipping, *J. Chem. Soc.*, **101**, 2113 (1912).

$PhSiCl_3$, 44 mole % Ph_2SiCl_2 and 5 mole % Ph_3SiCl. While this accounts for only 63% of the silicon, some definite statements concerning the reaction are still possible, on comparing the yield figures with the curves of Figs. 1 and 2. The reaction probabilities cannot be in the geometric ratio, because the yields of mono- and tri-chlorides are too low. It is clearly obvious that $\alpha > 1$; that is, unsymmetrical $RSiCl_3$ reacts much faster with Grignard reagent than symmetrical $SiCl_4$, despite the fact that the latter contains more halogen.

An interesting partially specialized case is obtained by setting $1:\alpha:\beta:\gamma = 1:3\gamma:{}^1/_2:\gamma$, *i. e.*, by setting the ratios of reaction probabilities for the pairs $AX_4 - R_2AX_2$ and $RAX_3 - R_3AX$ equal to their geometrical ratios, and leaving the relative probabilities for symmetrical and unsymmetrical compounds disposable as an arbitrary parameter. For this case

$$y_1 = (y_0 - y_0^{3\gamma})/(3\gamma - 1) \tag{16}$$

$$y_2 = [6\gamma/(6\gamma - 1)][2y_0^{1/2} + y_0^{3\gamma}/(3\gamma - 1) - (6\gamma - 1)y_0/(3\gamma - 1)] \tag{17}$$

$$y_3 = 3\gamma[y_0^{\gamma}/2\gamma(1 - 2\gamma)(1 - \gamma) - 4y_0^{1/2}/(6\gamma - 1)(1 - 2\gamma) + y_0^{3\gamma}/2\gamma(6\gamma - 1)(1 - 3\gamma) - y_0/(1 - 3\gamma)(1 - \gamma)] \tag{18}$$

$$4 - x = 3(4\gamma - 1)y_0^{3\gamma}/2(6\gamma - 1)(1 - 3\gamma) + 12\gamma(1 - 4\gamma)y_0^{1/2}/(6\gamma - 1)(1 - 2\gamma) + 3y_0^{\gamma}/2(1 - 2\gamma)(1 - \gamma) + (1 - 4\gamma)y_0/(1 - \gamma)(1 - 3\gamma) \tag{19}$$

Since (dy_0/dx) does not vanish for $0 < x < 4$, the maximum in y_2 is given by the root of $(dy_2/dy_0) = 0$. We find

$$y_2(\text{max.}) = 2(y_m^{1/2} - y_m) \tag{20}$$

where y_m is the value of y_0 at the x-value where the maximum in y_2 appears. The function

$$f(z) = 2(\sqrt{z} - z)$$

has a maximum of 0.5 when $z = 0.25$, so the yield of R_2AX_2 can never exceed 50% for the case considered in this paragraph.

For the general case, with α, β and γ arbitrary, the condition for a maximum in y_2 leads to

$$y_2(\text{max.}) = (y_m^{\beta} - y_m)/(1 - \beta) \tag{21}$$

where again y_m is the value of y_0 where y_2 is at its maximum. The maximum in y_2 depends only on β and the corresponding value of y_0; the latter, however, depends on α and γ in a complicated way. The function

$$\varphi(z) = (z^{\beta} - z)/(1 - \beta) \tag{22}$$

has a maximum when

$$z = \beta^{1/(1-\beta)}$$

The value of the maximum of $\varphi(z)$ is given by

$$\text{Max. } \varphi(z) = \Phi(\beta) = \beta^{\beta/(1-\beta)} \tag{23}$$

The following values give an estimate of the maximum possible yields of R_2AX_2, considered as a function of β, the relative probability of reaction of R_2AX_2 with Grignard reagent: $\Phi(0) = 1$, *i. e.*, if R_2AX_2 will not react, the final product is obviously R_2AX_2; $\Phi(^1/_4) = 4^{-1/3} = 0.6300$, $\Phi(^1/_3) = \sqrt{3}/3 = 0.5773$, $\Phi(^1/_2) = {}^1/_2$, $\Phi(1) = e^{-1} = 0.3548$, $\Phi(2) = {}^1/_4$, $\Phi(3) = 3^{-3/2} = 0.1925$; and $\Phi(\infty) = 0$, *i. e.*, no R_2AX_2 can accumulate if it has zero relative probability of not reacting.

SCHENECTADY, N. Y. RECEIVED SEPTEMBER 22, 1943

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Complex Ions. VII. A Solubility Method for the Determination of Instability Constants in Solution and the Ammines of Nickel, Cadmium and Magnesium[1]

BY PAUL F. DERR AND W. C. VOSBURGH

To determine the instability constant of a complex ion it is necessary to measure the concentration or activity of one ionic or molecular species at equilibrium, in addition to the total amounts of the reactants. For a metal-ammonia complex ion, for example, the concentration or activity of the uncombined ammonia, of the uncombined (aquo) metallic ion, or of the complex ion may be determined. From one of these together with the total amounts of metallic ion and ammonia and suitable activity coefficients the equilibrium constant can be calculated.

If more than one complex ion is formed, several determinations on mixtures containing varying amounts of the reactants are needed. Simultaneous equations can then be set up which on solution will give the instability constants.

The activity of an aquo-ion in equilibrium with a complex ion can be determined by solubility[2] or electromotive force measurements[3] and that of the ammonia by distribution between the solution and either an immiscible solvent[4] or air.[5] Two spectrophotometric methods applicable in special cases have been described by Job.[6]

Bjerrum[7] has determined the stabilities of a number of metal ammines and ethylenediamine complexes by means of electromotive force measurements with a glass electrode. The electromotive force was related empirically to the concentration of free ammonia under the conditions of

[1] Part of a thesis submitted by Paul F. Derr in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] Randall and Halford, THIS JOURNAL, **52**, 178 (1930).

[3] (a) Bodländer and Fittig, *Z. physik. Chem.*, **39**, 607 (1902); (b) Job, *Ann. chim.*, [10] **9**, 166 (1928).

[4] Dawson and McCrae, *J. Chem. Soc.*, **77**, 1239 (1900).

[5] De Wijs, *Rec. trav. chim.*, **44**, 663 (1925).

[6] (a) Ref. 3b, 113; (b) Job, *Ann. chim.*, [11] **6**, 97 (1936).

[7] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941.