

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY SCHOOL OF MEDICINE]

Oxidation-Reduction Potentials of the System: Selenourea-Formamidine Diselenide

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The oxidation-reduction potentials of the selenourea-formamidine diselenide system have been measured in acid solutions at platinum electrodes by a standard electrometric titration method. The stability of the potentials and their close correspondence to the expected values, based on the electrode equations applicable to the related thiourea-formamidine disulfide system, establish the ready reversibility of this system. The E_0 of the selenium system is +0.240 which is more reducing than its sulfur analog of +0.420. From pH 0 to pH 4.25, there is no change in E_0' , but there is the expected change of E_0' with the total concentration of the components.

Thiourea,¹ substituted thioureas^{2,3} and dithiobiuret and other compounds containing two thioureido ($-C=S.NH_2$) groups⁴ have been demonstrated to be readily reversible oxidation-reduction systems with their corresponding disulfides. The potentials were readily and accurately measurable at platinum electrodes by the standard potentiometric methods.

Since these compounds containing the thioureido group are the only RSH and RSSR types whose potentials are indisputably measurable by simple electrode means, it was considered of interest to determine whether related selenium compounds behaved similarly. Selenourea was selected because it is the simplest representative of the class and methods for its preparation are available.

The oxidation-reduction potential apparatus and procedure were the same as previously described.^{4,5} The potentials were measured at 30° with bright platinum wire electrodes against a saturated potassium chloride-calomel half-cell joined by a saturated potassium chloride-agar bridge. The junction potentials are ignored. The solutions were stirred with nitrogen gas purified by passage over hot copper.

Freedman and Corwin⁶ have suggested that the potentials obtained by Preisler and Berger⁴ at platinum electrodes might have been due to some unknown reaction with the platinum electrodes, basing their conclusion upon their inability to obtain satisfactorily stable potentials when using boron carbide or gold-plated platinum electrodes. Similar uncertain results were obtained with gold-plated electrodes by Preisler and Berger but were not there reported; the use of the customary gold-plated electrodes had been discontinued because of their instability and because on one occasion, after the disulfide had been formed by titration, the solution had been allowed to stand overnight during which time all of the gold had been dissolved off the electrode.

The reaction of gold with the disulfide was tested recently by subjecting a piece of pure gold foil of 25 sq. cm. area, at about 25°, to a saturated solution of formamidine disulfide ditrichloroacetate containing excess of the solid (being about 0.03 molar), in N sulfuric acid stirred with O_2 -free nitrogen gas for 20 hr. The loss in weight of the gold foil was 0.018 gram. Such reactivity with the metal of the electrode could easily account for the instability of the potentials, the electrode being no longer in the "unattackable" class.

The recorded potentials have been converted to E_h values (normal hydrogen electrode as zero).

The materials and solutions were prepared from commercial analytical grade reagents. The cyanamide was a highly purified sample obtained through the courtesy of the American Cyanamid Company.

Selenourea was prepared by passing hydrogen selenide through warm aqueous cyanamide solution.⁶ The resulting material was recrystallized from hot water, quickly filtered off while protecting from oxygen by nitrogen and dried in a

vacuum or nitrogen over calcium chloride. The melting point was 200-203° with decomposition. The color was slightly pink, probably due to a very small amount of red selenium.

Thallic sulfate solution, 0.200 N in thallic and 1.000 N in acid, was prepared by dissolving thallic oxide in warm standard sulfuric acid containing the proper excess acid. The titrating solutions were prepared by adding the proper amount of this solution to the respective buffering solutions. Ferricyanide solutions were prepared from potassium ferricyanide and the proper buffer. Potassium acid phthalate was used as buffer material from pH 3 to 4.5.

The titration of the reductant with an oxidizing agent was the only available method by which accurate mixtures of oxidant and reductant could be prepared, because the oxidant could not be isolated sufficiently pure by the methods of preparation at hand.

Analogue to the thiourea-formamidine disulfide system, the reaction in acid solution may be written

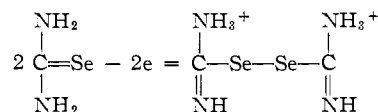


Table I gives the data of a typical titration of selenourea with ferricyanide. The analytical error at the end-point being less than 1%, the equivalents used per mole of selenourea were considered one. The E_h shown is the average of two platinum electrodes, which throughout the titration were always within 0.0001 volt. E_0' was calculated by the simplified equation applicable to this type system¹ when hydrogen ion does not enter into the reaction and there is a simple transfer of electrons.

TABLE I

Selenourea (0.000102 mole in 50 cc. of 1.0 N hydrochloric acid) (pH 0.05) titrated with potassium ferricyanide (0.005 N in the same acid); end-point at 20.4 cc., at 30°.

% Total equiv. of oxidant	E_h (v.) (measured)	E_0' (volts) (calcd.)	% Total equiv. of oxidant	E_h (v.) (measured)	E_0' (volts) (calcd.)
4.9	0.2721	0.238	68.6	0.3367	0.237
9.8	.2823	.237	73.5	.3425	.236
14.7	.2892	.238	78.4	.3490	.236
19.6	.2945	.237	83.3	.3562	.236
24.5	.2992	.237	88.2	.3671	.237
29.4	.3034	.237	93.1	.3791	.235
34.3	.3076	.237	95.0	.3905	.236
39.2	.3125	.237	95.9	.3961	.236
44.1	.3154	.238	96.9	.4008	.233
49.0	.3193	.237	98.0	.4094	.230
53.9	.3234	.237	99.0	.4205	.230
58.8	.3276	.238	100.0	.4360	...
63.7	.3322	.237			

(1) P. W. Preisler and L. Berger, *THIS JOURNAL*, **69**, 322 (1947).(2) P. W. Preisler and M. M. Bateman, *ibid.*, **69**, 2632 (1947).(3) L. D. Freedman and A. H. Corwin, *J. Biol. Chem.*, **181**, 601 (1949).(4) P. W. Preisler, *THIS JOURNAL*, **71**, 2849 (1949).(5) P. W. Preisler and L. H. Hemplemann, *ibid.*, **58**, 2305 (1936).

(6) W. Geisel, German Patent 607,382 (1934).

$$E_h = E_0' + \frac{RT}{2F} \ln \frac{(RSeSeR)}{(RSeH)^2}$$

which at 30° becomes

$$E_h = E_0' + 0.03 \log \frac{(RSeSeR)}{(RSeH)^2}$$

where E_h is the potential of the platinum electrode referred to the normal hydrogen electrode, E_0' is a constant characteristic of the specific system, and (RSeSeR) and (RSeH) are the concentrations in moles per liter of the oxidant and reductant, respectively. E_0' is defined for this system, as for other systems, as the E_h value when the logarithmic term becomes zero; that is, when $\log [(oxidant)/(reductant)^2] = 1$. The experimentally found value of E_0' is +0.240 volt over the pH range of 0.05 to 4.25. A more complete discussion of the mathematical considerations involved in this type of system has been presented for the analogous thiourea-formamidine disulfide system.¹

The effect of total concentration of the oxidant and reductant is to cause a rise in potential of 0.30 volt for each ten-fold decrease in total concentration of any fixed ratio of oxidant to reductant.

Table II gives the results of a dilution experiment conducted as follows: 0.0002 mole of selenourea (0.0242 g.) was dissolved, with nitrogen stirring, in 30 cc. of 1.0 *N* sulfuric acid and 20 cc. of deoxygenated 0.005 *N* thallic sulfate in 1.0 *N* sulfuric acid was added. The potential of this mixture was determined. Then 5 cc. of this mixture

was added to 45 cc. of deoxygenated 1.0 *N* sulfuric acid. The potential of this 1:10 dilution was then determined. A further 1:10 dilution was similarly prepared and the potential determined.

TABLE II

EFFECT OF DECREASE IN TOTAL CONCENTRATION OF OXIDANT AND REDUCTANT, AT CONSTANT RATIO OF THESE COMPONENTS, UPON THE POTENTIAL

Concn. oxid., moles/l.	Concn. red., moles/l.	$E_{1/2}$ expl. (v.)	$E_{1/2}$ calcd. (v.)	ΔE expl. (v.)	ΔE calcd. (v.)
0.001	0.002	0.314	0.312	0.029	0.030
.0001	.0002	.343	.342	0.031	0.030
.00001	.00002	.374	.372		

The average value of E_0' of +0.240 volt was used for the calculations.

The effect of pH or acidity upon the potential was determined by titrations of about 0.002 molar solutions of selenourea with suitable oxidizing agents. The E_0' were calculated by equation from the potential obtained when one-half of the original quantity has been oxidized. The differences between the potentials at $1/4$ and at $3/4$ completely oxidized and the potential at $1/2$ oxidized were computed. The results in Table III indicate that the system follows the mathematical equations expected for a two-equivalent oxidant and one-equivalent reductant, throughout the pH range of 0 to 4. Beyond pH 4, the oxidant decomposes too fast for accurate titrations.

TABLE III
 E_0' AT VARIOUS pH (AT 30°)

pH	E_0' (calcd.) (from $E_{h^{1/2}}$) v.	$E_{h^{1/2}} - E_{h^{1/4}}$ v.	$E_{h^{3/4}} - E_{h^{1/2}}$ v.	Oxidizing agent (0.005 <i>N</i>)	Buffering soln.
0.05	+0.237	-0.021	+0.024	Ferricyanide	1.0 <i>N</i> HCl
.32	.242	.021	.024	Thallic	1.0 <i>N</i> H ₂ SO ₄
.33	.240	.021	.024	Ferricyanide	0.5 <i>N</i> HCl .5 <i>M</i> KCl
.72	.241	.021	.024	Ferricyanide	.2 <i>N</i> HCl .8 <i>M</i> KCl
.74	.241	.020	.023	Thallic	.025 <i>N</i> H ₂ SO ₄ .175 <i>N</i> HCl .8 <i>M</i> KCl
1.37	.241	.021	.024	Thallic	.025 <i>N</i> H ₂ SO ₄ .025 <i>N</i> HCl .95 <i>M</i> KCl
3.15	.238	.021	.024	Thallic	.1 <i>N</i> KHPhth. .025 <i>N</i> H ₂ SO ₄ 1.0 <i>M</i> KCl
4.25	(.237)	(Decomposes)		Thallic	0.1 <i>N</i> KHPhth. 0.025 <i>N</i> NaOH 1.0 <i>N</i> KCl
	+ .240	-0.0208 - .0196 - .0143 - .0286	+0.0238 + .0233 + .0143 + .0286	(Av.) (Theor. for 2 equiv. oxid. 1 equiv. red.) (Theor. for 2 equiv. oxid. 2 equiv. red.) (Theor. for 1 equiv. oxid. 1 equiv. red.)	

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