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Studies on Oxidation–Reduction Mechanism. I. Potential Humps and the Equivalence Change Principle

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The purpose of this paper is to clear up differences of opinion between Weiss[1] and Shaffer[2] on the latter's theory of equi-valence change in ionic oxidation–reduction reactions, thereby extending the Shaffer theory. Weiss's chief criticism of the theory was based on the assertion that the rapid oxidation of stannous salts (didelectronators[3]) by ceric salts (monodelectronators[3]) is not in accord with the obvious absence of equi-valence change. He suggested that the general explanation of the existence of slow oxidation–reduction reactions between ions is to be sought in the existence of electrostatic repulsion between the complex ions formed in solution from the simple oxidizable or reducible ions.

There are, however, two other possible explanations of the rapid reaction between ceric and stannous salts. One is that the reaction might be catalyzed by the rare earths usually present in commercial ceric sulfate. The other is based on the theory of the potential hump[4] coupled with the magneto-optic evidence[5] that when stannous chloride is partially oxidized by dichromate about 0.01% of trivalent tin exists in equilibrium with the other forms. This means that if stannous tin is to be oxidized by successive one-electron steps, it must go over a potential hump and that a monodelectronator of sufficiently high potential, like ceric sulfate, would have no difficulty in bringing about a monodelectronation, whereas a monodelectronator whose potential is not quite as high as the potential hump could only surmount it slowly because the Maxwell–Boltzmann distribution of energy would only endow relatively few ions at a given moment with sufficiently high potential. A didelectronator would not have to surmount the hump.

The experimental work described below indicates the strong improbability that the fast oxidation of stannous ions by ceric ions is to be explained by the catalytic action of rare earths. That this reaction is rapid because of electrostatic attraction between positive ceric ions and negative $SnCl_4^-$ ions, as Weiss[1] suggested, also seems unlikely in view of the strong evidence presented by Smith and Getz[6] showing that quadrivalent

cerium exists as $Ce(SO_4)_3^-$ ions in aqueous sulfuric acid solutions, that in normal sulfuric acid solution the degree of formation of the complex ions is at a maximum and, in analogy to the closely similar hexanitratocerate ion in 2 N nitric acid, that almost all of the ceric ions are present in the complex form. It appears, then, that the reaction between ceric sulfate and stannous chloride is fast despite apparent electrostatic repulsion and unequal valence change.

This conclusion focuses interest on the potential hump theory. Table I gives the relevant data so far accumulated in support of this theory. The values of E_0 there given are the normal potentials of the mono- or didelectronators used. Considering first the monodelectronators, it will be observed that as the potential falls, fast reactions pass through the borderline case of molybdicyanide into a region of slow reactions and finally into one where no detectable reaction occurs. Obviously Shaffer's simple theory of equi-valence change does not explain the rapid reactions of the three most powerful monodelectronators unless it is extended by the potential hump theory.

TABLE I

FAST AND SLOW OXIDATIONS OF STANNOUS IONS IN 1–4 N SULFURIC ACID BY VARIOUS REAGENTS

Monodelectronators	E_0	Didelectronators	Speed of oxidation	Ionic charge of delectronator
*Ceric sulfate	1.45 v.		Fast	−
*Ferric phenanthroline ion	1.14		Fast	+
	1.2	Thallic ion	Fast	+
	0.91	Mercuric ion	Fast	
*Molybdicyanide	.79–0.82		3.5–5 min.	−
Silver ion	.80		Slow	
Ferric ion	.77		Slow	
	*.53–0.59	ᵃAuricyanide	Fast	−
	.53	Iodine in KI	Fast	−
	.34	ᵃCupric ion	None	
*Cupric ion	.17		None	

* Indicates data reported in the experimental part of this paper.

Considering next the didelectronators, one observes that no slow reactions are encountered and that the reactions are fast at potentials lower than those at which monodelectronation is slow. This accords with the idea that the didelectronation involves no hump and is contrary to the theory of compulsory univalent oxidation[7] which does not admit of the possibility of a one-step didelectronation.

(1) J. Weiss, J. Chem. Soc., 309 (1944).

(2) (a) P. A. Shaffer, THIS JOURNAL, 55, 2169 (1933); (b) J. Phys. Chem., 40, 1021 (1936); (c) Cold Springs Harbor Symposia Quant. Biol., 7, 50 (1939).

(3) R. E. Kirk and A. W. Browne, THIS JOURNAL, 50, 337 (1928).

(4) W. D. Bancroft and J. E. Magoffin, J. Franklin Inst., 224, 283 (1937); THIS JOURNAL, 57, 2561 (1935); 58, 2187 (1936).

(5) T. R. Ball and K. D. Crane, ibid., 55, 4860 (1933); T. R. Ball, W. Wulfkuehler and R. E. Wingard, ibid., 57, 1729 (1935).

(6) G. F. Smith and C. A. Getz, Ind. Eng. Chem., Anal. Ed., 10, 191 (1938).

(7) (a) L. Michaelis, Trans. Electrochem. Soc., 71, 107 (1937); Ann. Rev. Biochem., 7, 1 (1938); (b) L. Michaelis and E. S. Fetcher, Jr., THIS JOURNAL, 59, 1246 (1937).

Unfortunately the case of iodine is suspect inasmuch as Shaffer[2c] states that the experiment was made in the presence of iodide ions which would be expected to form complexes with the several tin ions and hence might well catalyze the reaction by lowering the potential hump. The auricyanide however, is practically free from suspicion on this score.

Experimental

The space limitations of THIS JOURNAL do not permit a detailed presentation of the experimental details so only the high points can be presented. The ceric sulfate solution used was prepared by Dr. G. R. Sherwood. The solution, when placed in an absorption cell 5-cm. wide, showed no absorption lines in the red end of the spectrum, thus indicating the absence of praseodymium and neodymium and indicating the high probability that other rare earths were also absent.

The potential of the auri–aurocyanide system cannot be satisfactorily determined in acid solution by the potentiometric method. Accordingly, it was determined roughly by finding out which reversible reducing agents in 1 to 2 N sulfuric or hydrochloric acid were oxidized by auricyanide and which were not. Auricyanide was found to oxidize iodide ion and leuco-indigodisulfonate whereas it failed to oxidize diphenylamine, toluhydroquinone, ferrous sulfate and bromide ions. It was concluded that the potential lies between 0.53 and 0.59 volt.

The experimental differentiation between fast and slow oxidations of stannous ions was carried out essentially in the absence of oxygen and, in the case where molybdicyanide was the oxidizing agent, with the complete exclusion of light. The results are shown in Table I in which the data marked with asterisks were obtained in this laboratory. The remaining data were taken from Shaffer's publications except for certain potential values which were chosen with care from the literature. Only in the case of the pure ceric sulfate was the sulfuric aid more concentrated than 4 N. In this case it was about 10 N. Comparable concentrations were used in all experiments.

Summary

1. Experiments were made which showed whether stannous ions in the absence of oxygen reacted rapidly or slowly in dilute sulfuric acid solution with ferric phenanthroline ion, potassium molybdicyanide, potassium auricyanide, cupric sulfate and highly purified ceric sulfate.

2. The reduction potential of the auricyanide-aurocyanide system in acid solution was determined approximately by observing whether or not reduction occurred with a series of reducing agents of graded potentials. It was found to lie between 0.53 and 0.59 volt in dilute acid solution.

3. The above facts were discussed in relation to the opposing oxidation–reduction theories of Shaffer and Weiss and it was shown that if Shaffer's theory were extended by introduction of the concept of potential humps it offers a satisfactory explanation of the observed facts. Weiss's suggestion that electrostatic repulsion is a sufficiently powerful influence to determine whether a given ionic oxidation–reduction reaction will be fast or slow is not borne out by the experimental facts.

Heats of Adsorption on Carbon Black. I

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The differential heats of adsorption on a number of commercial carbon blacks are being determined calorimetrically in an attempt to find a correlation between the state of surface of these blacks and their unique efficiency in rubber reinforcement. With the problem of reinforcement in mind, interest would naturally center on heat measurements with various olefins or diolefins as adsorbates. The results of such experiments, which are now in progress, will be reported in a subsequent publication.

Before investigating the hydrocarbon adsorbates, it was decided to make a series of measurements with nitrogen, oxygen and argon at liquid nitrogen temperature. It was felt that work with these elementary gases, especially nitrogen, would not only give information about any qualitative differences in the carbon black surfaces but that, in addition, it would yield data of general significance in the field of physical adsorption. This plan of investigation would have two possible points of advantage over many previous calorimetric measurements of heats of adsorption. First, the recently developed theory of physical adsorption due to Brunauer, Emmett and Teller[3] makes it possible to estimate the value of v_m, the volume of adsorbate necessary to fill the monolayer, and hence it is possible to relate the differential heats of adsorption to the fraction of surface covered. Second, although complex in physical structure and chemical constitution, the carbon blacks have highly reproducible surfaces and the large body of information concerning particle size and crystal structure of the blacks further enhances their value for use in fundamental adsorption studies.[4]