[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Effect of Hydrochloric Acid Concentration on the Reduction of Molybdate in the Silver Reductor

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In the course of a series of studies associated with an investigation of the thiocyanate complex of molybdenum, it was necessary to prepare relatively pure solutions of quinquevalent molybdenum. Among the various methods for preparing this substance there are three common quantitative procedures available. In all cases, a molybdate is reduced with moderately strong reducing agents in solutions approximately 2 normal with hydrochloric acid. Lang and Gottlieb[2a] used stannous chloride solution, Birnbaum and Walden[2b] used the silver reductor, and Furman and Murray[3] used metallic mercury. Because of certain requirements in our experiments, we selected the silver reductor for our investigations. In earlier studies, Walden, Hammett and Edmonds[4] obtained erratic results when they used silver for the reduction of molybdate. However, Birnbaum and Walden showed later that by regulating the normality of the acid, the rate of flow through the reductor tube and the temperature, molybdate was reduced completely to the quinquevalent state.

It will be recalled that high acid concentrations exert a pronounced effect upon quinquevalent molybdenum solutions as well as upon the reduction of molybdate.[5,6] A solution of five-valent molybdenum in 2 normal hydrochloric acid is amber in color while one in 8 normal hydrochloric acid is green. However, if molybdate is reduced with such vigorous agents as the Jones reductor (Zn) in 2 normal sulfuric acid solutions, the molybdenum is trivalent and the solution is green.[7] When molybdate is reduced electrolytically in 8 normal hydrochloric acid solutions, trivalent molybdenum is formed but the solution is pink instead of green.[8] The work of these authors has

been summarized in Latimer's "Oxidation Potentials"[9] in the following scheme

$$Mo^{3+} \text{ (green)} \xrightarrow{+0.25v.} Mo^{5+} \xrightarrow{-0.53v.} Mo^{6+}$$
$$Mo^{3+} \text{ (red)} \xrightarrow{-0.11v.}$$
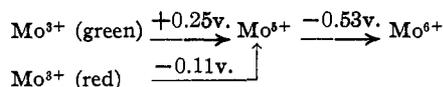
Relative stability of solutions of quinquevalent and trivalent molybdenum is another important consideration. It will be remembered that when molybdenum is reduced in the Jones reductor, the reduced solution of trivalent molybdenum is usually caught in ferric alum, or else the solution is protected from the air by an atmosphere of carbon dioxide. Solutions of quinquevalent molybdenum are much more stable. Furman and Murray have indicated that a solution of quinquevalent molybdenum can be titrated with ceric sulfate without any special precautions. In fact, the quantitative procedure for the estimation of molybdenum by means of the silver reductor depends on the fact that if some trivalent molybdenum is formed in the course of the reduction enough air will be dissolved in the solution to oxidize the molybdenum back to the quinquevalent state.

Reductor Technique.—Since we were interested in the true extent of the reduction, it was necessary to prevent oxidation by air. To this end, a one-liter flask was provided with a three-holed stopper and this was arranged in such a manner that it could be attached to the reductor and the air could be displaced in the attached flask by a stream of carbon dioxide before and during the reduction. In a regular procedure, the reductor was heated by passing through it about 200 ml. of boiling hot hydrochloric acid of the same concentration as that of the molybdate sample which was to be reduced. Following the warming process, a one-liter receiving flask was attached and the air displaced by a rapid stream of carbon dioxide. About 40 ml. of 0.02482 molar molybdate which was 8 normal to hydrochloric acid was diluted with the appropriate amount of boiled distilled water to bring the acid concentration to the desired value. This hot solution was passed through the reductor at a rate of about 60 drops per minute. The reductor was then washed with 100 ml. of hot hydrochloric acid which had the same concentration as that of the sample. The reduced solution was received in a molybdate solution which contained about four times as much molybdate as did the original sample. After suitable dilution to

(1) This paper is part of a thesis offered in fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) (a) Lang and Gottlieb, Z. anorg. Chem., **49**, 148 (1906); (b) Birnbaum and Walden, THIS JOURNAL, **60**, 64 (1938).

(3) Furman and Murray, ibid., **58**, 1689 (1936).

(4) Walden, Hammett and Edmonds, ibid., **56**, 350 (1934).

(5) Foerster, Fricke and Hausswald, Z. physik. Chem., **146**, 81 (1930).

(6) Foerster, Fricke and Hausswald, ibid., **146**, 177 (1930).

(7) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929.

(8) Foerster and Fricke, Z. anal. Chem., **36**, 458 (1923).

(9) Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

bring the whole solution to such a volume that the hydrochloric acid concentration was 2 normal, it was titrated with 0.07217 N ceric sulfate. Orthophenanthroline-ferrous complex was used as an internal indicator.

Results.—Table I shows the data for a series of samples which represent different acid concentrations. The extent of the reductions is indicated by the calculation of equivalent valence changes. A better picture of the trend of these reductions is shown in the graph in which acid concentration of the various samples is plotted against valence change.

TABLE I

All titrations were corrected by suitable blanks.

Normality HCl	Av. ml. of 0.02482 M MoO₄ taken	Av. ml. of 0.07217 N Ce⁺⁺⁺⁺ used	Av. calcd. valence change	Deviation in valence change
2	40.03	13.95	1.013⁺	±0.012
3	40.50	25.40	1.823	± .028
3.5	40.05	38.88	2.823	± .002
4	40.13	41.13	2.980⁺	± .030
4.5	40.61	42.30	3.028	....
5	40.11	41.90	3.037	....
6	40.02	42.04	3.055	± .050
7	40.09	42.30	3.068	......
8	40.02	42.44	3.083	± .030
8.6	40.11	42.53	3.090⁺	± .030
10.0	40.03	42.63	3.097	± .025
10.5	40.08	42.65	3.097	....
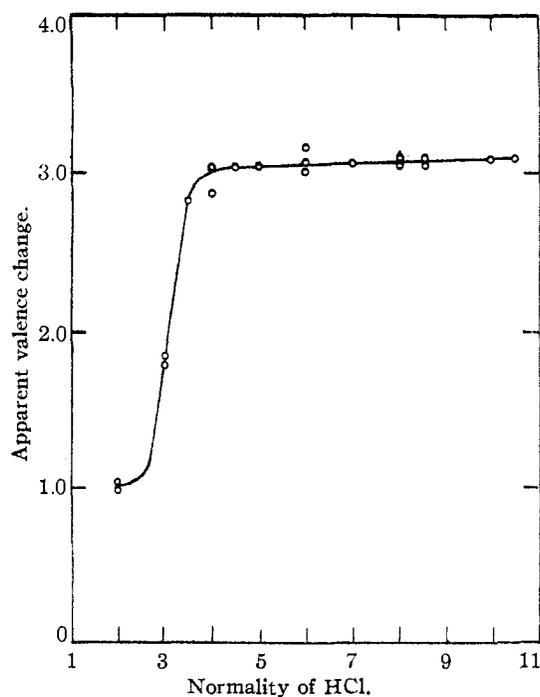
Fig. 1.

Examination of the results indicates that under the conditions of these experiments, a trace of

molybdenum is reduced below the five-valent state even in 2 normal hydrochloric acid. Above 4 normal, the molybdate appears to be reduced quantitatively to the trivalent state and the possibility exists that part of the molybdenum is being reduced to an even lower valence state.

In order to see whether such values as those obtained with the 2 normal acid were really due to a reduction of traces of quinquevalent molybdenum to the trivalent state, several samples were treated according to the Birnbaum–Walden procedure without using boiled water or the protective atmosphere of carbon dioxide. The reduced solutions were not caught in molybdate solution. Under such conditions the results obtained showed a valence change of one unit. Typical results for the apparent valence changes were 1.000, 0.9995 and 1.001.

Concerning the fact that in higher acid concentrations the reduction apparently produces a valence change of as much as 3.1, a possible interpretation is that some divalent molybdenum is being formed. The irregularity cannot be due to the titration since all of the titrations were performed in solutions 2 normal to hydrochloric acid. It seemed desirable to compare this behavior with that of Jones reductor under similar conditions. To this end, samples were reduced in the Jones reductor, care being used to avoid all possible oxidation by the air. Titrations were performed in the same manner as those in conjunction with the silver reductor. Some of the data obtained, when this type of reduction was used, are shown in Table II.

TABLE II

Normality HCl	Ml. of MoO₄ 0.02482 M	Ml. of Ce⁺⁺⁺⁺ 0.07217 N	Apparent valence change
3	39.99	41.30	3.006
	40.00	41.30	3.005
4	40.00	41.30	3.005
	40.03	41.34	3.006
6	40.05	41.41	3.013
	40.06	41.30	3.002

Although extremely high acid concentrations were not used, it is evident that the hydrochloric acid concentration does not affect the degree of reduction in the Jones reductor, at least up to 6 normal. One would want more substantial evidence before concluding that the effect in the silver reductor was due to reduction to a valence state lower than 3.

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Summary

1. It has been shown that when the reduction of molybdate is performed according to the method of Birnbaum and Walden in 2 normal hydrochloric acid, using a silver reductor, their conclusions are substantiated. Although traces of trivalent molybdenum may be formed in the process, exposure to the air oxidizes it to the quinquevalent state before the sample is titrated with ceric sulfate. Therefore their procedure produces quantitative reduction of the molybdate to the quinquevalent state.

2. When reduction of molybdate in 2 normal hydrochloric acid is performed in the silver reductor, using special precautions to avoid air oxidation, the reduction corresponds to slightly more than 1 equivalent in valence change of the molybdenum. If the acid concentration is greater than 4 normal, molybdenum in the molybdate is reduced mainly to the trivalent state. In high acid concentrations such as 10 normal, the reduction shows an apparent valence change as high as 3.1.

3. When reduction of molybdate is performed in a Jones reductor using precautions to prevent air oxidation, the apparent change of valence for molybdenum is not greater than three even though the acid concentration is as high as 6 normal.

Internal Rotation in 1,1,2-Trichloroethane[1]

BY ANTHONY TURKEVICH AND J. Y. BEACH

The problem of the freedom of rotation around the carbon–carbon single bond in halogen substituted ethanes recently has been attacked by the electron diffraction method. Studies have been made of ethylene chloride,[2] ethylene chlorobromide,[3] and ethylene bromide.[3] In all three cases it was found that the *trans* configuration was the stable configuration and that the potential barrier to internal rotation was 5 kcal./mole or greater. In this paper we shall report an electron diffraction investigation of the freedom of internal rotation in 1,1,2-trichloroethane.

The compound used was an Eastman Kodak Co. product, purified by fractional distillation in a 30-inch (76-cm.) column on which the reflux ratio could be controlled. The electron diffraction apparatus was similar to the one described by Brockway.[4] The electron wave length was 0.0590 Å. and the distance from the photographic plate to the nozzle was 12.19 cm. The photographs, taken with the compound warmed to about 65°, show seven irregularly spaced maxima. The fourth maximum is weaker than the third or fifth. The observed values of $s(= (4\pi \sin \Theta/2)/\lambda)$ and the visually estimated intensities, I, of the maxima and minima are tabulated in Table I.

TABLE I

VALUES IN PARENTHESES NOT INCLUDED IN THE AVERAGE

Max.	Min.	I	C	s_0	s^a	s^a/s_0	s^b	s^b/s_0
1		15	20	2.937	2.85	(0.907)	3.12	(1.062)
	2	−13	−35	3.993	3.76	(.942)	3.86	(0.967)
2		20	44	4.835	4.82	.997	4.89	1.011
	3	−12	−51	6.851	6.08	.887	6.15	0.898
3		16	51	7.654	7.61	.994	7.64	.998
	4	− 2	− 9	8.645	8.59	.994	8.63	.998
4		8	29	9.387	9.18	.978	9.24	.984
	5	− 7	−35	10.92	10.17	.931	10.21	.935
5		12	48	11.85	11.86	1.001	11.87	1.002
	6	− 5	−24	12.88	13.06	1.014	13.07	1.015
6		3	14	13.65	13.95	1.022	14.03	1.028
	7	− 3	−14	14.59	14.45	0.990	14.45	0.990
7		2	14	15.29	15.08	.986	15.10	.988
					Average	0.981		0.986
					C–Cl	1.73 Å.	C–Cl	1.74 Å.

[a] Calculated for a model in which the interactions are assumed to be electrostatic plus exchange. [b] Calculated for a model in which the interactions are assumed to be electrostatic plus "corrected" exchange.

The photographs were interpreted by the radial distribution method[5] and the usual visual method.[6] Two radial distribution functions are shown in Fig. 1. Curve A was calculated by a method somewhat improved over the original one[5]

(1) These results were presented to the American Chemical Society at the Boston, Mass., meeting, September, 1939.

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(3) J. Y. Beach and Anthony Turkevich, THIS JOURNAL, **61**, 303 (1939).

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(6) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).