On the Rhodanate Reaction of Molybdenum.

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Since Braun(1) has reported the colour reaction of molybdenum produced by stannous chloride and rhodanate, the reaction has been in general adopted in the detection as well as in the estimation of the element. It is well known that the red colour once developed gradually disappears if the solution is treated with too much reducing agent. Thence some complex ions of *quinquivalent* molybdenum, such as $MoO(SCN)_5''$, are considered to be responsible for the reaction. The fact is well recognized by some investigators but others are in the opinion that the red colour is due to the *tervalent* molybdenum, such as $Mo(SCN)_6'''$. The latter consideration still prevailing to a certain extent is by no means correct, however. The present writers(2) recently studied the absorption spectra of rhodanate- and chloro-complexes of molybdenum and have found that the solutions are, at least in the visible region, most hyperchromic when the element is in the *quinquivalent* state. And it was proved, moreover, that the solution of $K_3[Mo(SCN)_6]$, which could be isolated in the crystalline state by the reaction between $K_3[MoCl_6]$ and KSCN, had but a faint yellowish tinge, and that it became more hyperchromic only when some oxidizing agent was added.

It is often emphasized that *p*H of the solution in which molybdate-rhodanate reaction takes place should be very carefully controlled because the colour intensity depends largely upon the acidity of the medium. The reduction potential of a reducing agent, e.g., stannous chloride, is a function of the acid concentration of the solution so that *p*H should naturally play an important rôle in this colour reaction. Hurd and Allen(3) studied the effect of variables involved in the colorimetric determination of molybdenum. It is recommended by these authors that the concentration of hydrochloric acid should be kept at 5.0%, potassium rhodanate at 0.6%, and stannous chloride above 0.1%. To make a test of the molybdate-rhodanate reaction, stannous chloride is usually added to the solution of molybdate which already contains hydrochloric acid and rhodanate. In some books, however, the directions are given that the reducing agent should be added in advance and rhodanate be added afterwards. We thus notice that stress has never been laid on the order of priority in which the reagents are added. Nevertheless, this is a matter of no small importance. The colour intensity of the reaction products is not found to be identical when the order is reversed, even though the amounts of the reagents used are exactly the same. Experiments have therefore been carried out to elucidate what really causes this difference.

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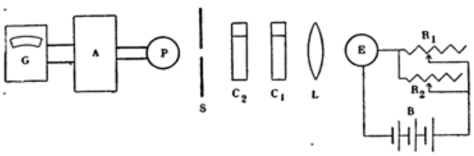
(1) C. D. Braun, *Z. anal. Chem.*, **2** (1863), 36.

(2) Y. Uzumasa and K. Doi, *J. Chem. Soc. Japan.*, **59** (1938), 1047.

(3) L. C. Hurd and H. O. Allen, *Ind. Eng. Chem.*, *Anal. Ed.* **7** (1935), 396.

Experimental. *Comparison of the colour produced by different procedures.* Two series of molybdate solutions each containing 1∼24% hydrochloric acid were prepared. One series was coloured by adding rhodanate first and then stannous chloride (A), while the other coloured by the addition of stannous chloride followed by rhodanate (B). Both series were examined by means of a photoelectric colorimeter constructed by the writers. Its essentials are illustrated in Fig. 1.



B: Lead storage batteries. 6V, Cap. 100A.
R_1, R_2: Slide resistances.
E: Mazda talkies-bulb. 5V, 5.5A.
L: Condensing lens.
C_1, C_2: Solution cells.
S: Slit.
P: Photocell. Elevam Cs-PV-65.
A: Amplifier.
G: Siemens box-type galvanometer. 0.25×10^{-6}A.

Fig. 1.

A beam of light from the lamp E passes through the condensing lens L and the cell C_1 containing the filter liquid. The beam then traverses the second cell C_2 which contains the solution to be examined and enters the slit S by which it is defined. The unabsorbed light finally strikes the photocell P. The filter liquid is composed of an aqueous solution of cupric sulphate, the concentration of which is 20 mg. $CuSO_4$/c.c. This solution serves for cutting off the infrared component of the light. The photoelectric current is amplified and can be read on a Siemens box-type galvanometer G. The amplifier circuit applied by us is that proposed by Hogness, Zschelle, Jr. and Sidwell, Jr.⁽⁴⁾ In this circuit the so-called "electrometer bulb" Mazda UX 54 is used by which a sufficient constancy of amplification during operation can be obtained.

Table 1. Transmission (%).* Thickness: 1 cm.

Procedure	A					B				
Conc of HCl \ t (min.)**	1	30	60	90	120	1	30	60	90	120
1	36	66	73	75	88	91	85	87	87	88
2	34	45	50	58	66	89	82	77	82	84
3	32	38	45	47	56	35	58	54	62	67
5	25	16	19	20	20	76	44	20	20	20
6	26	15	22	23	23	76	43	25	28	30
8	29	27	34	36	48	68	29	25	40	50
10	27	28	35	40	65	51	39	45	68	73
15	44	86	88	90	91	68	67	77	85	91
20	52	90	91	91	91	82	86	90	91	91
24	54	91	91	91	91	83	88	90	91	91

* Distilled water: 93%. ** Time after the addition of the last reagent.

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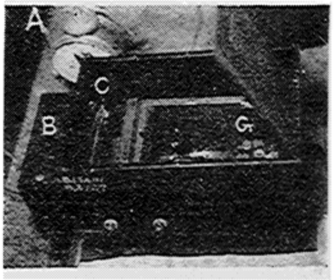
(4) T. R. Hogness, F. P. Zschelle, Jr. and A. E. Sidwell, Jr., *J. Phys. Chem.* **41** (1937), 379.

The results of the experiments carried out with two series of molybdate solutions coloured respectively in the manner described above are summarized in Table 1.

It has been recognized by a number of investigators that the colour produced by molybdenum and rhodanate undergoes considerable changes with the duration of time. With the object of following these changes, we constructed an apparatus by means of which any change in the colour of a given solution is autographically recorded. Fig. 2 shows the principal features of the apparatus.



G: Shimazu box type galvanometer.
C: Cylindrical lens.
B: Metallic box containing a rotating drum.
A: Alarm clock.

Fig. 2.

The rays reflected from the mirror of the galvanometer are converged by a cylindrical lens C upon a sheet of bromide paper which is stretched round a drum held in a metallic box B. The shaft of the drum is, by means of a pair of cog-wheels, so connected with the shaft of the hour-hand of an alarm clock that the latter gives the former one complete turn in two hours. The difficulty of keeping either the light source or the amplifier at a constant condition often makes the autographic recording unsuccessful. To overcome this difficulty it is necessary not only that the storage batteries should be always kept in a perfect condition but also that as a light source a lamp which gives least fluctuation throughout the observation should be adopted. We found that the bulb used for automobile headlight was not suitable for the present purpose because of its unsteadiness of the filament. Instead, Mazda talkies-bulb is highly recommended, for its filament is extremely steady. As resistance in the main amplifying circuit, Nihonmusen Company's radio rheostats of variable type are used. These rheostats markedly, though not completely, excluded the possible fluctuation of the galvanometer.

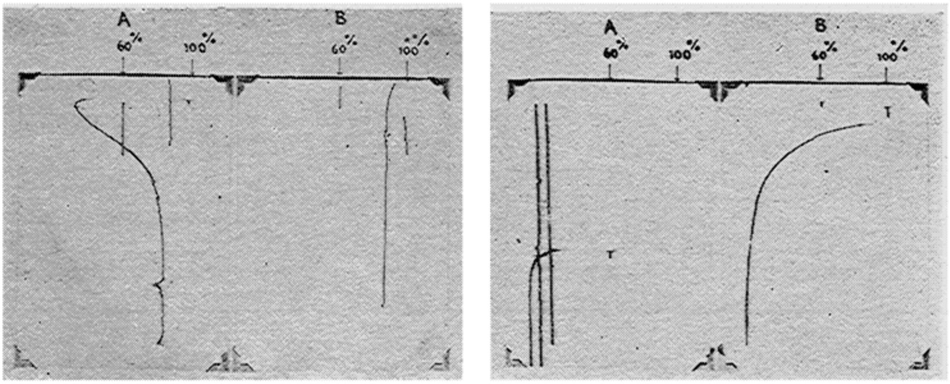
Some autographical results are given in Fig. 3.

Acid concentration and the formation of molybdenum brown. We next studied at what concentration of hydrochloric acid molybdenum brown is most easily formed. To 1 c.c. of neutral molybdate solution

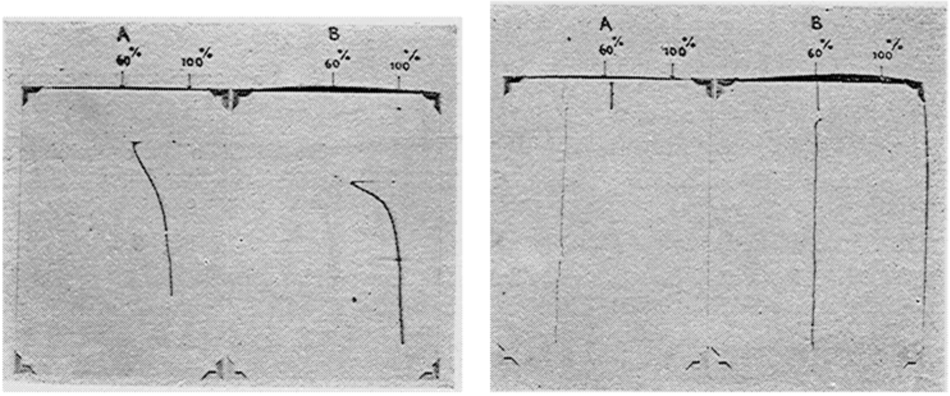
Table 2.

x	y	Resultant conc. of HCl (%)	M/100 K_2MoO_4	M/10 K_2MoO_4
0	8	1	brownish*	yellowish brown*
1	7	2	colourless	yellowish
2	6	3	,,	colourless
3	5	4	,,	,,
4	4	5	,,	,,

* These colorations indicate the formation of molybdenum brown.



HCl 1% HCl 5%



HCl 10% HCl 5% + acetone 2%

Fig. 3.

were added *x* c.c. of 10% hydrochloric acid and *y* c.c. of water. Each solution was then treated with 1 c.c. of 10% stannous chloride in 10% hydrochloric acid solution. The results are given in Table 2.

Spectrographic examination of the reaction products. In the next place, we examined spectrographically the reaction products of the procedure A and B. To the mixture of 1 c.c. of M/20 molybdate solution, *x* c.c. of 10% hydrochloric acid and *y* c.c. of water were added 1 c.c. of 10% KSCN, and then 1 c.c. of 10% $SnCl_2$(5) (A); or 1 c.c. of 10% $SnCl_2$ and then 1 c.c. of 10% KSCN (B). Ten minutes after the addition of the last reagent, 1 c.c. was pipetted out from each solution and diluted with a proper amount of water and hydrochloric acid so that the resultant solution might contain 1, 3, 5 or 8% HCl respectively. Their absorption spectra were then photographed with a small quartz spectrograph. The results are shown in Table 3.

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(5) Stannous chloride should not be added more than this amount, because it has its own absorption in the ultraviolet region which masks the band of molybdenum in question.

Table 3.

x	y	Resultant conc. of HCl (%)	Absorption bands (Å)	
			A	B
0	7	1	3100 + *	3000 + *
2	5	3	3150 ++	3000 ++
4	3	5	3150 +++	3000 ++
7	0	8	3150 +++	3000 +++

* +, ++ and +++ indicate the relative intensities of the bands.

If the reaction products are shaken with ether, the coloured substance is extracted into the other layer, leaving stannous chloride in aqueous solution. The masking effect of stannous chloride may be thus avoided. The solutions obtained by the process A as well as by the process B were both allowed to stand for just ten minutes and then were extracted with 10 c.c. of ether. 1 c.c. was pipetted out from the ether layer, and diluted to 50 c.c. with ether. It was then observed spectrographically (Table 4). In case of A, the coloured substance was thoroughly extracted into ether, and the aqueous layer was almost colourless, while, in case of B, the extraction was always incomplete, the aqueous layer remaining more or less yellowish.

Table 4.

Conc. of HCl (%)	Absorption bands (Å)	
	A	B
1	3300 +	2600 +
3	3300 ++ , 3100 ++ , 2600 +	
4	3300 ++ , 3100 ++ , 2600 +	
5	3300 +++, 3100 +++, 2600 ++	3300 +, 2600 +
8	3300 +++, 3100 +++, 2600 ++	3300 +, 2600 +

Discussion of Results. As it will be seen from Table 1 and also from the autographical results, the process A almost always develops a colour much more intense than the B. This is a fact which was hitherto disregarded. The optimum concentration of hydrochloric acid for the production of the maximum intensity of red colour is found to be approximately 5~6%. This is in accordance with the result of Hurd and Allen.(3)

Why the colour produced in the process A surpasses in intensity that produced in the process B may be explained in two ways.

I. In the process B, some intermediate compounds, e.g., molybdenum blue, molybdenum brown, etc., are expected to form, even when an excess of stannous chloride and hydrochloric acid is used. Those compounds are stable and may prevent the production of complexes of *quinqui-* or *tervalent* molybdenum.

II. When chloro-complexes of molybdenum, such as $K_2[MoOCl_5]$, $K_2[MoO_2Cl_3]$ or $K_3[MoCl_6]$, are once formed, their transmutation into corresponding rhodanate-complexes on the addition of potassium rhodanate may take place with considerable difficulty.

Our experiments indicate that, as shown in Table 2, the formation of molybdenum brown takes place only when the acid concentration is below 2%. The concentration of acid in which molybdenum blue is formed is likely to be much lower again; while the colour produced in the process B is weaker at *all* the concentration of acid than that produced in the process A (see Table 1). Consequently the formation of molybdenum blue or brown may not be responsible for the colour difference of the two processes.

Table 3 shows that the reaction products of the process A are always hyperchromic than those of the process B. The band of the former is situated between 3100Å and 3150Å while that of the latter is at 3000Å. It is also found that all the bands are more pronounced with increasing conecntration of hydrochloric acid. According to our recent studies⁽²⁾ on the absorption spectra of the molybdenum complexes, $K_2[MoO(SCN)_5]$ has its band at 3200Å while $K_2[MoOCl_5]$ has at 2940Å. The band produced by the process B is, therefore, ascribed to chloro-complexes of molybdenum. Probably these chloro-complexes may be rather stable and not easily changeable into rhodanate-complexes, even in a large excess of rhodanate.

The spectrographical examination of the ether extracts indicates that the more hydrochloric acid they contain, the more pronounced the bands appear. The extracts from the product of the process A are more hyperchromic than those from the process B (Table 4). When a solution of rhodanate complex of *quinquivalent* molybdenum, $K_2[MoO(SCN)_5]$, was acidified with hydrochloric acid and shaken with ether, a deep red extract was obtained which showed the absorption bands at 3300Å and 3100Å. These bands are in accord with those observed in the experiment with the ether extract from the process A.

On the basis of these results, it is concluded that the red colour observed in the rhodanate test for molybdenum is due to rhodanate complexes of *quinquivalent* molybdenum, possibly and chiefly $K_2[MoO(SCN)_5]$, and that when stannous chloride is added in advance, there may be formed some chloro-complexes, such as $K_2[MoOCl_5]$ or $K_2[MoO_2Cl_3]$, which positively interfere the formation of red rhodanate compounds. The fact that the addition of potassium rhodanate to the aqueous solution of $K_2[MoOCl_5]$ causes no remarkable coloration is in favour of this view. To make the test, therefore, it is always necessary to add ammonium or potassium rhodanate first and then some reducing agent, otherwise the sensitivity of the reaction might be more or less reduced.

The influence of acetone on this colour reaction was also studied. No doubt the presence of this organic solvent makes the colour developed more durable, but it neither increases the sensitivity of the reaction nor prevents undesirable effect of great excess of reducing agent. It is probable that the presence of acetone makes the reducing action milder and a long duration of time is necessary for over-reduction. The coloured substances formed may thus remain much longer in the intermediate state of reduction. The colouring in the presence of acetone is also shown more constant in the records taken by the autographic apparatus.

Summary.

(1) By means of a photoelectric colorimeter, the reaction products between molybdenum and rhodanate under various conditions were examined. The colour changes with the duration of time were recorded by an autographic apparatus constructed by the writers.

(2) The spectrographic observations of the products were also carried out.

(3) The red colour observed in the rhodanate test for molybdenum is ascribed to rhodanate complexes of *quinquivalent* molybdenum, possibly and chiefly $K_2[MoO(SCN)_5]$.

(4) It is emphasized that, to attain the maximum sensitivity of the reaction, rhodanate should be added in advance of the reducing agent.

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