TABLE II

COMPARISON OF EQUILIBRIUM CONSTANTS OF 8-QUINOLINOL[15] AND 8-QUINOLINOL-5-SULFONATE

M^{n+}	8-Quinolinol log K_{MA}	8-Quinolinol log K_{MA_2}	8-Quinolinol-5-sulfonate log K_{MA}	8-Quinolinol-5-sulfonate log K_{MA_2}	Δ log K_{MA}	Δ log K_{MA_2}
Co^{2+}	10.91	9.9	8.11	6.95	2.8	3.0
Ni^{2+}	11.65	10.4	9.02	7.75	2.6	2.6
Cu^{2+}	15.0	14.0	11.92	9.95	3.1	4.1
Zn^{2+}	10.91	9.9	7.54	6.78	3.4	3.1

Acid dissociation constants[11]: $pK_1 = 5.02$; $pK_2 = 9.81$

Ni(II) and Co(II) were calculated by the algebraic method described above. All of the other formation constants were determined by the method of Bjerrum.[9]

In Table II the relative stabilities of the Co(II), Ni(II), Cu(II) and Zn(II) chelates of 8-quinolinol-5-sulfonate are compared with the corresponding stabilities of 8-quinolinol chelates reported by Irving (Table II).[15] The lower basicity of the sulfonated ligand is reflected in a correspondingly lower stability of the metal chelates of 8-hydroxyquinoline (average Δ log $K_1 = 3.0$ and average $\Delta \log K_2 = 3.2$).

It is of interest to compare the dimerization tendencies of the 3:1 thorium, 2:1 uranyl and 2:1 ferric chelates as listed in Table I. The more positive charge (-1) of the ferric chelate relative to that of the chelate of uranyl or thorium (-2) plus the smaller radius of the ferric ion combine to produce an iron(III) chelate which is less resistant to hydrolysis ($pK_a[FeA_2^{1-}] = 5.02$; $pK_a[ThA_3^{2-}] = 6.2$; $pK_a[UO_2A_2^{2-}] = 6.68$). Because of the greater affinity of the ferric hydroxo chelate for additional donor groups, polymerization takes place more readily than in the cases of the chelates of uranyl or thorium ions. In addition the coulombic barrier is less for the polymerization of two binegatively charged ferric hydroxo complexes than for that of the trinegatively charged hydroxo chelate species of uranyl or thorium. In Fig. 9 are plotted the fractions of chelate present in the binuclear form as a function of $-\log[H^+]$ for a solution which is 1×10^{-3} molar in metal chelate. It may be seen that the uranyl chelate polymerizes only to a maximum extent of about 8%, whereas nearly 70 and 90% of the thorium and ferric chelates, respectively, are ultimately present in the binuclear form.

It should be pointed out that the hydrolysis reactions observed for the 8-quinolinol-5-sulfonate chelates have no counterpart in the reactions of the unsulfonated compound, since the metal chelates formed from the latter are insoluble and do not react further with water.

WORCESTER, MASS.

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[15] H. Irving, Paper No. 4, "A Discussion on Coördination Chemistry," Butterwick Research Laboratory, I. C. I., Sept. 21-22, 1950.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

The Nature of the Chromium(VI)-1,5-Diphenylcarbohydrazide Reaction. I. Extraction Studies[1]

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The magenta-colored product of the chromium(VI)-1,5-diphenylcarbohydrazide reaction was extracted into isoamyl alcohol. Analysis of the isoamyl alcohol extract revealed that chromium was present. The amount of color left in the aqueous extract agreed closely with the amount of chromium found in that extract. The results of this and other pertinent extraction experiments show that the colored product of the chromium(VI)-1,5-diphenylcarbohydrazide reaction contains chromium.

The reaction of 1,5-diphenylcarbohydrazide (diphenylcarbazide) with an acidified chromate solution yields an intense magenta color. This reaction has been known and used for many years, although the nature of the colored substance is not clear. There is even a difference of opinion in the literature as to whether it contains chromium. Cazeneuve[2] first proposed that the colored substance is an organometallic derivative of chromium. Babko and Paliĭ[3] then found that it contains no chromium and is rather an oxidation product of 1,5-diphenylcarbohydrazide. The most recent investigators have sided with Cazeneuve's proposal. Bose[4] concluded that the colored substance is a complex of chromium(II) and diphenylcarbazone, while Das Sarma and Ray[5] and Pflaum and Howick[6] postulate that the colored species is a complex of chromium(III) and diphenylcarbazone.

When the experimental evidence adduced by the various investigators is examined, the most direct proof is found to be that of Babko and Paliĭ. They extracted the magenta-colored substance with isoamyl alcohol. On oxidation of the organic extract with sodium peroxide and subsequent determination of chromate ion, no chromium was found. All of the chromium was found to be retained in the colorless aqueous layer. It was therefore concluded by these workers that no organometallic complex is formed in the reaction and that the colored substance is an oxidation product of 1,5-diphenylcarbohydrazide.

Evidence supporting the majority opinion may be summarized as follows.

(a) Pflaum and Howick found that it was possible to detect chromium in an isoamyl alcohol extract of the colored substance; chromium was not

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[1] This work was assisted by a research grant from the National Science Foundation.

[2] P. Cazeneuve, *Bull. soc. chim. France*, **25**, 758 (1901).

[3] A. K. Babko and L. A. Paliĭ, *Zhur. Anal. Khim.*, **5**, 272 (1950).

[4] M. Bose, *Anal. Chim. Acta*, **10**, 201, 209 (1954).

[5] B. Das Sarma and J. N. Ray, *Sci. and Culture (India)*, **21**, 477 (1956).

[6] R. T. Pflaum and L. C. Howick, THIS JOURNAL, **78**, 4862 (1956).

extracted under identical conditions in the absence of 1,5-diphenylcarbohydrazide. However, these their results were qualitative, and a relatively small amount of chromium might have been extracted. Furthermore, the control experiment was done with chromium(VI),[7] whereas it is generally agreed that chromium(VI) is reduced in the reaction. Also, Pflaum and Howick do not mention any disagreement between their results and those of Babko and Paliĭ.

(b) Solid reaction products of varying composition, which appear to be organometallic complexes of chromium, have been isolated by Cazeneuve and by Das Sarma and Ray. But these substances might be dissociated when in solution, and thus their results do not necessarily conflict with those of Babko and Paliĭ.

(c) Bose, and Pflaum and Howick, have pointed out that if the conclusions of Babko and Paliĭ are correct, then the oxidation by chromium(VI) must be highly selective, as it has not been observed with any other oxidizing agents. While this is true, it does not necessarily follow that the results of Babko and Paliĭ are in error.

(d) It has been reported that the same colored substance also is formed in the reaction of chromium(II) with diphenylcarbazone[4–6] or diphenylcarbodiazone,[5] by reaction of chromium(III) with diphenylcarbazone,[5,6] and in the presence of oxygen, by the reaction of chromium(III) and 1,5-diphenylcarbohydrazide.[5,6] It is conceivable, however, that the magenta-colored substance might be an organic compound intermediate between 1,5-diphenylcarbohydrazide and diphenylcarbazone, as for example the free radical, or its dimer, obtained by removal of one hydrogen atom from 1,5-diphenylcarbohydrazide.

The extraction experiments of Babko and Paliĭ are therefore of critical importance, and it is essential to determine, quantitatively if possible, whether chromium is extracted along with the color into organic media.

Experimental

Reagents.—The 1,5-diphenylcarbohydrazide was from Eastman Organic Chemicals, lot 42. Matheson Coleman and Bell double compound[8] of 1,5-diphenylcarbohydrazide and phenylsemicarbazide (labeled 1,5-diphenylcarbohydrazide, lot 301623), was used in one of the runs. Technical grades of isoamyl alcohol (isopentyl alcohol), containing some active amyl alcohol, and of boiling range 128–132°, were employed for extraction. All other chemicals were reagent grade. $CrCl_3 \cdot 6H_2O$ was used for tests of the extraction of chromium(III).

Procedures.—In procedure A, sixty ml. of a solution which was 2.7×10^{-3} *M* in 1,5-diphenylcarbohydrazide, 0.10 *N* in HCl and 17 vol. % in acetone were added to 25.0 ml. of 1.209×10^{-4} *M* $KHCrO_4$. Ten g. of NaCl was added, the solution was transferred quantitatively to a separatory funnel and extracted four times with 25-ml. portions of isoamyl alcohol.

In procedure B, ten ml. of a solution which was 4.2×10^{-2} *M* in 1,5-diphenylcarbohydrazide, 0.50 *N* in H_2SO_4 and 50 vol. % in acetone was added to 6.0 ml. of a solution which was 1.008×10^{-3} *M* in $KHCrO_4$ and 1.0 *N* in H_2SO_4. After quantitative transfer of the resulting solution to a separatory funnel, it was extracted once with an equal volume of isoamyl alcohol. The amount of color retained in the aqueous fraction was determined spectrophotometrically.

For Procedure C, 0.1 g. of 1,5-diphenylcarbohydrazide was dissolved in 5 ml. of acetone plus 5 ml. of 5 vol. % H_2SO_4. To this was added a solution containing 0.001 g. of $K_2Cr_2O_7$ in 5 ml. of 5 vol. % H_2SO_4. This solution was then extracted with 15 ml. of isoamyl alcohol.

In all runs, a reagent blank containing all components except chromium was carried through the entire procedure.

Analysis for Chromium.—The residue remaining after evaporation of water or isoamyl alcohol was treated with a mixture of 3 ml. of concd. H_2SO_4 and 10 ml. of concd. HNO_3 and fumed to dryness. This oxidation step was repeated until a residue devoid of brown organic tars was obtained. The residue was next heated with a mixture of 3 ml. of concd. HCl and 5 ml. of concd. HNO_3 to convert any insoluble chromium compounds to soluble chromium salts.[9] Then the colorless or green residue was dissolved in water, the solution thus obtained made strongly basic with aqueous NaOH, and 1 g. of Na_2O_2 was added. The solution was heated and boiled for several minutes after the evolution of oxygen had ceased. After neutralization with HCl, a 1,5-diphenylcarbohydrazide solution similar to that described in procedure A was added. The absorbancy at 546 mμ was measured with a Beckman DU spectrophotometer. From the observed absorbancy and the molar absorbancy index of the colored substance (4.17×10^4, based on chromium(VI) concentration),[8] the amount of chromium present was determined quantitatively.

Results

Some representative results are given in Table I. The first experiment was done by Procedure A, which is similar to that of Pflaum and Howick in that chloride ion is added to aid extraction. Almost all of the chromium is extracted along with the magenta color into isoamyl alcohol. This result is therefore in agreement with the qualitative result of Pflaum and Howick.

TABLE I

RESULTS OF EXTRACTION EXPERIMENTS WITH ISOAMYL ALCOHOL

			% Cr found		
Expt. no.	Substance to be extracted	Procedure	Aqueous phase	Organic extracts	Total
1	Cr(VI)–DPC[a]	A	2	96	98
2	Cr(VI)–DPC	B	80[b]	14	94
3	Cr(VI)–DPC	B[c]	19	73	92
4	Cr(VI)–Dble.Cpd.	B	81	13	94
5	Cr(VI)–DPC	C	39[d]	52	91
6	Cr(VI)–DPC	C[e]	14	78	92
7	Cr(III)	A	87	0	87
8	Cr(III)	B	98	0	98
9	Cr(VI)	A	21	55	76

[a] DPC = 1,5-diphenylcarbohydrazide. [b] 77% of the color was retained in the aqueous phase. [c] Eight extractions. [d] 42% of the color was retained in the aqueous phase. [e] Four extractions.

In the second experiment Procedure B was used. This procedure is similar to that of Babko and Paliĭ, H_2SO_4 being used in place of HCl, and with no salts added to aid extraction. The extractability of the colored substance is markedly affected by the nature of the anion present in the aqueous phase,[4,6] and with this procedure most of the color remained in the aqueous layer. Fourteen per cent. of the chromium was found in the isoamyl alcohol extract, and there is good agreement between the amount of color left in the aqueous fraction (77%) and the amount of chromium

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(7) L. C. Howick, Univ. of Arkansas, Fayetteville, Arkansas, private communication.

(8) T. L. Allen, *Anal. Chem.*, **30**, 447 (1958).

(9) P. F. Urone and H. K. Anders, *ibid.*, **22**, 1317 (1950).

subsequently found in that fraction (80%). As shown in expt. 3, repeated extraction removes most of the chromium from the aqueous phase. These results directly contradict the findings of Babko and Paliĭ.

The double compound of 1,5-diphenylcarbohydrazide and phenylsemicarbazide has a m.p. close to that of pure 1,5-diphenylcarbohydrazide. As the double compound has been mistaken for and sold as 1,5-diphenylcarbohydrazide,[8] Babko and Paliĭ might unintentionally have used this reagent in place of 1,5-diphenylcarbohydrazide. It therefore was of interest to study the reaction of chromium(VI) with the double compound and this was done in expt. 4. The results are almost identical with the results of expt. 2, so that the results obtained by Babko and Paliĭ cannot be attributed to use of the double compound.

Although our results are in disagreement with those reported by Babko and Paliĭ, it seemed possible that the discrepancy could be caused by differing concentrations or other experimental conditions. For example, Babko and Paliĭ did not state what concentration of H_2SO_4 was used in their work. Professor Babko kindly supplied us with the details of his reaction and extraction procedure.[10] This procedure has been given in the Experimental section as Procedure C. It has been assumed that "5% H_2SO_4" meant 5 volume % H_2SO_4. This interpretation results in a final concentration in the aqueous phase of 1.3 N H_2SO_4, and Babko[10] maintains that chromium remains almost completely in the aqueous phase at 1 to 1.5 N H_2SO_4, even after repeated extraction has removed almost all of the colored substance.

In expt. 5, Babko's procedure was followed as closely as possible, but over half of the chromium was found in the isoamyl alcohol extract. In expt. 6, it was found that after four extractions only 14% of the chromium remained in the aqueous phase. The amount of color left in the aqueous fraction in expt. 5 (42%) was in good agreement with the amount of chromium found in that fraction (39%).

The findings of Babko and Paliĭ and the results of this investigation thus remain at variance. It should be noted that Babko and Paliĭ have presented no quantitative data for chromium analyses of the aqueous and organic phases. Furthermore, they have given no details of their analytical procedures. Our repeated efforts to obtain these details have been unsuccessful.

Since it is possible that some form of chromium can be extracted independently of the colored substance into organic media, runs were made in which the extraction of chromium(III) and chromium(VI) into isoamyl alcohol were studied without the use of 1,5-diphenylcarbohydrazide. In the attempted extraction of chromium(III), (expts. 7 and 8), no chromium was found in the organic extract. A considerable amount of chromium(VI) was extracted (expt. 9). This result is in disagreement with the control experiment of Pflaum and Howick, which was, however, based on visual observation.[7] Since it is known that chromium(VI) can be extracted from an aqueous solution 1 N in HCl by 4-methyl-2-pentanone,[11] it is not surprising that it can be extracted by isoamyl alcohol under approximately the same conditions.

Conclusions

The possible forms in which chromium might be present after reaction are chromous ion, chromic ion, hydrogen chromate ion ($HCrO_4^-$) and an organometallic complex of chromium. We may eliminate the first three possibilities. Chromous ion is oxidized rapidly by air to chromic ion. Chromic ion is not extracted by isoamyl alcohol. Hydrogen chromate ion is extracted but not as readily as the chromium species resulting from the reaction of chromium(VI) and 1,5-diphenylcarbohydrazide (compare expts. 1 and 9). Furthermore, if the chromium were present after reaction as $HCrO_4^-$, it would have survived the reaction unchanged. Therefore we may conclude that after reaction the chromium is present as an organometallic complex.

The organometallic complex and the magenta-colored reaction product show the same extraction behavior, at least to within the experimental error. It is conceivable but most improbable that this is a coincidence, and therefore we conclude that the magenta-colored reaction product is an organometallic complex of chromium.

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(10) A. K. Babko, Inst. of Inorg. Chem., 9-a Leontovitch St., Kiev, Ukrainian S.S.R., U.S.S.R., private communications (1957 and 1958).

(11) H. A. Bryan and J. A. Dean, *Anal. Chem.*, **29**, 1289 (1957).